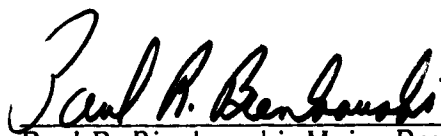


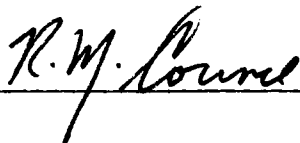
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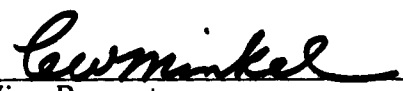

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**THE ADSORPTION AND DESORPTION CHARACTERISTICS OF THE
CELLULOSE/WATER VAPOR SYSTEM ABOVE 50 °C**

**A THESIS
PRESENTED FOR THE
MASTER OF SCIENCE DEGREE
THE UNIVERSITY OF TENNESSEE, KNOXVILLE**

ANDREW T. CHAMPAGNE

MAY 1990

DEDICATION

This work is dedicated to my mother,
Elisabeth Alice Champagne

ACKNOWLEDGEMENTS

I appreciate greatly all the people who assisted me in this endeavour. My thanks to Dr. Paul Bienkowski for his guidance and direction throughout my graduate program and, in particular, this research. I would also like to thank Dr. Hank Cochran and Dr. Pete Counce for serving on my committee. Special thanks goes to Vinod Shah for his patience in offering guidance and advice, and Bob Moore, who rankled me enough to finish and still gave me rides to and from the airport. The support and love of my parents is greatly and always appreciated. A very special thanks to my grandmother, Mrs. Elisabeth Duncan, for providing a place to stay and great suppers; this was an invaluable resource. Finally, for the understanding, love, and support of my wife, Karen, I am greatly in her debt.

ABSTRACT

A flow apparatus was constructed and used to determine some adsorption/desorption characteristics of a water vapor/cellulose system for the temperature range of 343-363 K. The mass transfer zone heights, heats of adsorption, mass transfer coefficients, and adsorption/desorption isotherms were determined. Two independent methods were used for data analysis : the areas under the breakthrough curves (AUC) were determined then used to calculate the amount of water adsorbed, the second "simple" method was weighing the adsorption column (WGT) before and after each experimental run. A modified Henderson's equilibrium equation was used to correlate the experimental data. Calculated values for the heats of adsorption, 11.6-14.8 kcal/mol, are similar to those previously reported for a physical adsorption process. A rigorous method for determining the mass transfer coefficients for this system is given. These data extend knowledge of the equilibrium behavior of water and cellulose to temperatures encountered in the selective adsorption of water from alcohol mixtures.

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I. INTRODUCTION

Many of the industrialized nations of the world are facing increasing problems with the availability of liquid fuels. The petroleum used to make these fuels is becoming exhausted; and in this country, it is a commodity vital to our national security; however, most of the petroleum is now imported thus subject to availability or lack of from the oil exporting countries, e.g., gas shortage of the 1970's. A possible solution, supported by the U. S. Federal Government, is the use of ethanol produced by the fermentation of renewable biomass as a cleaner burning extender or replacement of gasoline for transportation fuel.

Traditional technology for producing ethanol by fermentation uses inefficient, energy intensive distillation (azeotropic or extraction) to separate the ethanol from the fermentation mixture. This mixture of water and ethanol, forms a difficult-to-separate azeotrope. In the past, benzene has been added as a third component to break the azeotrope. The use of benzene, however, causes additional problems. Benzene is toxic to the environment and, therefore, must be strictly controlled. Its removal from the final product is difficult and lowers product quality. Alternative means of separating this azeotropic system are needed. The separation process of adsorption is thought to be a viable solution.

Adsorption is the selective concentration of one or more components of either a gas or liquid (adsorbate) at the surface of a contacting solid or liquid (adsorbent). Desorption is the reverse of adsorption. Both are general phenomena, and almost all solids will adsorb and desorb an adsorbate to a certain extent. The usefulness of an adsorbent depends upon its affinity for an adsorbate, chemical nature, prior history, manufacture, and surface area. As an example, some of the more important industrial adsorbents such as silica, charcoal, zeolites, and certain clays, have a specific attraction for a substance and large surface areas. The key is to find the correct adsorbent for the adsorbate to be separated.

Because cellulose has an affinity for water vapor, it could be used as an industrial adsorbent to remove water from aqueous mixtures, such as the ethanol/water azeotrope, waste water, other alcohol mixtures, etc. Cellulose is a polymer of glucose found in the cell wall of plants. It is cellulose that gives plants their rigid structure. A common example of pure cellulose is cotton. Cellulose is useful in separating the ethanol/water vapor azeotrope because it will not adsorb the ethanol to any appreciable extent (Hong, 1982); it will not degrade and due to its high purity will not give off material during the adsorption/desorption process cycle (Stamm, 1964). It has the added attraction of being inexpensive and readily available, making

adsorption with cellulose potentially an economically feasible separation process.

The study of the adsorption and desorption characteristics of the water vapor/cellulose system will be discussed in this paper. The transport and equilibrium properties determined will be: mass transfer coefficients, heats of adsorption, height of the mass transfer zone, and the adsorption/desorption isotherms. The hysteresis effect and column regeneration will also be examined. These properties will begin to provide information on the equilibrium capacity and adsorption rate of the water vapor/cellulose system above 60 °C.

These data will be derived from experimental breakthrough curves. If the feed composition, temperature, pressure, and flow rate are kept constant through a properly designed and built apparatus, then measurement of effluent adsorbate concentration over time will provide the experimental points necessary for the curves. This dynamic method allows easier determination of the heat and mass transfer quantities.

II. LITERATURE REVIEW

A. The Nature of Adsorption and Desorption

Adsorption processes can be classified as physical or chemical in nature depending upon the forces involved. Chemical adsorption or chemisorption involves an exchange or sharing of electrons between the adsorbent and the adsorbate. This sharing of electrons liberates an amount of heat that is approximately equal to the heat of a chemical reaction, 20-155 kcal/mol (Oscik, 1982). Although chemisorption is important in catalysis, as in the large scale manufacturing of aromatics, certain reactions involving the polymerization of plastics and synthetic rubber, the production of hydrogen and hydrogen peroxide, and many others, it will not be discussed further in this paper.

Physical adsorption, also known as van der Waals adsorption, is caused by intermolecular attraction forces between the adsorbent and adsorbate at the adsorbent surface. Physical adsorption can be thought of as a condensation process, the amount of heat liberated approximates the heat of condensation, 8-20 kcal/mol (Oscik, 1982). The heat of adsorption of water vapor onto cellulose has been reported ranging from 9.7-11.4 kcal/mol (Stamm, 1964). Adsorption can occur even when the adsorbate's partial pressure is less than its vapor pressure at a prevailing temperature.

The reverse process of adsorption is desorption. The removal of an adsorbate from an adsorbent (desorbing) can be accomplished by four basic means or combinations thereof :

1. Thermal Swing :

After equilibrium is reached between adsorbate in the feed and on the adsorbent at an initial temperature, the bed or column temperature is raised, thus driving more adsorbate from the adsorbent.

2. Displacement Purge :

A second adsorbate is introduced that adsorbs just as strongly or more strongly than the original adsorbate.

Therefore, the desorption is facilitated by the concentration reduction in the fluid phase around the adsorbent particles or lower adsorbate partial pressure in the bulk gas and by competitive adsorption of the second adsorbate.

3. Pressure Swing :

The total pressure of the feed gas is reduced thus reducing the partial pressure of the adsorbate in the bulk gas phase.

4. Inert-Gas Purge :

A nonadsorbing gas containing very little or no adsorbate is passed through the bed. This has the effect of lowering the partial pressure or concentration of the adsorbate around the adsorbent particle.

The inert-gas purge was used during these experiments. By using pure nitrogen as the column feed, the water vapor concentration around the adsorbing particles of cellulose was decreased; in other words, the partial pressure of the water vapor in the bulk gas phase was decreased below the equilibrium partial pressure of the adsorbed phase promoting the mass transfer of the water vapor from the cellulose to the nitrogen purge stream.

Advantages of using the inert-gas purge process come from the adiabatic operation plus using moderate pressure ratios between the adsorption and desorption steps. These advantages include: shorter cycle times, usually <10 min; the use of relatively small amounts of adsorbent, and if the effluent purge containing the desorbed fluid can be discarded, minimal auxiliary equipment required for the purge stream, all of these having favorable economic impacts.

Commercial inert-gas purge cycles, as shown in Figure 1, have previously been used to separate normal and isoparaffins from petroleum; however, these cycles are more and more being applied to the removal of large amounts of water from organic streams, such as the drying of ethanol (Garg, 1983).

B. Adsorption Models

1. Langmuir's Model. Irving Langmuir, in 1918, was the first to describe the relationship between the amount of gas adsorbed and the equilibrium pressure of the gas at a constant temperature (Langmuir, 1918). His model was based on the assumption of a monomolecular adsorbed layer with singular molecules adsorbed at singular sites on the surface. He visualized adsorption equilibrium as a dynamic process: The gas molecules strike the surface; most become adsorbed and stay on the surface for awhile; then they acquire enough energy to leave the surface. At equilibrium, the amount adsorbed has a definite value; therefore, the rate of adsorption must equal the rate of desorption.

The number of molecules striking a unit area of surface per unit time, μ , is given by the kinetic theory of gases:

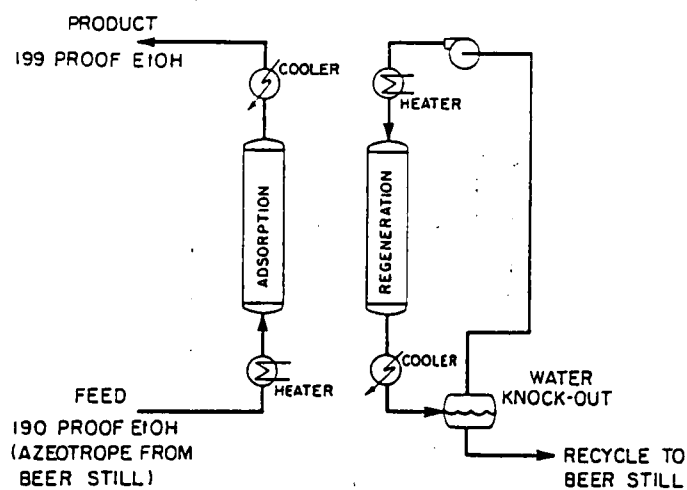


Figure 1. Inert-gas Purge Process for Removal of Water From Ethanol. (Garg, 1983).

$$\mu = P / (2\pi mkT)^{0.5} \quad (1)$$

Since the surface forces have a very short range, only molecules that strike a bare surface are adsorbed, whereas those that strike an already adsorbed molecule will be elastically reflected back into the gas phase. The rate of adsorption of molecules per unit area of surface is then :

$$Ra = \alpha(1 - \emptyset)\mu \quad (2)$$

Where $\emptyset$ is the fraction of surface covered with adsorbed molecules and α is a "condensation coefficient" (the ratio of the inelastic collisions resulting in adsorption to the total number of collisions of gas molecules with the surface) on the bare surface.

The number of adsorbed molecules evaporating from unit area of surface per unit time, v , is dependent on the energy of binding between the molecules and the surface :

$$v = k_0 \exp(-q / kT) \quad (3)$$

If q is the heat evolved when a molecule is adsorbed, then only those molecules that acquire an energy quantity equal to or greater than q will be able to desorb. The term k_0 is a constant dependent on the

entropy of adsorption. Therefore, the rate of desorption per unit area of surface is given by :

$$R_d = \nu \emptyset \quad (4)$$

At equilibrium, the opposing rates must be equal :

$$a(1 - \emptyset)\mu = \nu \emptyset \quad (5)$$

solving for $\emptyset$ gives the Langmuir equation :

$$\emptyset = (a\mu / \nu) / (1 + (a\mu / \nu)) \quad (6)$$

which can be written as :

$$\emptyset = bP / (1 + bP) \quad (7)$$

where :
$$b = a \exp(q / kT) / k o (2\pi m k T)^{0.5} \quad (8)$$

Because elastic collisions with the bare surface are rare, the value of a is close to unity. Langmuir considered b a constant, which is equivalent to considering ν constant. This implies a constant free energy of adsorption, and is a correct assumption if the free energy of adsorption does not vary with $\emptyset$ (Flood, 1967). Therefore, equation (7) can be linearized by letting $\emptyset = V / V_m$, the fraction of surface

covered by adsorbate, where V is the volume of gas adsorbed at the equilibrium pressure P , and V_m is the volume of gas necessary to cover the entire surface with a complete adsorbed monolayer. Upon substituting into (7) :

$$V = V_m bP / (1 + bP) \quad (9)$$

At low pressures or in the low adsorption region, bP , can be neglected in comparison with 1 in the denominator, therefore :

$$V = V_m bP \quad (10)$$

The amount adsorbed becomes directly proportional to the pressure, i.e., the adsorption obeys Henry's Law.

In the high-pressure or high adsorption regions, 1 can be neglected in comparison with bP in the denominator and :

$$V = V_m \quad (11)$$

The amount adsorbed becomes independent of pressure. This is seen as saturation is approached.

In the intermediate range, the complete equation must be used and (9) can be linearized :

$$P/V = 1/V_m b + P/V_m \quad (12)$$

Where a plot of P/V vs P should give a straight line and the constants V_m and b .

Similar derivations of Langmuir's model have originated from the law of mass action, from the theory of absolute reaction rates, statistical thermodynamics, and from the Maxwell-Boltzmann distribution law (Young, 1962; Flood, 1967). There have since been many analogues of Langmuir's original model, each taking into account something different to better describe the experimental results obtained and overcome the very limiting Langmuir assumptions. These modifications provided for multi-molecular layers, mobile monolayers, two dimensional adsorption, and heterogeneity of the adsorbent surface including porous surface layers and capillary effects (Young, 1967).

2. BET Model. In 1938, Brunauer et al. (1938) overcame some hindering mathematical difficulties to develop a practical equation for multimolecular adsorbed films, and thus, the next step in adsorption theory was taken. They discarded Langmuir's unimolecularity

assumption and postulated that molecules in the vapor phase can be adsorbed on top of already adsorbed molecules. They did retain the rest of Langmuir's concepts of adsorption and assumed that each adsorbed layer obeyed a Langmuir equation. They derived 2, 3, and 4 parameter model equations. The linear 2 parameter model is given :

$$x / V(1-x) = 1/V_m C + (C-1)x/V_m C \quad (13)$$

where a plot of $x/V(1-x)$ vs x should yield a straight line and the constants C and V_m .

The five types of isotherms observed (shown in Figure 2) have been classified by Brunauer et al., in 1940. Type I is the well known Langmuir adsorption isotherm for an adsorbed monomolecular layer. Type II is the s-shaped or sigmoid type isotherm, which is the typical isotherm found for the adsorption of water on polysaccharide adsorbents. Type III isotherms describe cases where the heat of adsorption is less than the heat of liquefaction, or the attraction forces between the adsorbate and the adsorbent are less than the attraction forces between the molecules of the gas in the liquefied state, opposite that of Type II isotherms. Types IV and V are cases that relate capillary condensation since they level off as the saturation pressure of the adsorbate vapor is reached. Cellulose exhibits a type II

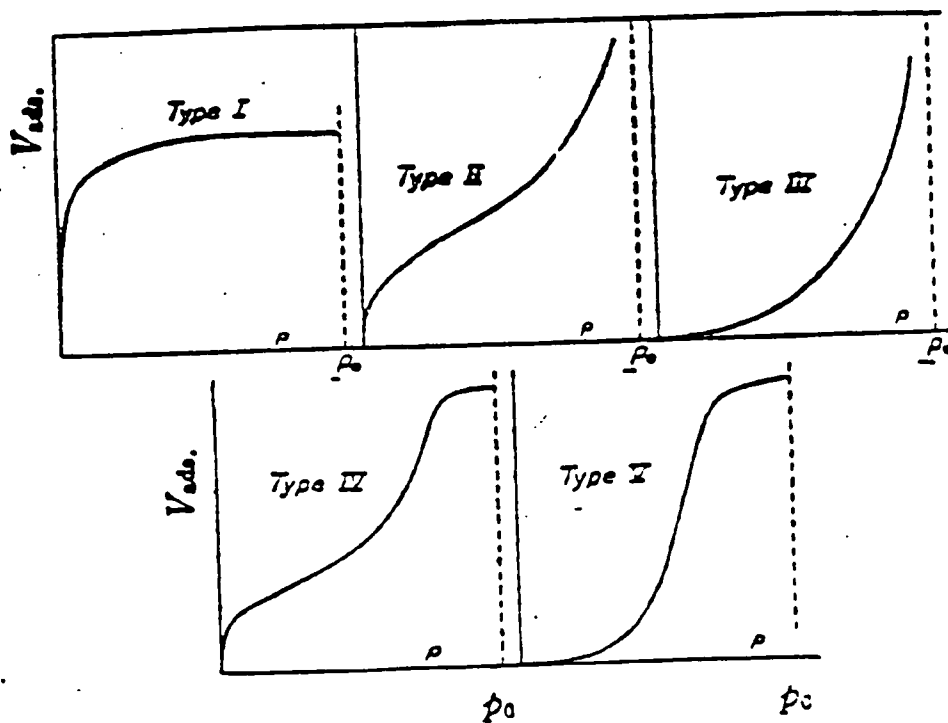


Figure 2. The Five Types of van der Waal's Adsorption Isotherms.

isotherm when adsorbing water vapor. A brief discussion describing this curve is given.

The Type II curve is divided into three regions. The first region goes from 0% to about 10% relative humidity and represents the range of partial pressures required to form a monomolecular layer of water molecules on the available surface, presumably, held on the surface by each polar (OH) group; the curve shows rapid uptake which is readily reversible. The formation of some secondary layers may also occur before the first layer is completed. This part of the curve generally follows Langmuir's or the extension of Brunauer, Emmett, and Teller's equation.

The second, practically linear region of the sigmoid curve, extends roughly from 10% to 50% relative humidity. The straightness of the curve demonstrates the proportionality between adsorption and pressure; however, whether this implies the gradual completion of the surface-bound layer (monolayer) with gradually decreasing attraction; the build-up of several layers; or the filling of narrow crevices and interstices of gradually increasing spacing or radius, assuming swelling produces new surfaces, is not clear.

The final region from about 50% relative humidity to saturation, where the linear part of the curve gives way to a rapid curvature upwards, represents the filling up of intercrystalline crevices, canals, and capillary spaces as the cellulose swells as attraction forces between the cellulose chains are overcome (Ward, 1955).

Brunauer et al., in 1940, extended their previous equation (13) to describe all five types. Their basic theory has been modified and extended by several authors (Young et al., 1962) who have noted that there are some problems concerned with it, such as negative surface tension at $P=P_0$ due to a disregard of interaction forces, questions as to whether or not the adsorbed phase is liquid-like, and the heat and entropy contributions predicted by the BET are only in semi-quantitative agreement at best. However, the BET theory is still useful today for describing some adsorption results. The classification scheme is still widely used even though the theory does not provide a complete description of all observed adsorption isotherms.

C. Adsorption/Desorption and Hysteresis Involving Cellulose

Since cotton (cellulose) is such an integral part of the textile industry, its adsorption/desorption characteristics have been studied for quite some time. The first precise work on cellulose was done by

Williams and Urquhart in 1924 (Urquhart, 1924). In a series of papers, they set down their studies of raw and soda-boiled cotton at 20 and 25 °C respectively. These studies led to several important observations concerning water uptake in cellulose. It was noted that pretreatment of the material had a significant effect on the amount of water which could be adsorbed. Pretreatment is defined as the type of heating and deformation the material had undergone prior to exposure to a humid atmosphere. Second, the hysteresis effect was definitely established as a property of cellulose during adsorption; more will be said about the hysteresis effect later.

Pidgeon and Maass measured adsorption and desorption of water on coniferous woods and cellulose in the temperature range of 12 to 42 °C (Pidgeon, 1930). Their data showed the typical s-shaped curve of a Type II adsorbing vapor, see Figure 3. They indicate three areas of interest on the curve. The first 1-2% of water is highly adsorbed causing a lowering of partial pressure which brings about a flattening of the isotherm curve near the origin. Between 2 and 10%, the curve is essentially a straight line indicating adsorption is proportional to pressure. As saturation is approached, the curve begins to flatten out again and becomes parallel to the adsorption axis, showing that a small increase in partial pressure will cause a large increase in

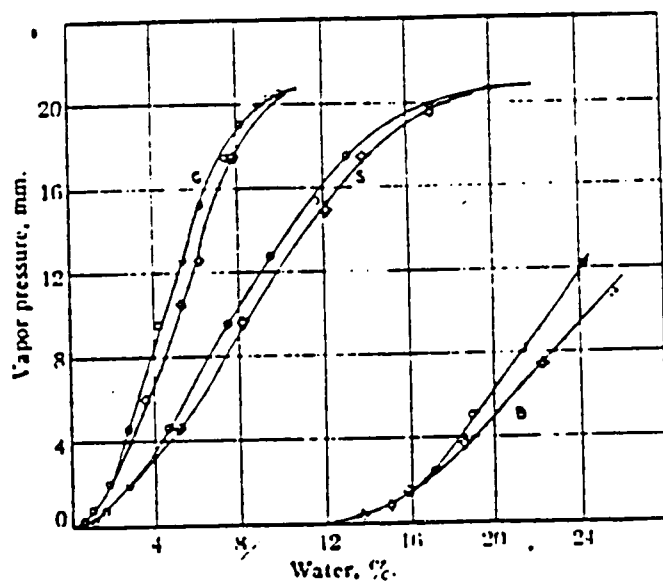


Figure 3. Adsorption Isotherm at 23°C, C, cotton cellulose; S, spruce wood; B, S enlarged.

adsorption. They also compared adsorption by wood to gel absorption theory and found reasonable agreement.

The gel theory assumes that gels possess a heterogenous structure in which the actual gel particles or micelles are separated by ultra-microscopic spaces or capillaries. When the dry gel is brought into contact with an adsorbing vapor, the vapor quickly adsorbs to the large internal surface of the structure. As the partial pressure of the adsorbate is increased, liquid adsorbate begins to appear in the capillaries. If the gel is the non-swelling type, adsorbate uptake is continued at a constant vapor pressure until saturation is reached. If the gel swells when adsorbate is added, the micelles move apart increasing the size of the intramolecular spaces causing an increase in partial pressure, thus a swelling gel takes up water with an increase in partial pressure until saturation is reached. The hysteresis effect was also observed.

Much of the previous work has been continued and enhanced by Sheppard, Maass, Campbell, and others (Maass, 1935; Russell, 1937; Sheppard, 1964). Babbitt used the then new BET theory to analyze the adsorption of water vapor by cellulose (Babbitt, 1942). He related the previous work mentioned to his own and concluded that the s-shaped adsorption isotherm could be explained by several mechanisms :

1. at low humidities, adsorption occurs in monomolecular layers obeying Langmuir's equation.
2. between 20 and 80 % relative humidity, adsorption agrees with the polymolecular layer BET equation.
3. between 80 % relative humidity and saturation, it appears that capillary adsorption is predominant.
4. the heats of adsorption for cotton and wood do not differ appreciably.
5. there is an increase in internal energy of the adsorbed state as adsorption takes place.
6. the swelling of the cellulose and the increase in internal energy of the adsorbed state might be accounted for by the two hydrogen bonds formed between the water and cellulose molecules.

Several other authors have developed general isotherm equations for the adsorption of water vapor by cereal grains and other farm products (Henderson, 1957; Chung, 1967). Henderson's equation is of particular use. His empirical equation is in exponential form with two constants k , and n that vary with the material used as adsorbent :

$$1 - rh = \exp(-kTM^n) \quad (14)$$

He derived (14) by a rigorous thermodynamic method from the Gibbs relationship :

$$\partial\sigma / \partial v = -(\partial P / \partial s)_T \quad (15)$$

Which relates the surface tension of the adsorbed liquid and liquid volume to the wetted solid surface and osmotic pressure.

The equation is capable of extrapolating limited data to other relative humidities and moisture content, to determine the temperature effect upon the relative values of moisture content and relative humidity, and to provide a complete isotherm from a minimum of two observations. Henderson calculated values for the constants k and n for seventeen various farm products. For cellulose, the values are $k = 0.0000491 \text{ K}^{-1}$, $n = 1.70$ at 77°F . The calculated and observed points for each isotherm showed good agreement. Henderson's equation will be used to model the data obtained in these experiments for the adsorption/desorption isothermal curves.

Since the early 80's, there have been several studies with cellulose and farm products used as adsorbents for the separation of the water/ethanol azeotrope (Bienkowski, 1986; Hong, 1982; Ladisch, 1983, 1984; Neuman, 1986; Pitt, 1983). All have shown that the use

of farm products as adsorbents is a viable means of azeotropic separation of organic streams.

From Figure 4, the spatial arrangement of cellulose can be seen and how the long, thread-like chains are possible. It also shows the spatial distribution of the hydroxyl groups allowing for the chains to combine laterally through hydrogen bonding. This bonding can be so regular and organized that cellulose gains the appearance of a crystalline structure. This crystalline structure does not appear throughout the cellulose chain however. Small, not-crystallized amorphous regions are also dispersed throughout the chain. When the cellulose is crystallized along several chains, the interstitial spaces that result between the chains are the proper size to allow sorption of water molecules. Sorption is being defined here as the molecular diffusion of the water molecules through the bulk gas to the cellulose surface, being adsorbed onto the surface and then diffusing into the interstitial spaces (Honeyman, 1959). This is slightly different from adsorption, which is the selective concentration, by diffusion through the bulk gas phase, of the water to the cellulose surface and being adsorbed there.

The driving forces for sorption are represented in Figure 5. C to C_1 is the concentration difference from the bulk gas phase to the

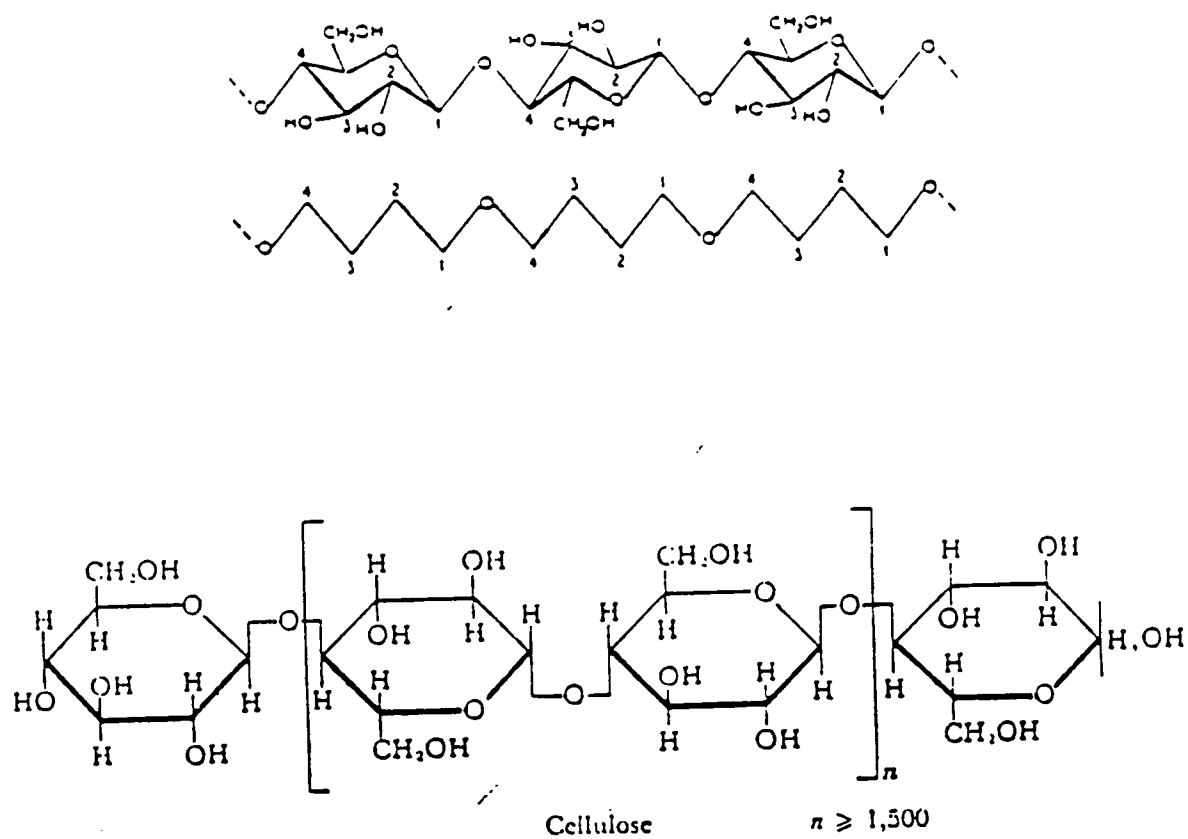


Figure 4. Spatial Arrangement of Cellulose. (Honeyman, 1959).

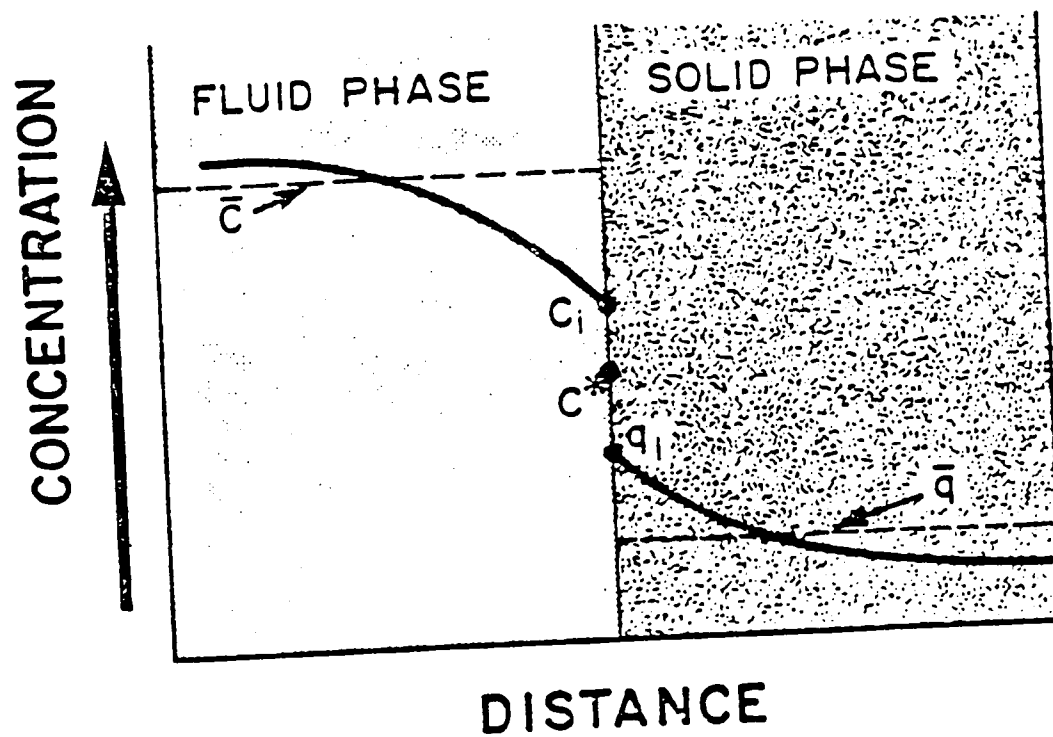


Figure 5. Concentration Profiles at the Gas/Solid Interface.

gas/solid interface. C^* represents the adsorbate concentration in the gas phase, at the interface, in equilibrium with an average adsorbate concentration in the bulk solid, q . The second driving force is represented by the difference q_i to q ; the concentration of the adsorbate in the solid phase at the interface to the average adsorbate concentration in the bulk solid phase.

As noted previously, the water vapor/cellulose system exhibits a hysteresis effect. This effect can be described as the amount of adsorbate in the vapor phase, in equilibrium with a given adsorbate concentration on the adsorbent, is greater on adsorption than desorption, or the equilibrium partial pressure differs depending on whether adsorption or desorption is taking place for the same moisture content. See Figure 6. Several authors have proposed explanations for hysteresis in cotton (Chung, 1967; Newns, 1959; Sheppard, 1934; Treyball, 1980; Urquhart, 1930; Wahba, 1975; disagreement over this phenomenon is a major concern that has to be solved in adsorption systems (Watt, 1980).

One of the first and most favored explanations is the one given by Urquhart and Eckersall (Urquhart, 1930). They attribute the effect to the change in availability of the polar hydroxyl groups of the cellulose chain, which are believed to bond the water through hydrogen

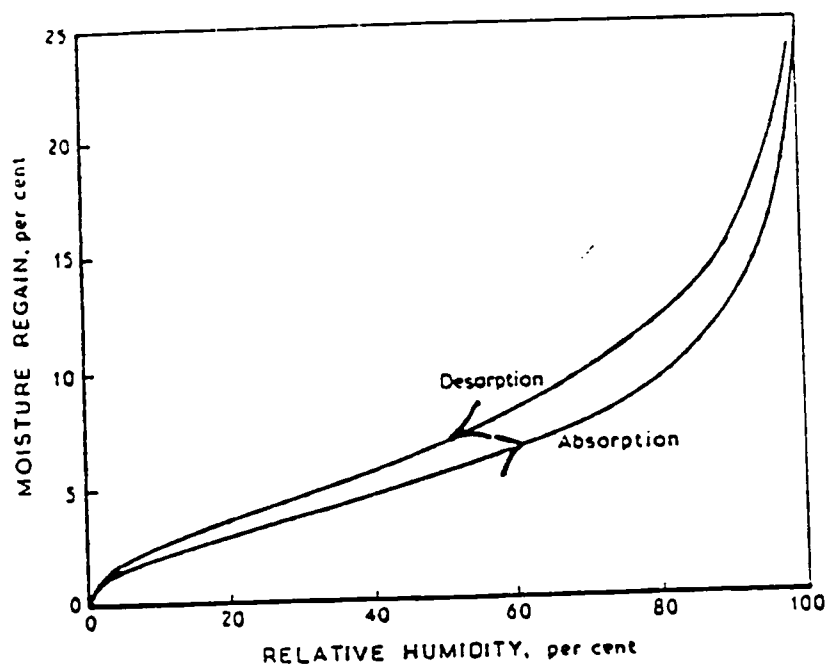


Figure 6. Adsorption Isotherm Showing Hysteresis Loop.

bonding. If the cellulose is wet initially, the hydroxyl groups (OH) of the chain are almost entirely saturated with attached water molecules. When the cellulose is dried (desorbed), a number of the hydroxyl groups are freed, and as shrinkage occurs, they are drawn close enough together that their residual valencies satisfy each other. Upon subsequent adsorption, part of the hydroxyl groups that mutually satisfy each other are not freed for water adsorption, thus resulting in a decreased amount of adsorbed water and hysteresis.

III. EXPERIMENTAL WORK

A. Objectives

The objectives of this work were to obtain the adsorption/desorption isotherms from the constant pattern breakthrough curves, then calculating certain mass and heat transfer characteristics for the water vapor/cellulose system at temperatures between 60-100 °C. Little work has been done at these higher temperatures involving cellulose (Urquhart, 1924). This temperature range could become important if adsorption is coupled with another separation process, such as distillation.

B. Experimental Apparatus

An experimental apparatus was designed and constructed to provide a dynamic means of measuring the adsorption and desorption isotherms of the water vapor/cellulose system. This dynamic method will allow measurement of the rate at which adsorption takes place. The design is a second generation modification of a system previously developed by Dr. Paul Bienkowski et al. (Ladisch, 1984), who adapted their system design from Michaels et al. (1952). Figure 7 shows the apparatus and its component parts : N₂ supply tank, mass flow

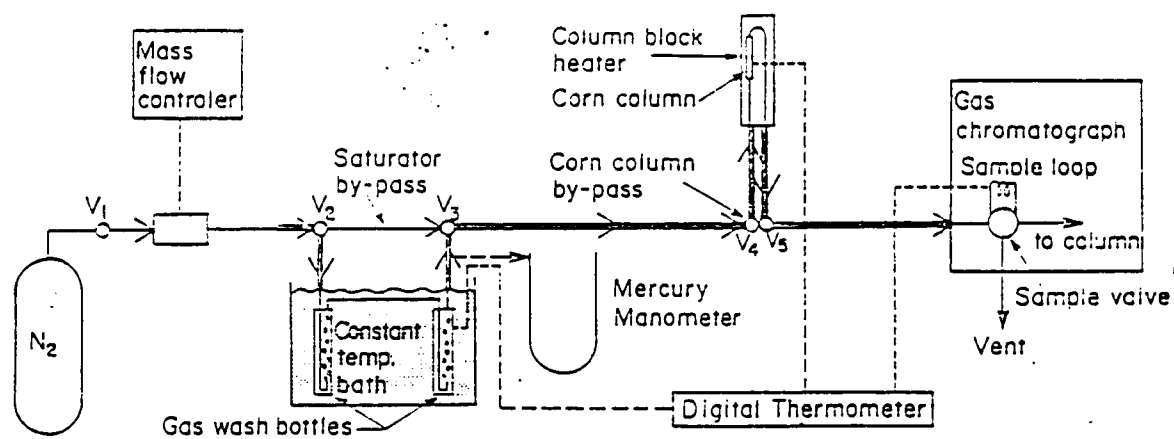


Figure 7. Original Dynamic Adsorption Apparatus.

controller, saturator bath and wash bottles, column, and gas chromatograph (GC).

Figure 8 shows a schematic diagram of the experimental apparatus used for this work, Table 1 gives a list of major equipment components. The carrier gas, nitrogen, was saturated with water by passing it through three gas wash bottles in series, two filled with double distilled, deionized water and the third with glass wool to act as a detainer. The gas washing bottles were submerged in a water bath which was kept at constant temperature with an immersion circulator.

The carrier gas flow rate was controlled with two mass flow controllers, MFC-1 and MFC-2. A modification to the Bienkowski system was the addition of the second mass flow controller, MFC-2, note Figure 8, to the saturator effluent stream to regulate the saturation (humidity) level entering the column. This eliminated the need to change the temperature of the saturator water bath when alterations in the saturation level were required, thus decreasing overall experimental run time.

With the partial pressure of the water vapor leaving the saturators fixed by the temperature of the water bath and atmospheric

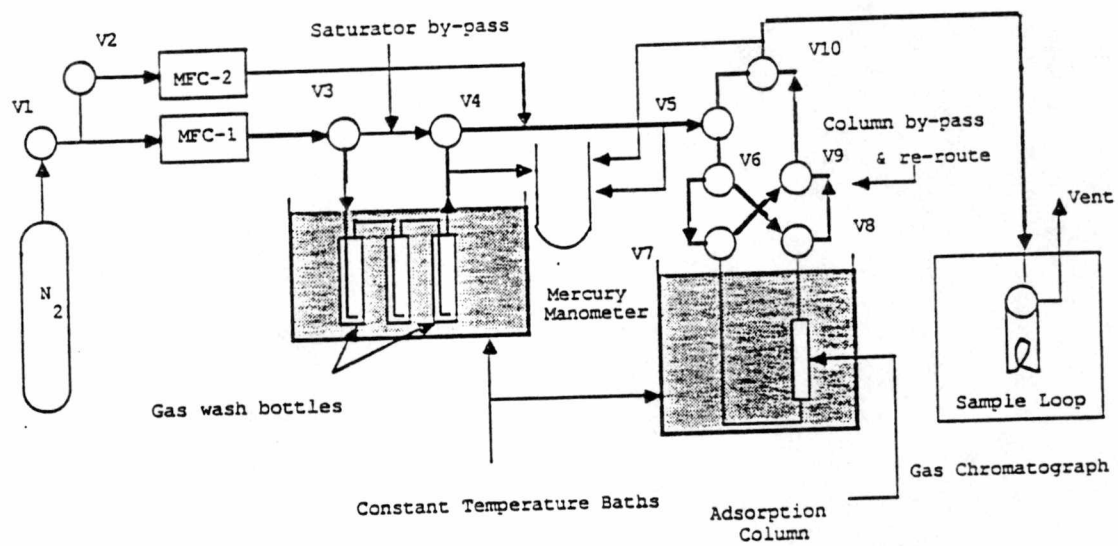


Figure 8. Modified Dynamic Adsorption Apparatus.

TABLE 1. EQUIPMENT LIST FOR ADSORPTION APPARATUS

Quantity	Item	Description
2	Immersion Bath Heaters/ Circulators	Haake Model #E3 25-140 °C
2	Mass Flow Controllers	Brooks Model 5850C
1	Analytic Balance	Mettler AE 163
3	Gas Wash Bottles	Ace Glass 40/35 25-50 Frit Pore Dia
1	Gas Chromatograph	Varian Vista 6000
1	Gas Chromatograph Column	Porapak N 80/100 2m*1/8 in. SS
1	Reporter Integrator	Hewlett Packard 3390A
1	Precision Thermometer	Fisher Scientific
1	Mercury Barometer	
3	Heating Tapes	
2	Water Bath	40L Fish Tank and 20L Insulated Vessel
10	Whitey Directional Valves Assorted Pieces of Stainless Tubing	1/8" and 1/4" Dia.

pressure, the flow rate for MFC-1 was set. The desired saturation level was obtained by adding pure nitrogen through MFC-2. The nitrogen, saturated to the desired level with water vapor and heated in a copper coil in the saturator bath, was then fed into the column. All the connections between the saturators and the column were traced with heating tapes to avoid condensation as well as to keep the gas at the saturator temperature.

The adsorbent was packed in a stainless steel column (1.26 cm o.d. x 25.5 cm) by tapping on the side of the column, while rotating it, after each incremental addition of cellulose. Two different columns were alternated throughout the experiments, one being dried while the other was in use. The column effluent was fed into a gas chromatograph (GC), where it was passed through a packed column (Porapak N) to separate the constituents of the effluent. The resulting signals from the thermal conductivity detector (TCD) in the GC were then output through the reporting integrator. An analytical balance was used to determine the weights of the columns after each run. All the exposed tubing and connections from the column to the GC were wrapped with heating tapes to avoid condensation.

The α -cellulose, trade name Avicel (Sigma Chemical Co., St. Louis, MO), used during the experiments was of a consistent nature (99.5 % pure) to eliminate inconsistencies that have been found in previous work due to variable cellulose content. The cellulose has a bulk density of 0.1445 g/cm³ and an average particle size of 180 microns. The cellulose should not be permanently affected by the column temperatures used. Cellulose does lose some water of constitution at temperatures of 105 °C and higher, but only after prolonged exposure (Stamm, 1964). The cellulose, during these experiments, was exposed for only a few hours to temperatures less than 91 °C. The water adsorbed by the cellulose should cause its strength properties to decrease, but because it is not in contact with the water vapor for a great length of time, there should be no permanent change (Stamm, 1964).

C. Instrument Calibration

The two mass flow controllers were checked for accuracy of flow by connecting them in series to one another. The controller with a 0-50 sccm flow range (MFC-2) was first in the series, so that its outflow was the inflow of the 0-100 sccm range (MFC-1) controller (measured at a reference state of 21 °C and 1 atm). MFC-1 was opened all the way, but reading zero flow; MFC-2, connected to a

nitrogen tank with an inlet pressure of 60 psig, was opened to read 50 sccm or any flow designated. The flow reading of MFC-1 was then read and compared to the set flow of MFC-2. The comparisons of the readings were well within 1% of each other.

The controllers were then exchanged, with MFC-1 first in the series, and the same procedure repeated up to the limit of MFC-2 (50 sccm). Since the total flow through both controllers was never to exceed 50 sccm for any experimental run, MFC-1 (0-100 sccm) would never operate above 50 sccm and this process would establish the reliability of MFC-1 up to that point. Again, comparison of the set and reading controllers were within 1% . Because the comparisons were close, it was accepted that both controllers would give consistent flow readings.

Calibration of the gas chromatograph was attempted by two methods. The first was injecting a known volume of liquid water, by syringe, into the GC and noting the output on the HP integrator. This method turned out to be hard to reproduce due to "eyeing" the amount in the syringe and uncertain because the water was mixed with an alcohol for dilution, and the alcohol, being hygroscopic, had an ever changing water content depending on the atmospheric humidity. This method was discarded for these reasons.

The method used involved passing the carrier gas through the saturators at a specific flow rate (MFC-1), and saturator bath temperature, and passing pure carrier gas through MFC-2 to obtain a calculated relative humidity in the carrier stream. After allowing the system to stabilize, the stream was fed directly into the GC, and after obtaining several responses for the given conditions, using the average as the calibration point. By changing the flow rates of the flow controllers and the saturator bath temperature, the whole range of relative humidities (0-100%) could be obtained for use in calibrating the GC.

This method implied, however, an assumption that the nitrogen carrier stream was being fully saturated when passed through the gas wash bottles. To validate this assumption, the saturated carrier stream was passed through a Drierite-filled column for a specific length of time. The Drierite should adsorb all the water vapor in the carrier stream for the duration of the experimental run. The difference in weight of the column before and after the run should give the amount of water vapor that flowed in the nitrogen stream. This was checked against the calculated value assuming 100% saturation. Appendix A lists the raw data.

An advantage of doing the calibration as previously described is that the system is actually operated and any problems can be identified and corrected, and indeed problems were found. The first experimental runs through the Drierite column gave results that showed saturation of the nitrogen stream ranged from 17 to 123 %. Condensation was found in some of the stainless steel tubing; the scale used was found to be out of balance; the water level in the saturators and bath was low. The condensation problem was solved by adding heating tapes to the tubing not covered; a new balance was obtained that worked properly; the water level in the saturators and saturator bath was increased; the heating tapes and bath now covered all exposed tubing.

Additionally, at the higher flow rates, the nitrogen bubbled quite vigorously through the saturators, and it was thought the nitrogen stream might be entraining some of the saturator water. To solve this, the third gas wash bottle, filled with glass wool, was installed to act as a detrainer.

After fixing leaks at several connections and letting the system stabilize longer, consistent saturation results were obtained. These results were accepted as showing the assumption of saturation to be a valid one.

The results obtained, for the GC calibration, at one flow rate, were now consistent; however, when the flow rate was increased through the saturators, the results became erratic. As Figure 9 shows, the initial GC responses increased as the flow rate did, i.e., more water was found in the GC sample loop than could be accounted for due to saturation. Since the entrainment problem was thought to be solved, cooling of the sample loop by the saturated stream causing condensation and accumulation of water was thought to be the problem.

To increase the distance travelled by the saturated nitrogen stream within the GC before reaching the sample loop, thus adjusting its temperature to that of the GC; a 6 ft. coil of stainless steel tubing was attached before the sample loop and embedded in a beaker filled with crushed rock, see Figure 10. This solved the sample loop cooling problem. During the calibration procedures, it was noted that the two sample loops used were of differing sizes, thus necessitating two GC calibration curves. Figure 11 shows the resulting calibration plots used and Appendix A contains the data used. The variable R or R^2 in the Figure and in several Figures following is the correlation coefficient representing the fit of the model to the data points.

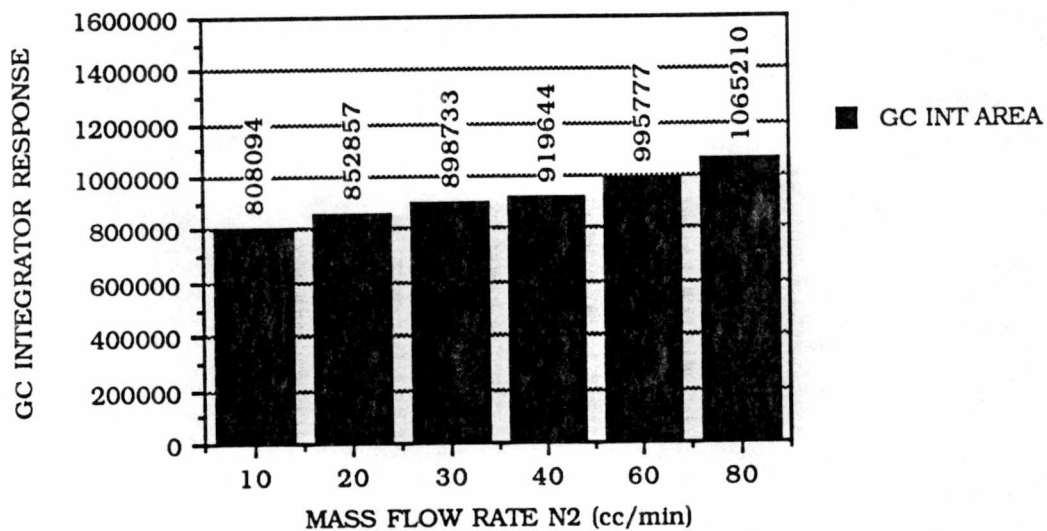


Figure 9. Initial GC Response to Change in Flow Rates.

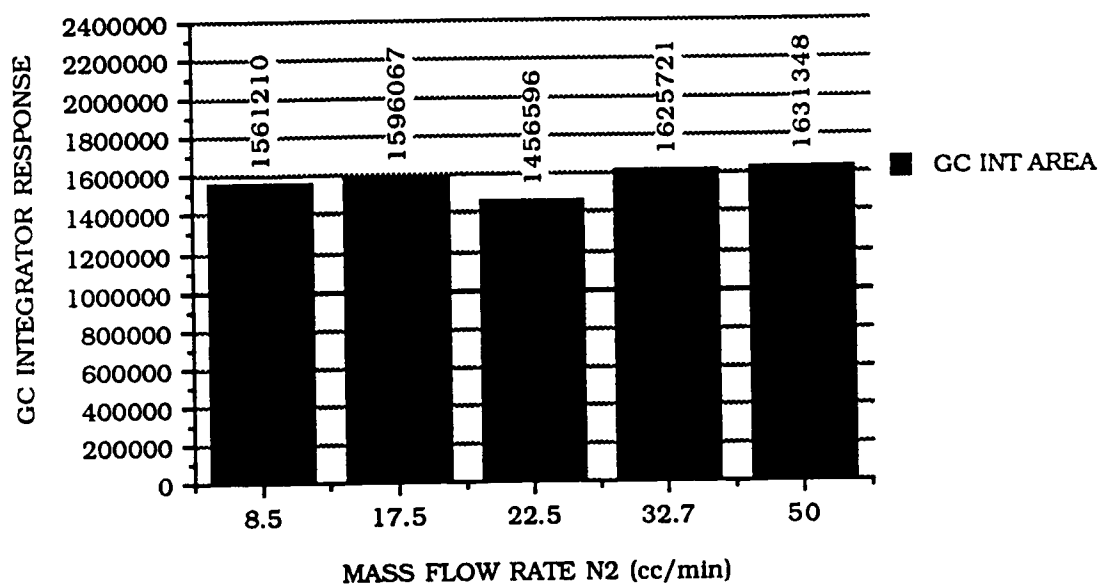


Figure 10. Final GC Responses after Corrective Actions.

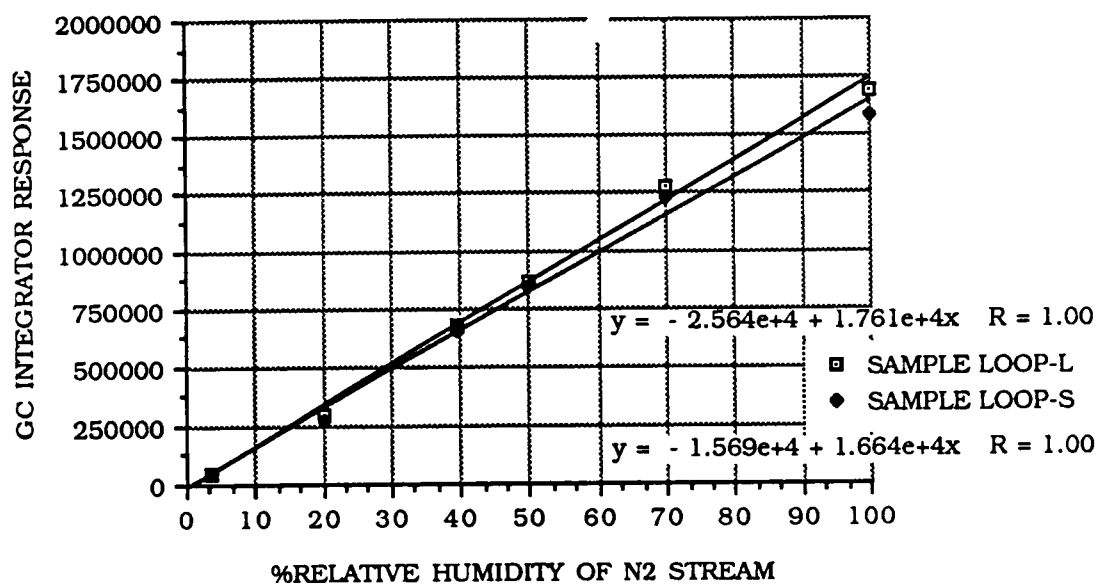


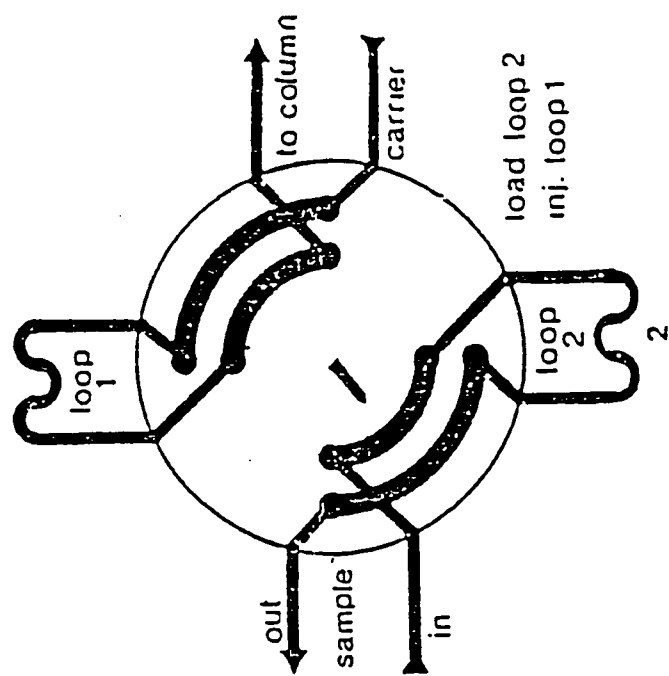
Figure 11. GC Calibration Plot.

Two sample loops were used in the GC because of the pressure pulses caused in the system with just one. The pulses adversely affected mass transfer of the water vapor to the cellulose. Figure 12 shows the sample valve used in the GC for these experiments.

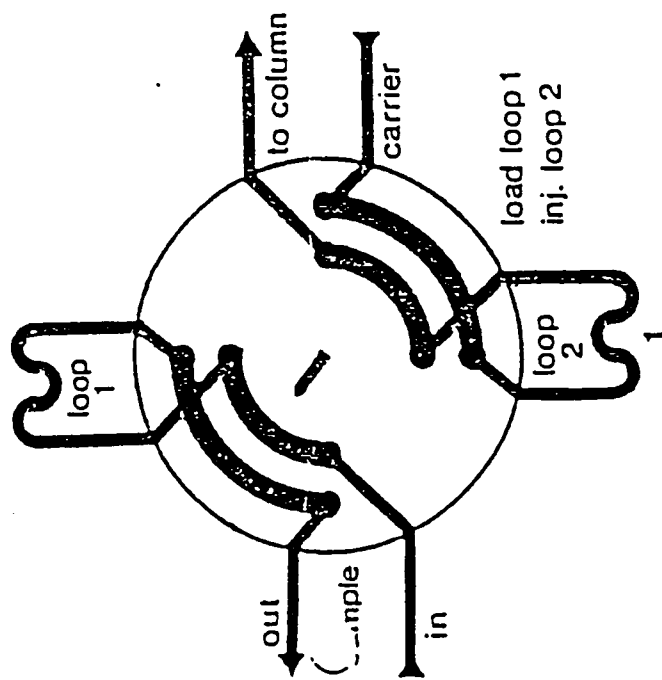
D. Experimental Procedure

Six points (% relative humidities) on three isotherms were taken during these experiment. The isotherm temperatures and thus the column bath temperatures were at 70, 80, and 90 °C. The relative humidities for each isotherm were approximately 10, 20, 40, 50, 70, and 100 %. The saturator bath was at 60 °C, except for the 10 % humidity point where it was 40 °C. Table 2 gives the flow rates and temperatures used to obtain these conditions.

The flow rates through both controllers, MFC-1 and MFC-2, varied according to the humidity level desired; however, the combined total flow through both was always 50 sccm. The reason for the 50 sccm flow was to keep the pressure drop across the column at a reasonable level. If the flow rate was too high, the pressure drop would become too great across the column, interfering with mass transfer of the water vapor to the cellulose. If the flow rate was too low, then measurement of the rate would be a problem. This is the reason for the saturator bath being decreased to 40 °C for the 10 % humidity



B



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Figure 12. Sample Loop Valve Design Used in the GC.

TABLE 2. APPARATUS OPERATING CONDITIONS.

% RH	Sat. Bath Temp., °C	MFC-1, sccm	MFC-2, sccm	Tot.Flow, sccm
10	40	5.0	45.0	50.0
20	60	8.5	41.5	50.0
40	60	17.5	32.5	50.0
50	60	22.5	27.5	50.0
70	60	32.7	17.3	50.0
100	60	50.0	0.0	50.0
12*	60	5.0	45.0	50.0

* The column regeneration isotherm used the 80 °C conditions for adsorption, and for desorption, 12 % humidity.

Note: 70 °C Isotherm

- Column Bath Temp. = 70 °C

80 °C/Regeneration Isotherm

- Column Bath Temp. = 80 °C

90 °C Isotherm

- Column Bath Temp. = 90 °C

point; the flow rate through MFC-1 would become too low to measure accurately at the saturator bath temperature of 60°C. By decreasing the temperature, the water vapor pressure decreased and allowed a higher flow rate through MFC-1 at this low humidity.

An experiment was started by setting the temperature of the two immersion baths, one which contained the saturators and the other the adsorption column, allowing four hours for stabilization. The two way valves were then positioned to by-pass the saturators and column, see Figure 8. The nitrogen flow rate through MFC-1 and MFC-2 was set to the values specified in Table 2. The flow of MFC-1 was then allowed to pass through the saturators until steady state was established; this was checked by direct analysis with the GC. Once the responses became uniform, the system had reached steady state, and they could be recorded as the column feed. The saturated nitrogen stream was now directed through the column.

Throughout each experimental run, the immersion bath temperatures and flow rates were continuously monitored. The flow meters were connected through their controller to a Keithely 195A Multimeter and 705 Scanner which were connected to an IBM PC Model XT. The bath temperatures were measured with hand held mercury thermometers and platinum resistant thermometers (PRTs)

which were calibrated by Mr. Vinod Shah and interfaced with the IBM PC.

Through software written by Mr. Shah, the IBM would continuously log the flow rates and temperatures during each experimental run. These data could then be checked at any time during or after completion of the experiment to note any changes.

At the same time the system was approaching steady state, the GC analyzer was doing the same. During calibration of the GC, the optimum operating conditions were determined. The GC separation column temperature was set at 150 °C, the thermal conductivity detector and the TCD filament were set at 200 and 250 °C respectively, the Helium carrier gas flow rate was set at 30 ml/min. The attenuation and range for the output signal were respectively set at 8 and 0.5, the HP integrator's operating parameters were set to receive the output signal.

The barometric pressure was recorded before, during, and after each experimental run. The pressure drops in the saturators and across the column were measured by the mercury manometers, see Figure 8. The pressure drop across the column was continually checked during all experimental runs because cellulose swells as adsorption takes place, causing increased bed length and thus

increased pressure drop. As noted previously, the pressure drop must not be allowed to reach a point (>5 psi) where it affects adsorption. This did not occur during any experimental run.

Once the GC and the flow system reached steady state, the column feed was recorded, and the column was weighed; then, the combined flow of MFC-1 and MFC-2 was directed through the column and the following measurements were taken as a function of time :

1. Saturator temperature
2. Adsorption column temperature
3. GC column temperature
4. Barometric pressure
5. Saturator pressure
6. Quantity of adsorbate leaving the adsorption column
7. Composition of stream leaving the adsorption column

The experimental run was terminated when the concentration of adsorbate in the nitrogen stream leaving the column approached the value obtained prior to passing the gas stream through the column, i.e., the column feed. The column was then taken off line (by-passed), and the quantity of adsorbate in the gas stream checked again with the GC to compare it with the value (column feed) obtained before the start of adsorption to check that no significant changes had occurred.

The adsorption column was then removed and weighed to get a second independent determination of the amount of adsorbate adsorbed.

The column was then put back on-line, but the valves were left turned so it remained isolated. The saturator valves, see Figure 8, were then turned so that MFC-1 flow by-passed the saturators to allow pure nitrogen to flow through the system, drying it. Once the system was dry (checked by getting no adsorbate response from the GC on the integrator) the column valves were turned to allow the dry nitrogen stream to pass down the column, in the opposite direction of adsorption, to desorb the column.

The desorption process was accomplished in the same manner as the adsorption step; the same information was recorded. Termination of the desorption run occurred when the integrator no longer registered adsorbate in the column effluent. The column was again isolated, removed, and weighed. The column was then put on a pure nitrogen drying line.

To do the next breakthrough curve, the second column, which had been drying with the pure nitrogen for +12 hours, was weighed and put on-line, but isolated. The saturator bath temperature was changed, if needed, and the flow rates were changed to get the

humidity level desired. The system was then allowed to come to steady state, and the process, previously described, was repeated for this new breakthrough curve, i.e., change in humidity.

An additional adsorption/desorption isotherm was done to see the effects of water vapor in the column regenerating gas during the desorption process. After completion of the adsorption phase, the column was desorbed with a regenerating nitrogen stream of 12 % relative humidity instead of 0% or pure nitrogen. The procedure was essentially the same except for setting the flow controllers to achieve 12 % relative humidity in the column influent instead of by-passing the saturators altogether for the desorption process.

F. Data Analysis

1. Breakthrough Curves. Figure 13 presents a typical constant pattern breakthrough curve obtained during these experiments. The data points (see Appendix C) represent the quantity of water which passes through the column versus time. Initially, the adsorption column is dry, so the cellulose adsorbs all of the incoming water. As the cellulose becomes saturated, some of the water begins to breakthrough the column, as seen by the increased water content of the effluent stream. When equilibrium is reached, the cellulose is saturated and the quantity of water leaving the column will equal the

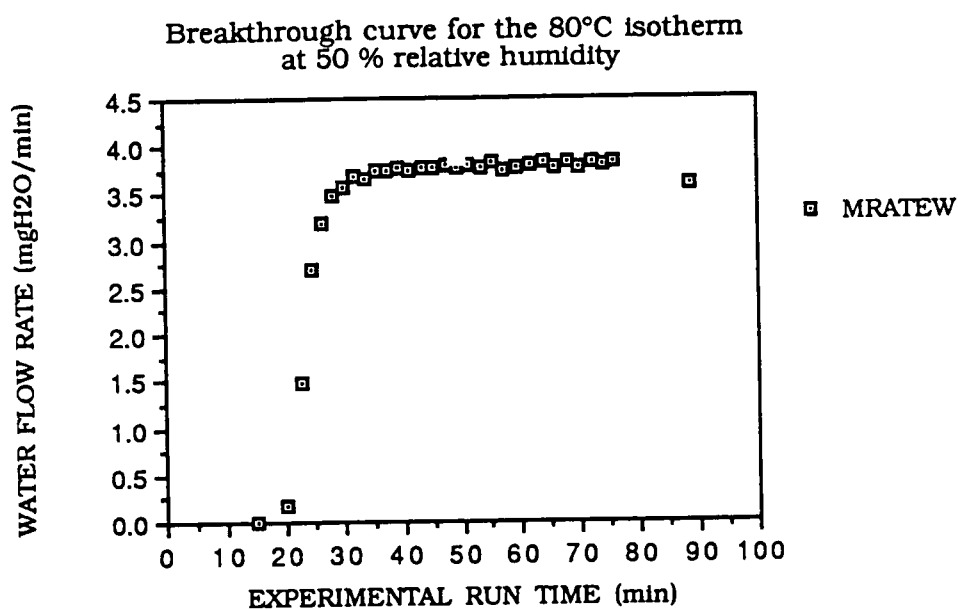


Figure 13. Typical Breakthrough Curve Obtained From the
Dynamic Adsorption Apparatus.

amount in the column feed. This is evidenced by the data points becoming tangential to the horizontal line representing the column feed, with the area between the two curves representing the amount of water adsorbed.

The breakthrough data were fitted to a function of the form :

$$X = F[1.0 - B\exp(-B1 \cdot RT/60) - C\exp(-C1 \cdot (RT/60)^2)] \quad (16)$$

which was chosen to satisfy the boundary conditions at breakthrough and exhaustion.

A Fortran program was written using a commercial regression package, **SAS** (1985), to perform the non-linear regression analysis on the breakthrough data using the model equation above and estimated initial parameters : B, B1, C, C1. See Appendix B. The analysis was performed using the Gaussian method of least squares to determine the four coefficients. Several guesses at the initial values were required on several of the breakthrough curves in order to get the best possible fit. Once the constants of the empirical equation were obtained for the given breakthrough data, the same run time values as the actual data were inserted into the model and plotted with the experimental values overlaid, as in Figure 14.

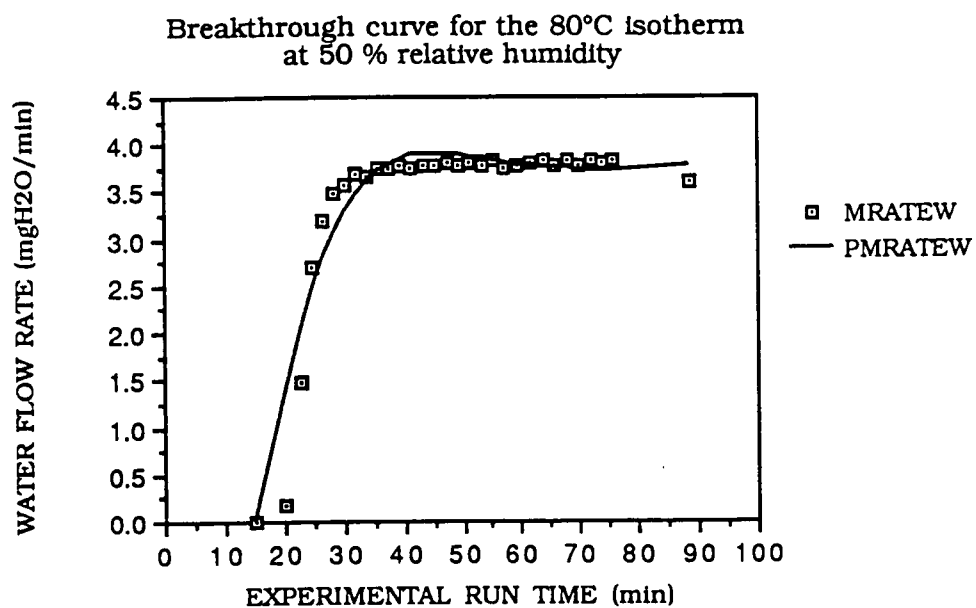


Figure 14. Breakthrough Curve from Figure 13 With Model Overlaid.

A typical desorption profile with the empirical equation overlaid is shown in Figure 15. The formula used was the converse of (16) :

$$X = F - B\exp(-B1 \cdot RT/60) - C\exp(-C1 \cdot (RT/60)^2) \quad (17)$$

Again, **SAS** was used to do the regression analysis to determine the constants for each breakthrough profile formula.

2. Adsorption/Desorption Isotherms. Once the adsorption and desorption model equations were obtained, they were integrated using a Fortran subroutine, QAGS, (see Appendix B) to obtain the areas under the curves. These areas, in turn, were subtracted from the areas under the column feed lines to obtain the amount of water adsorbed/desorbed to or from the cellulose. See Figure 16. These data was then plotted versus the equilibrium partial pressure of the water in the column feed to obtain the isotherm, as in Figure 17.

Henderson's equation (14) was used initially to model the isotherms and gave satisfactory results. The parameter n did not vary significantly with temperature while k was strongly temperature dependent. Therefore, equation (14) was modified much as Neuman et al. (1986) did where they assumed n is temperature and k can be expressed by an Arrhenius-type function of temperature. The modified Henderson's equation then :

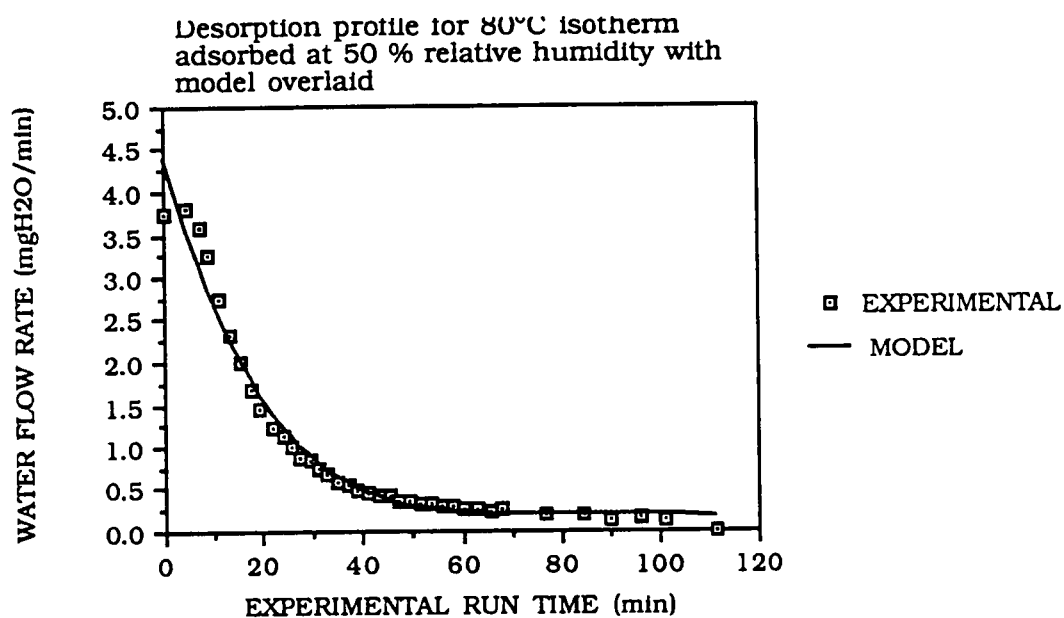


Figure 15. Typical Desorption Profile for the Cellulose/Water Vapor System.

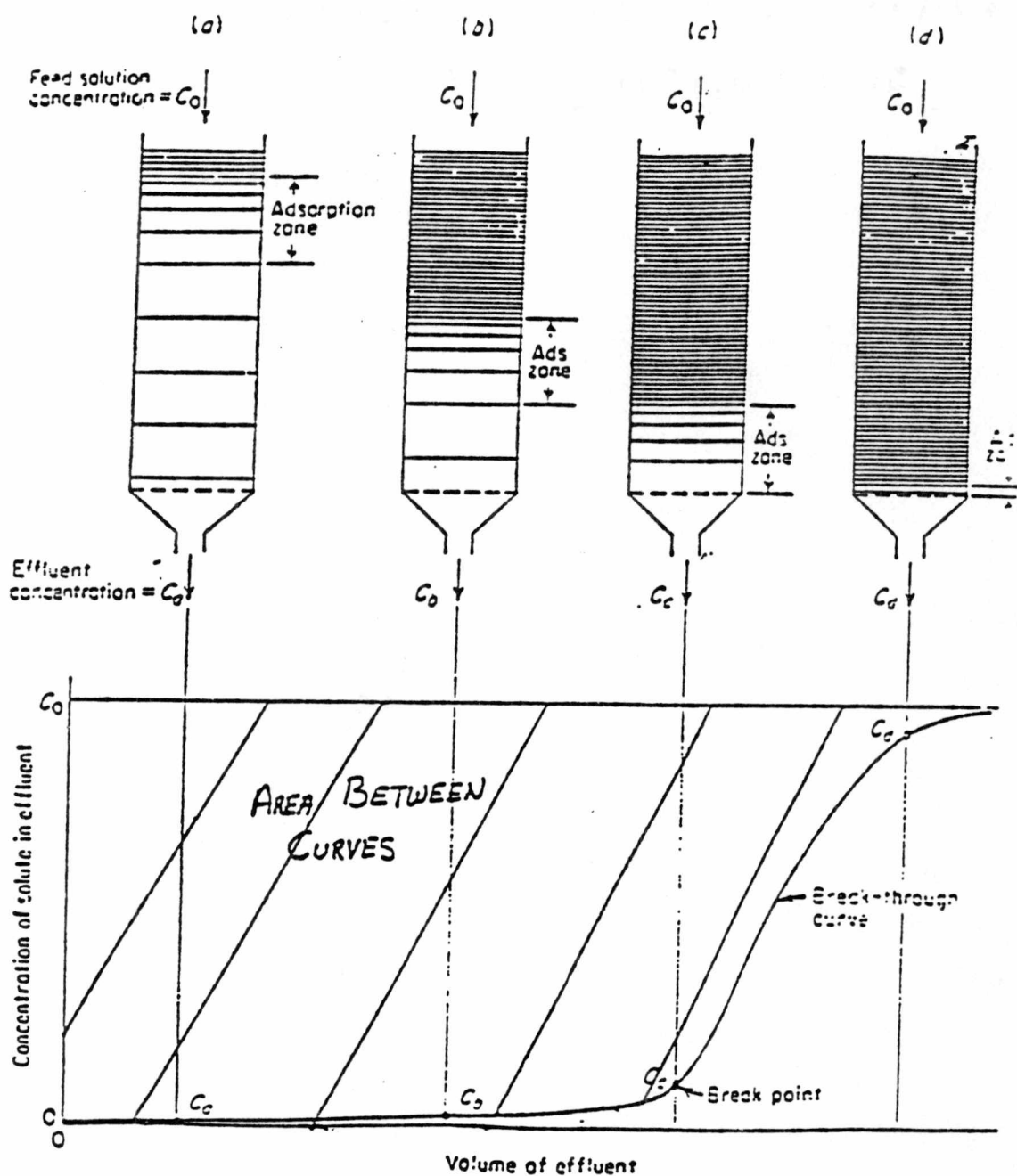


Figure 16. Areas Under the Curves Used to Calculate the Amount of Water Adsorbed by the Cellulose.

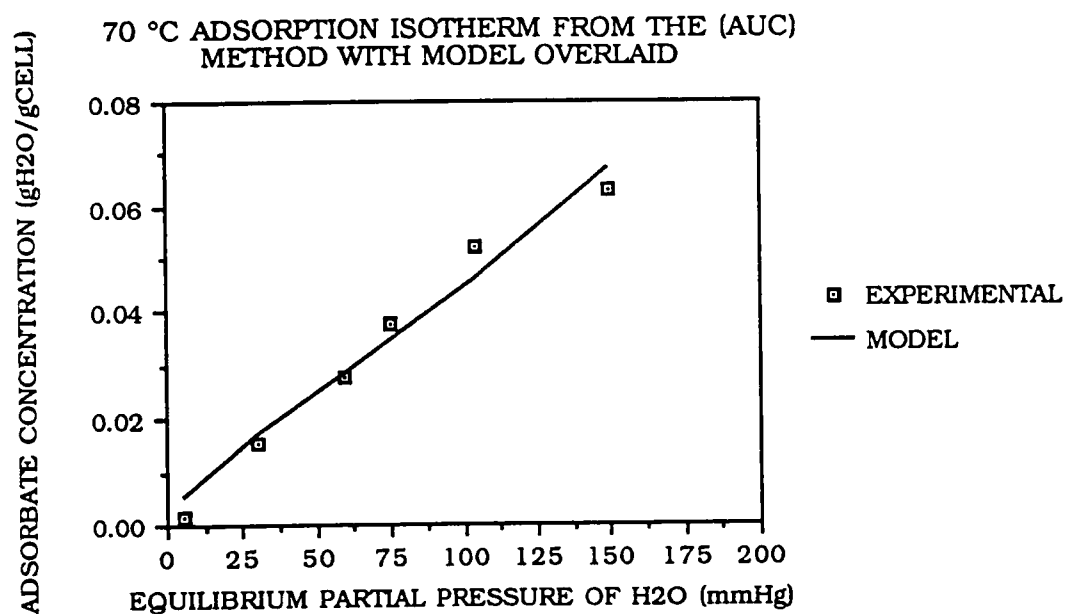


Figure 17. Isotherm Obtained from the Breakthrough Data.

$$\ln(1 - p^*/P) = [-kT][M^n] = [-k_0T\exp(-E/RT)][M^n] \quad (18)$$

which can be rearranged to give :

$$Z = 0.01M = 0.01[-\ln(1 - p^*/P) / k_0T\exp(-E/RT)]^{1/n} \quad (19)$$

Use of equation (19) allowed all of the experimental data obtained at different temperatures to be fitted with one correlation, again using the **SAS** regression routine to get the constants k_0 , E , and n . See Appendix B.

The preceding discussion concerns deriving the adsorption/desorption isotherms from the experimentally obtained points via the GC response (breakthrough curve). The isotherms were also determined by an independent method, column weight difference before and after each experimental run. See Appendix C. The weight difference was then divided by the total amount of cellulose in the column to get the equilibrium concentration of water adsorbed by the cellulose. This was then plotted versus the equilibrium partial pressure of the water vapor in the column and the modified Henderson's equation (18) fitted to the isotherm, exactly as described before.

3. Heats of Adsorption. The differential heats of adsorption were calculated by plotting isosteres. The data for the isosteres were generated by using equation (19) and the regressed constants k_o , E , and n to calculate values of p^* and P as indicated in Figure 18. The differential heat of adsorption, $-H$, can then be calculated via equation 11.1 from Treybal (1980) :

$$-H = -\gamma(P / p^*)(dp^* / dP) \quad (20)$$

where the slopes of the isostere lines in Figure 18 represent dp^*/dP . The latent heats of condensation, γ , for water at the three isothermal temperatures of 343, 353, and 363 °K used in equation (20) are respectively : 10.04, 9.94, 9.83 kcal/mol. (Perry, 1984). Table 3 shows the data used in equation (20) for the prediction of the differential heats of adsorption.

4. Height of the mass transfer zone. The mass transfer or exchange zone is defined, for these experiments, as the region of the bed within which the water vapor concentration in the nitrogen carrier stream flowing through the bed falls from 95 to 5% of its influent value. The concentration limits chosen to define the zone are arbitrary and are based on past use in other adsorption experiments.

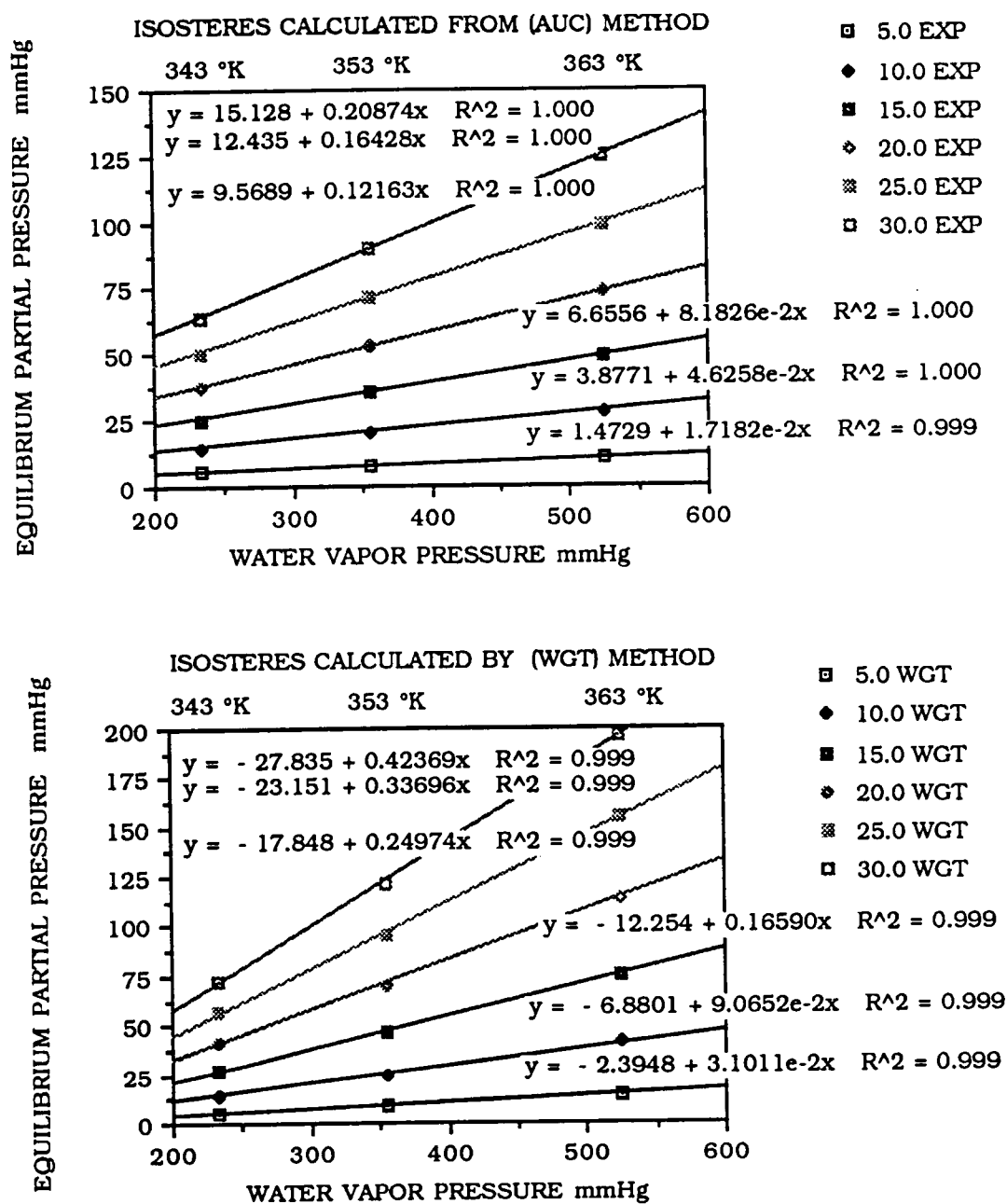


Figure 18. Isosteres for Water-Cellulose System Calculated by Using Equation (20).

TABLE 3. HEAT OF ADSORPTION DATA.

Area-under-the-curve isosteric points (AUC)

Z mgH ₂ O/gCell	70°C p*mmHg	80°C p*mmHg	90°C p*mmHg
5.0	5.45	7.64	10.48
10.0	14.59	20.47	28.13
15.0	25.61	36.00	49.56
20.0	37.75	53.18	73.35
25.0	50.50	71.33	98.58
30.0	63.51	89.94	124.60

Weight difference isosteric points (WGT)

Z mgH ₂ O/gCell	70°C p*mmHg	80°C p*mmHg	90°C p*mmHg
5.0	4.95	8.45	13.98
10.0	14.58	24.84	40.98
15.0	27.00	45.83	75.32
20.0	41.21	69.65	113.96
25.0	56.48	94.99	154.65
30.0	72.22	120.84	195.68

P/p* for AUG and WGT Methods

343°K		353°K		363°K	
AUC	WGT	AUC	WGT	AUC	WGT
42.48	47.21	46.48	42.02	50.17	37.61
16.02	16.03	17.35	14.30	18.69	12.83
9.13	8.66	9.86	7.75	10.61	6.98
6.19	5.67	6.68	5.10	7.17	4.61
4.63	4.14	4.98	3.74	5.33	3.40
3.68	3.24	3.95	2.94	4.22	2.69

From Figure 19, the breakthrough point, designated at the 5% value of the water concentration in the influent, and the exhaustion point, designated at 95% of the water's value in the influent, are shown on a typical s-shaped breakthrough curve. If conditions within the zone remain unchanged with time, then the s-curve should give a true picture of the water concentration variation across the exchange zone.

The time, Θ_z , required for the exchange zone to move its own height down through the bed under steady state conditions is proportional to the volume of effluent, V_z , see Figure 19 :

$$\Theta_z = V_z / (U_g * A_t) \quad (21)$$

The time, Θ_t , required for the zone to establish itself at the top of the bed and to move down out of the bed is proportional to the total volume of effluent, V_t , see Figure 19 :

$$\Theta_t = V_t / (U_g * A_t) \quad (22)$$

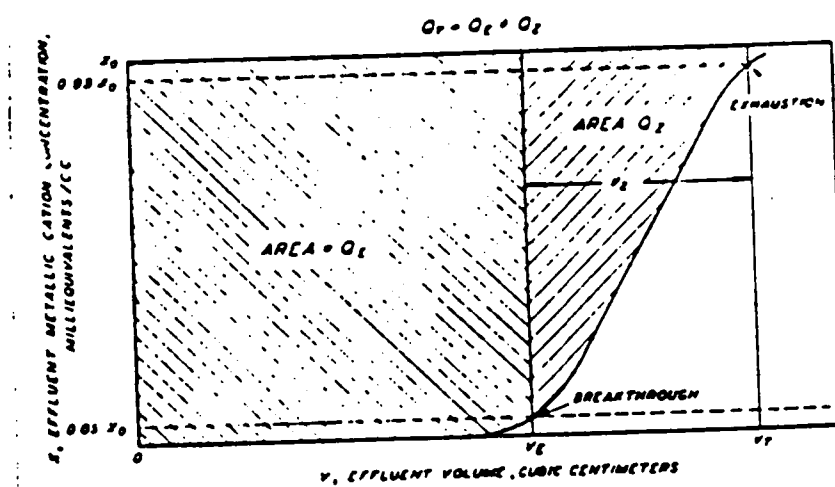


Figure 19. Breakthrough Curve Showing Representative Volumes : V_z ,
 V_t , V_e . (Michaels, 1952).

The zone is descending through the bed at a constant rate, except for the time during which it is forming at the beginning of the process and is expressed by :

$$U_z = H_t / (\Theta_t - \Theta_f) \quad (23)$$

The height of the exchange zone is determined by the relation :

$$H_z = U_z * \Theta_z = H_t (\Theta_z / (\Theta_t - \Theta_f)) \quad (24)$$

The only unknown is the zone formation time, Θ_f . However, in many cases the s-shaped curve is symmetrical so that Θ_f can be represented by :

$$\Theta_f = 0.5 \Theta_z \quad (25)$$

So, H_z can be calculated :

$$H_z = H_t (V_z / (V_t - 0.5V_z)) \quad (26)$$

The height of the adsorption bed, H_t , was 21.0 cm. V_z and V_t were calculated from a Fortran program using the model breakthrough

equation. See Appendix B. Table 4 gives the calculated zone heights and water flow rates.

TABLE 4. CALCULATED MASS TRANSFER ZONE HEIGHTS AND WATER FLOW RATES.

<u>343°K</u>		<u>353°K</u>		<u>363°K</u>	
<u>MFR</u>	<u>H_z</u>	<u>MFR</u>	<u>H_z</u>	<u>MFR</u>	<u>H_z</u>
(mgH ₂ O/min)	(cm)	(mgH ₂ O/min)	(cm)	(mgH ₂ O/min)	(cm)
0.28	10.20	0.29	13.81	0.28	8.14
1.48	9.75	1.48	14.41	1.49	15.20
3.05	14.29	3.03	13.31	3.07	18.24
3.92	21.00	3.96	15.72	3.89	20.53
5.67	20.38	5.76	38.33	5.67	17.73
8.63	22.74	8.63	14.66	8.66	38.93

5. Mass transfer coefficients. In a fixed bed adsorber, the adsorption zone in reality moves downward through the solid. Imagine instead that the solid (cellulose) moves upward through the column countercurrent to the fluid (nitrogen/water vapor) fast enough for the adsorption zone to remain stationary within the column, as in Figure 20. The solid leaving the top of the column is shown in equilibrium with the entering gas, and all the solute (water vapor) is shown as having been removed from the effluent gas. This would

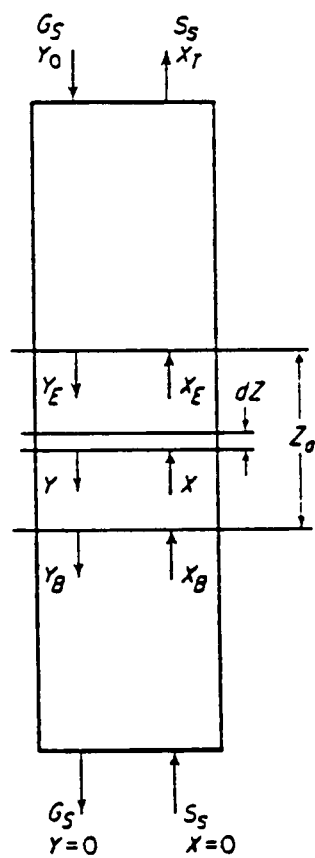


Figure 20. The Adsorption Zone.

require an infinitely tall column; however, the only concern will be the concentrations at the levels corresponding to the extremities of the adsorption zone, the 5 and 95% concentrations of the water vapor in the column influent. The operating line is :

$$G_s(Y_o - 0) = S_s(X_t - 0) \quad (27)$$

or
$$S_s / G_s = Y_o / X_t \quad (28)$$

Since the operating line passes through the origin (Figure 21) at any level in the column, the concentrations of solute in the gas Y and of adsorbate upon the solid X can be related by :

$$G_s Y = S_s X \quad (29)$$

Over the differential height dZ , the ratio of adsorption is :

$$G_s dY = K_y a_p (Y - Y^*) dZ \quad (30)$$

rearrange :
$$K_y a_p = G_s / (Y - Y^*) \, dY / dt^* dt / dZ \quad (31)$$

where :
$$dt / dZ = 1 / U_z \quad (32)$$

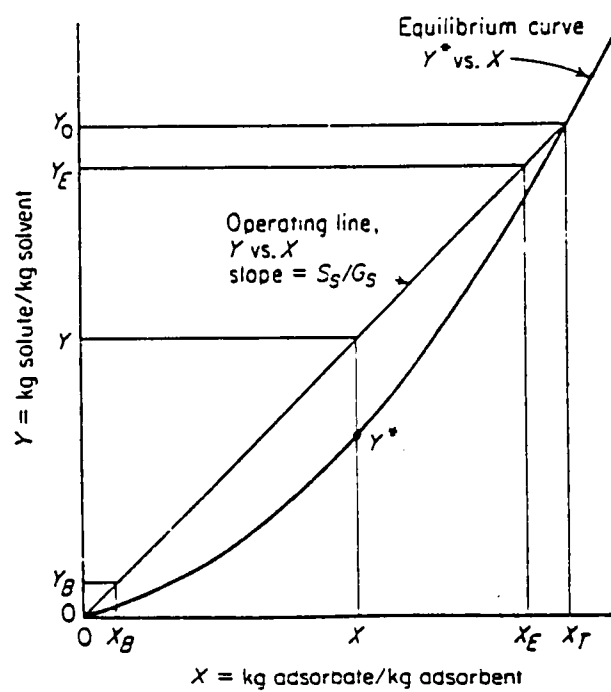


Figure 21. Equilibrium and Operating Curves.

is the inverse of the superficial velocity of the nitrogen and water vapor through the adsorption zone, assumed constant through the column. Therefore :

$$K_y a_p = G_s / U_z (Y - Y^*) \, dY / dt \quad (33)$$

The term dY/dt is represented by the breakthrough curve. A Fortran program was written to take the derivative of the model equation of the curve at its mid-point height, i.e., the slope of the breakthrough curve at 50 % of the column feed (Vermuelan, 1983). See Figure 22. The slope is in units of $\text{mgH}_2\text{O}/\text{min}^2$ and must be converted to the proper units of $\text{gH}_2\text{O}/\text{gN}_2\text{s}$. This can be easily done once the volumetric flow rate and density of the N_2 , at column conditions, are determined. G_s is the mass velocity of the unadsorbed gas (nitrogen) and $Y - Y^*$, the driving force, is represented by the vertical distance between the operating line and equilibrium curve (Figure 23) where Y^* is the equilibrium composition in the gas corresponding to the adsorbate composition X .

As seen from Figure 23, the equilibrium curve was plotted for an isotherm; then the six operating lines corresponding to the six relative humidities used to determine the isotherm were plotted. The driving force, $Y - Y^*$, was taken at Y equal to 50 % of the column feed,

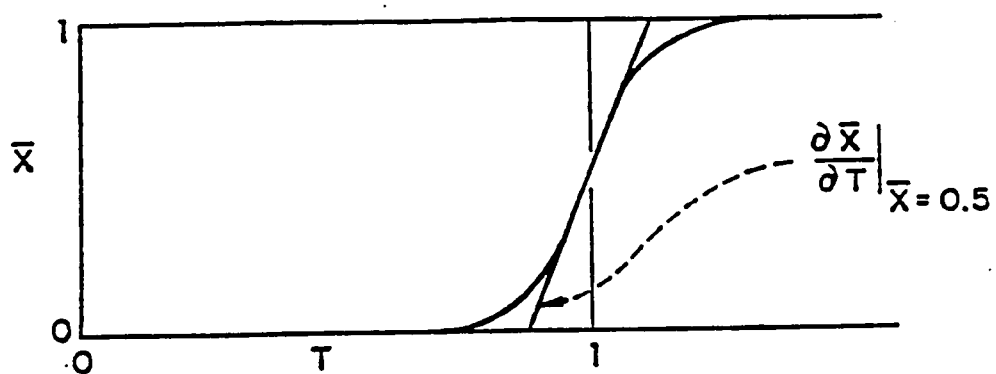


Figure 22. Calculation of Mid-Height Slope from Breakthrough Curve.

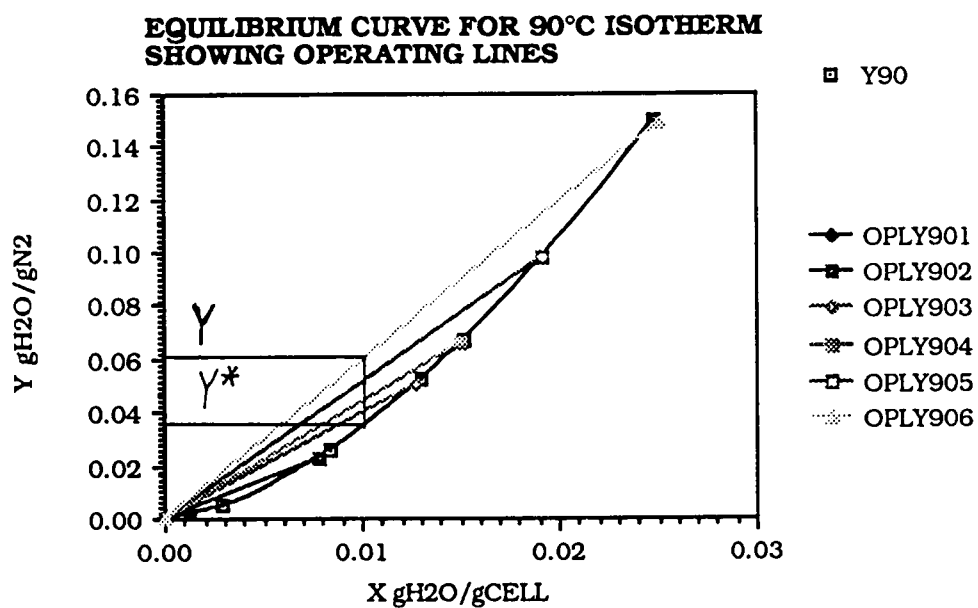


Figure 23. Calculation of Y^* from Equilibrium and Operating Curves.

the same point where the slope of the breakthrough curve was taken as previously mentioned. The equilibrium curve was plotted from the weight difference data only, the area-under-the-curve (breakthrough) data was too erratic to give a good equilibrium curve.

Besides the assumption of constant superficial velocity, an assumption was made that the model breakthrough curve equation was straight between 5 and 95 % of the column feed for the slope determination. As seen from Figure 24, this is only an approximation.

Breakthrough curve for the 80°C isotherm
at 50 % relative humidity showing the Mid-Height Slope

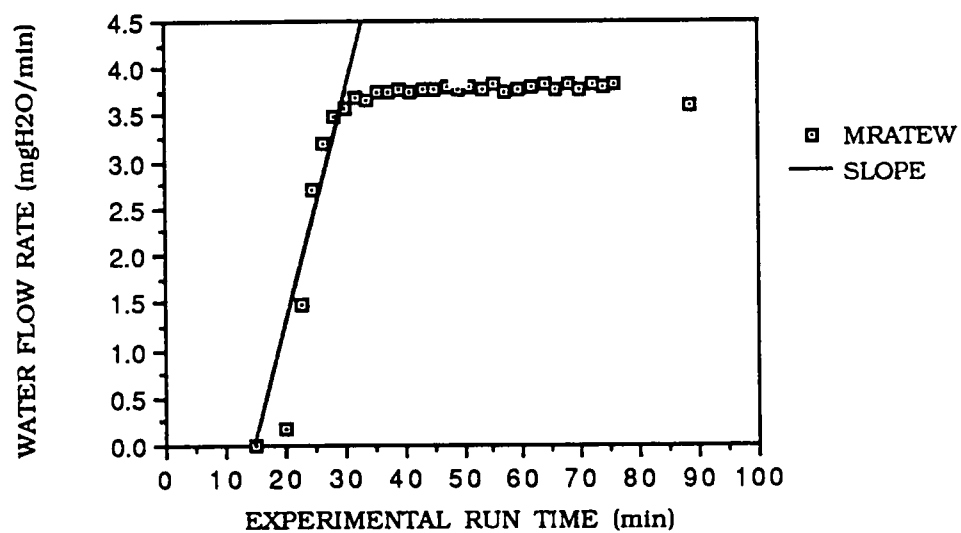


Figure 24. Calculated Slope of Breakthrough Curve.

IV. RESULTS AND DISCUSSION

A. Adsorption / Desorption Isotherms

Figures 25 and 26 present the experimental data for the isotherms obtained from both the area-under-the-curve and column weight difference methods. Clearly, the weight difference values correlate much better with the modified Henderson's equation than the former.

The shape of the isotherms in Figure 25 show a Type II adsorption process, with a "flattening" of the curves as the temperature increases. This reflects the decreased amount of adsorbate on the adsorbent due to the temperature increase, thus marking a decrease in the cellulose's capacity for water uptake.

From the two graphs, one can see that the (AUC) method gives steeper isotherms, showing more water being adsorbed than the physical (WGT) method. This can be attributed to the empirical equations used to model the breakthrough data. When the equations are integrated to get the area under the curve to subtract from the column feed area (part 2 of previous section), a smaller area than is actually represented by the data is determined, thus more area is calculated to represent the amount of water adsorbed.

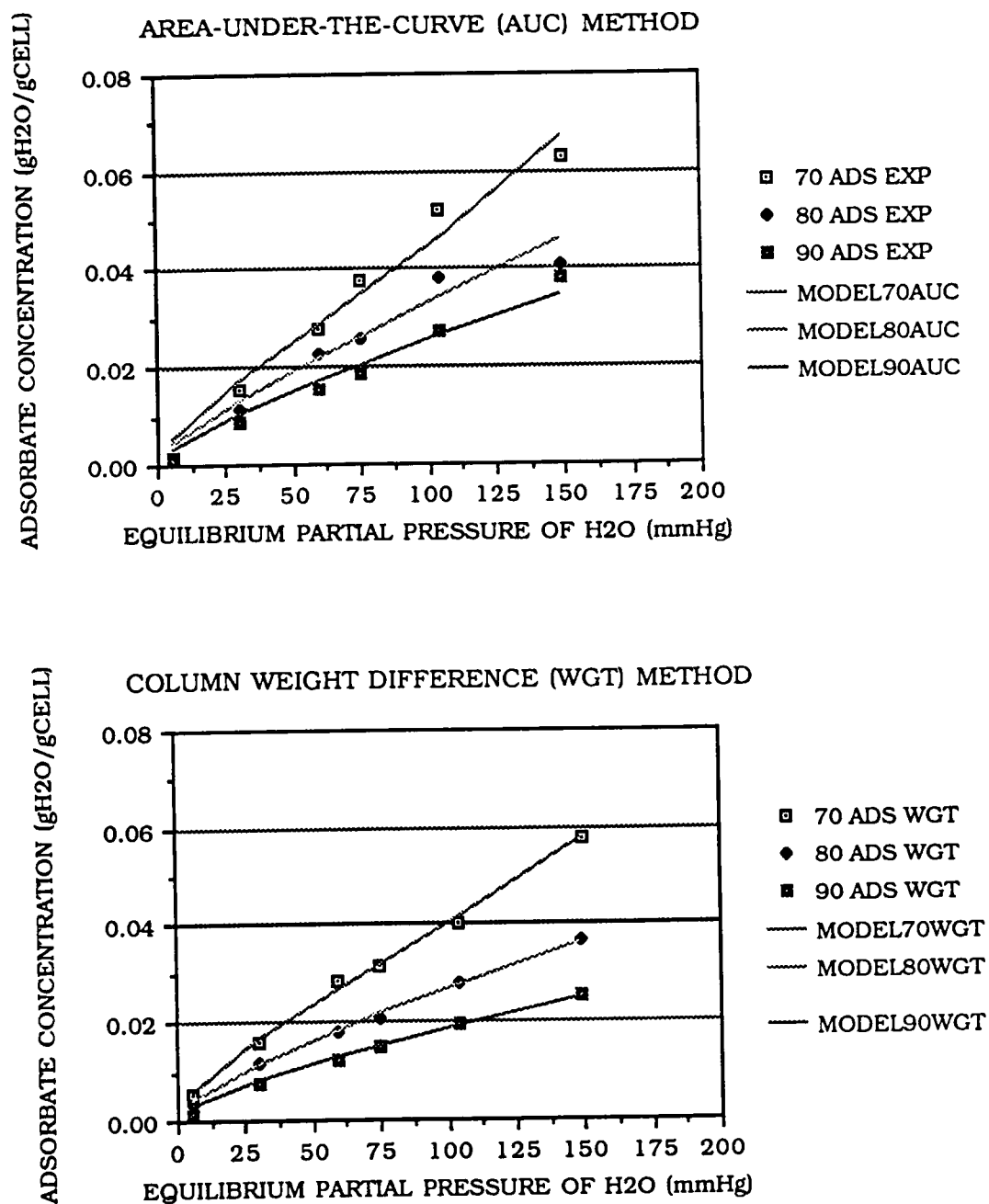


Figure 25. Adsorption Isotherms for the Water Vapor/Cellulose System.

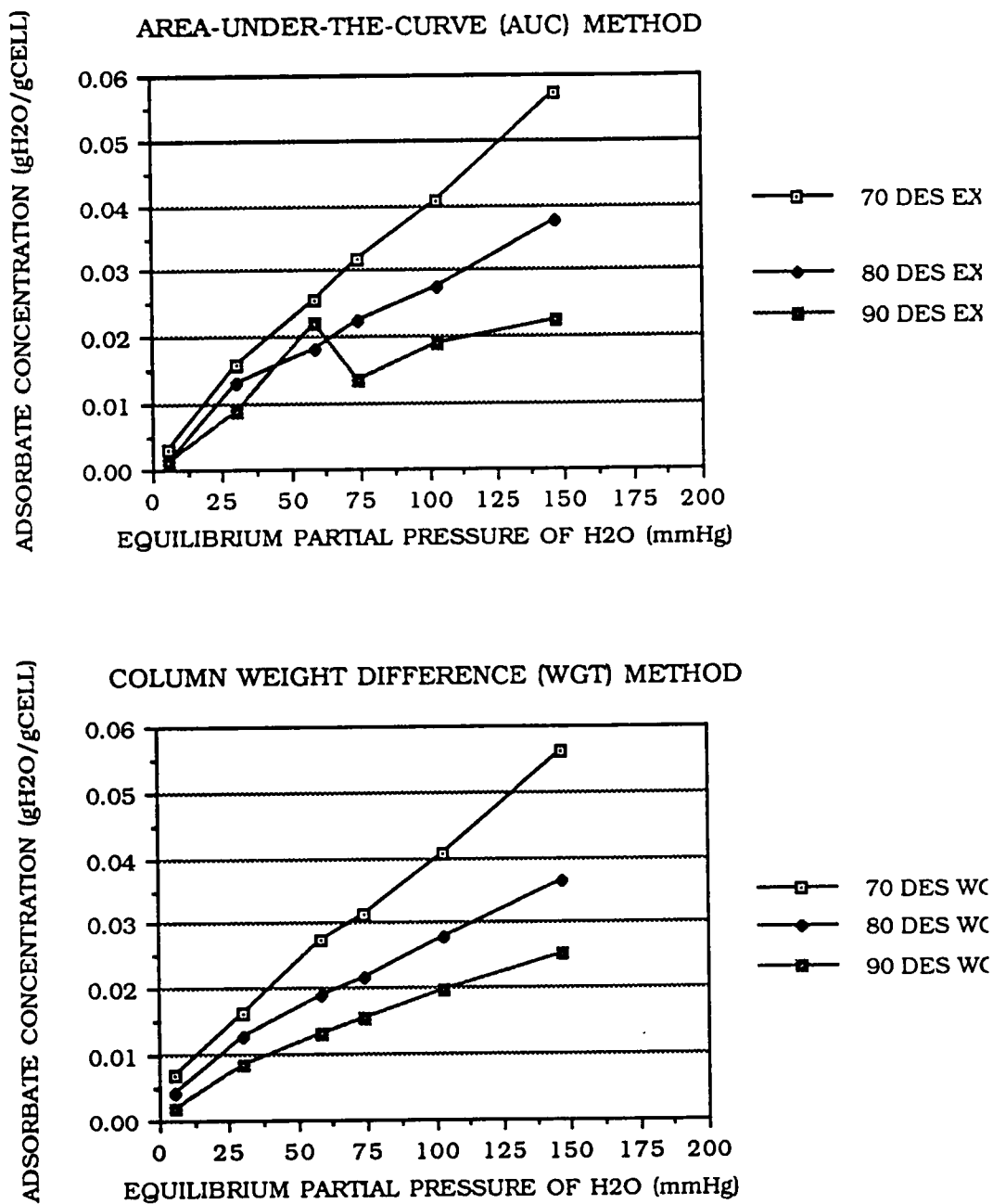


Figure 26. Desorption Isotherms for the Water Vapor/Cellulose System.

The modified Henderson's equation (18), when regressed against the data, gave the constants E , n , k_o , for the area-under-the-curve as : $E = -2.67$ kcal/mol, $k_o = 1.67 \cdot 10^{-10} \text{ K}^{-1}$, $n = 1.45$; and for the column weight difference : $E = 2.15$ kcal/mol, $k_o = 7.48 \cdot 10^{-8} \text{ K}^{-1}$, $n = 1.59$. Henderson calculated his constants for cellulose at 298K to be : $k_o = 4.91 \cdot 10^{-5} \text{ K}^{-1}$, and $n = 1.70$.

The desorption profiles in Figure 26 are typical of profiles obtained from polysaccharide adsorbents, in this case cellulose, exhibiting the Type II isotherm.

B. Type of Adsorption / Heats of Adsorption

One of the easiest indicators for determining the type of adsorption occurring is the amount of heat liberated during the adsorption process. From the amounts calculated from equation (20) and shown in Table 5, a plot was constructed showing the heats of adsorption as a function of equilibrium moisture content, Figure 27. The extrapolated values, at zero moisture content, fall within the range of 11.6 to 14.8 kcal/mol. This appears to indicate a physical adsorption phenomena because the range is near the latent heats of condensation for water of 9.7 - 10.0 kcal/mol for the experimental temperatures used.

TABLE 5. CALCULATED HEATS OF ADSORPTION.

<u>%Rh</u>	(kcal/mol)					
	<u>343°K</u>		<u>353°K</u>		<u>363°K</u>	
	<u>AUC</u>	<u>WGT</u>	<u>AUC</u>	<u>WGT</u>	<u>AUC</u>	<u>WGT</u>
10	7.40	14.70	7.90	12.90	8.49	11.50
20	7.50	14.60	8.00	12.80	8.50	11.40
40	7.50	14.40	8.00	12.78	8.53	11.39
50	7.60	14.20	8.10	12.67	8.60	11.30
70	7.60	14.00	8.10	12.50	8.59	11.27
100	7.70	13.80	8.20	12.40	8.67	11.22

This range of values are close to the values reported by Chung and Pfoest (1967) for adsorption of water onto corn, 10.6-13.2 kcal/mol at 304 K, and 9.7-11.4 kcal/mol at 298 K for water onto cellulose reported by Stamm (1964).

As seen from Figure 27, the heats of adsorption from the breakthrough data (AUC) go in the wrong direction (positive slope), with increased adsorbate concentration, for an exothermic process. These values therefore were used for comparison only and not included in any calculations. The systematic difference between the methods, in Table 5, can again be attributed to the approximate nature of the breakthrough formula.

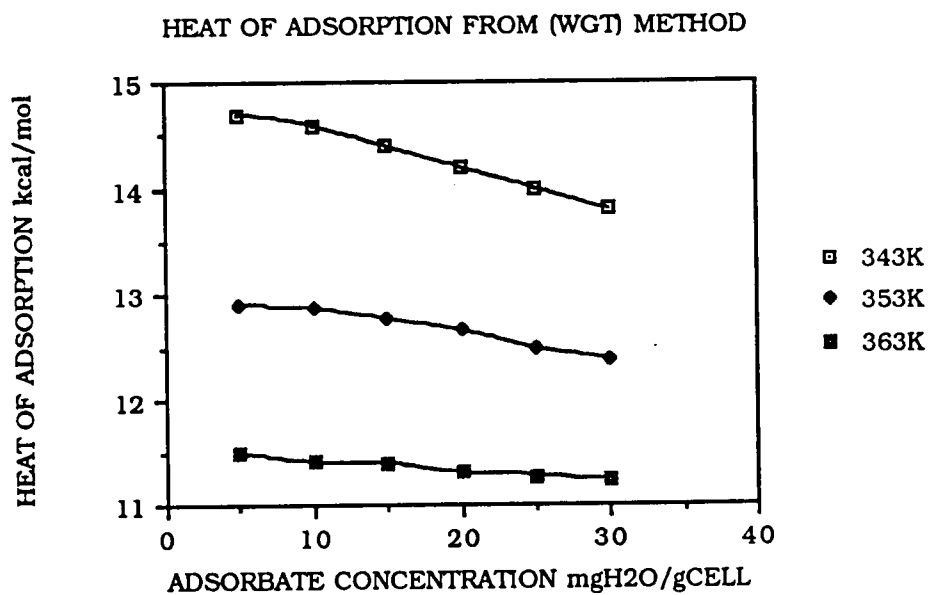
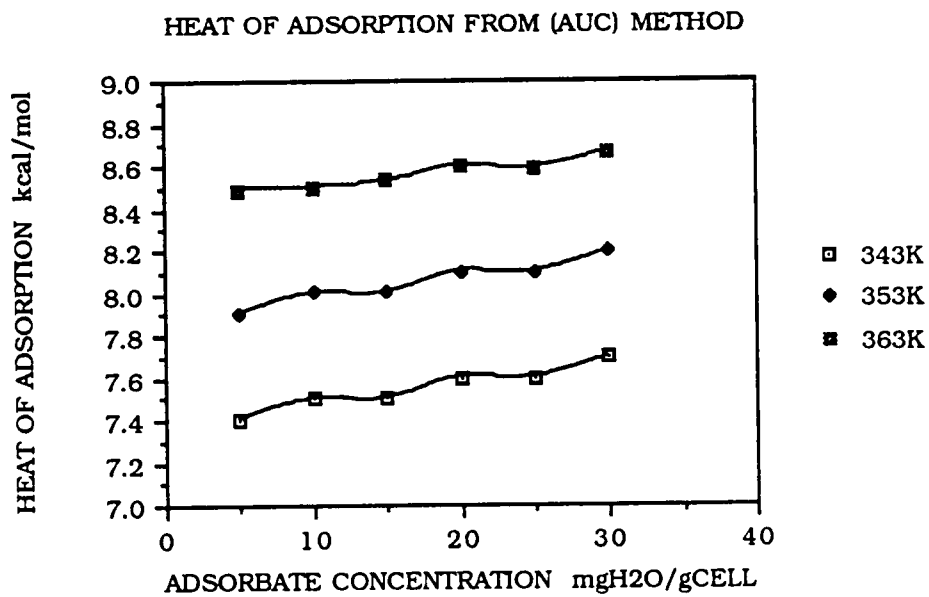


Figure 27. Heats of Adsorption Plot from Table 5.

C. Mass Transfer Zone

Figure 28 plots H_z , height of the mass transfer zone, versus the mass flow rate of water. The three points of each vertical group correspond to the three isothermal points with the same relative humidities, e.g., 70, 80, 90°C isothermal points at 10% relative humidity.

This graph indicates that the mass transfer zone increases with increasing flow rate. For most of the flow rates, the average zone height is smaller than the bed height of 21 cm. This indicates that most of the column would be saturated before the zone passes out of the column.

D. Mass Transfer Coefficients

Table 6 gives the calculated overall mass transfer coefficients for each point (% relative humidity) determined on the isotherms. The values are based on the fluid-phase resistance only; the solid phase resistance was assumed negligible.

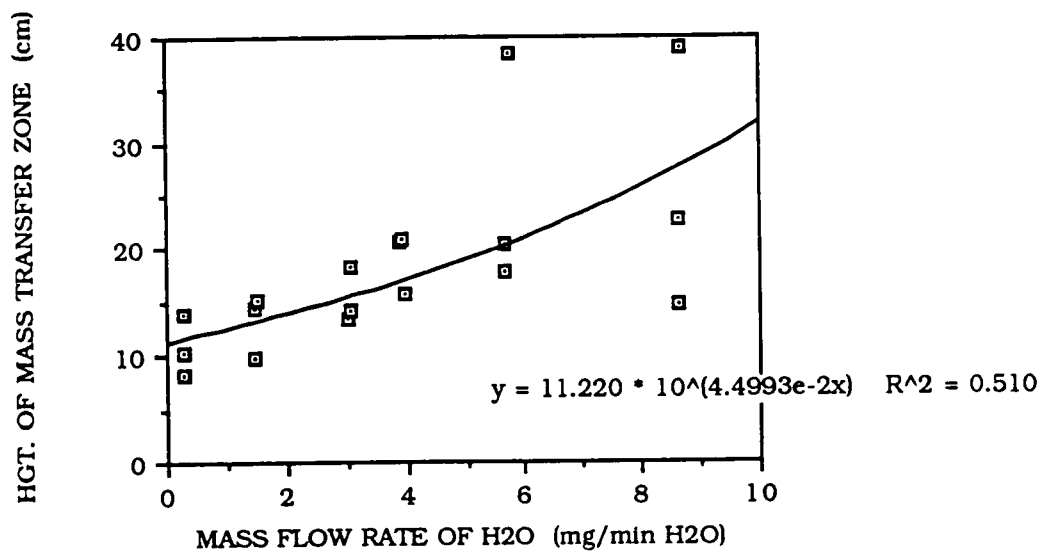


Figure 28. Height of the Mass Transfer Zone as a Function of Water Flow Rate.

TABLE 6. CALCULATED MASS TRANSFER COEFFICIENTS.

%Rh	<u>Kya_p</u> (Kg/m ³ hr)		
	70°C	80°C	90°C
10	33.08	47.16	98.64
20	25.63	15.59	21.24
40	21.17	31.32	19.12
50	31.57	21.38	26.46
70	32.58	34.38	29.48
100	48.96	37.08	74.52

The specific solid surface, per volume of bed, a_p , was calculated by :

$$a_p = 6(1 - \epsilon) / d_p \quad (34)$$

from Treybal (1980). For cellulose, the bed void fraction, ϵ , was assumed 0.3 cm³ void/cm³ bed (Ladisch et al., 1979), and the average particle diameter, d_p , was 0.018 cm. This gave an external surface area, a_p , of 233 cm² cell/cm³ bed.

No other coefficients were found in the literature for the cellulose/water vapor system; therefore, these are offered for use in future experiments or comparisons.

E. Hysteresis

Figure 29 shows the three adsorption/desorption isotherms determined by the column weight difference method, plotted against each other. The area-under-the-curve method was not conclusive (criss-crossing isotherms) thus the isotherms are not given. The Figures show very little hysteresis, and the effect that is noted, could be attributed to experimental error. The lack of hysteresis is probably caused by the higher temperatures used to obtain the equilibrium isotherms.

For swelling adsorbents, like cellulose, the effect should decrease with increased temperature, this is, to a small degree, due to the lower uptake at higher temperatures, as seen from the isotherms in Figure 25; and to the increased mobility of the molecular chains as the temperature increases. This changing of the structural conformation among the inter-chain bonds impedes desorption of the adsorbate molecules (Watt, 1980).

F. Column Regeneration

The adsorption and desorption isotherms for the column regeneration run are shown in Figure 30. The adsorption profile follows the 80°C isotherm in Figure 25 showing reproducibility. The

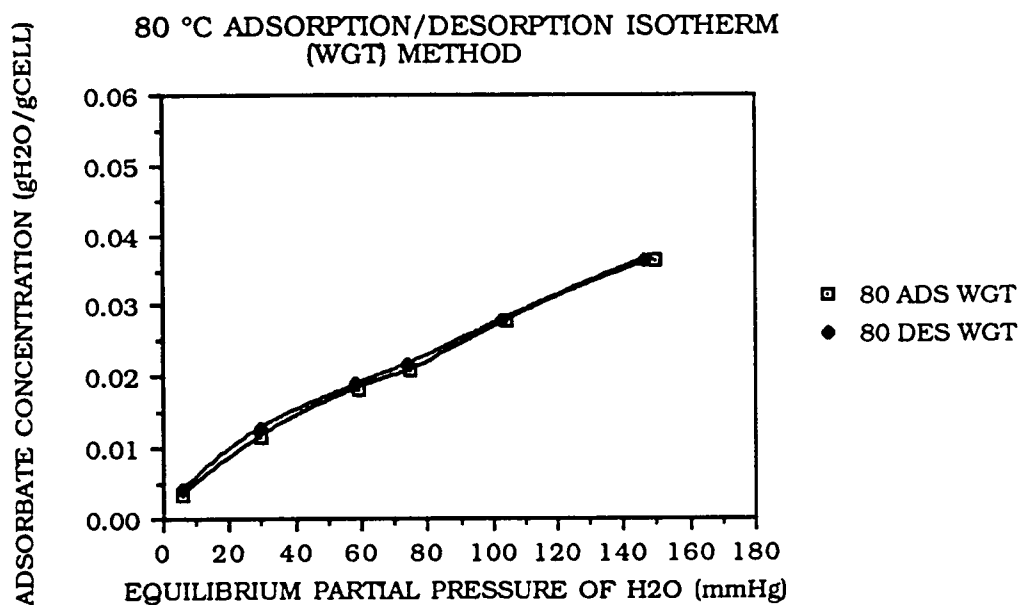
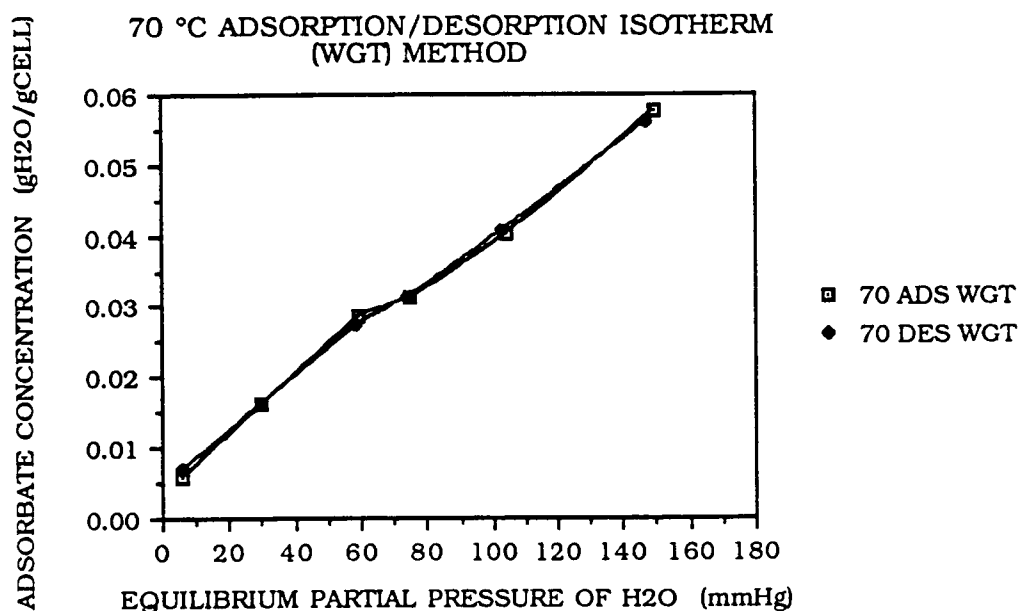


Figure 29. Adsorption/Desorption Isotherms Showing Hysteresis Effect.

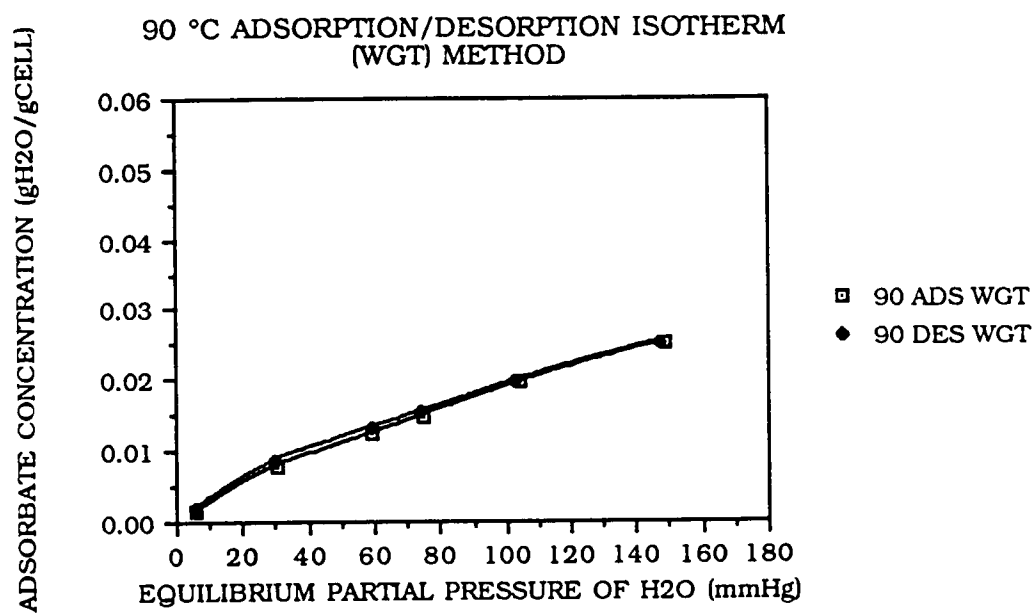


Figure 29. Continued.

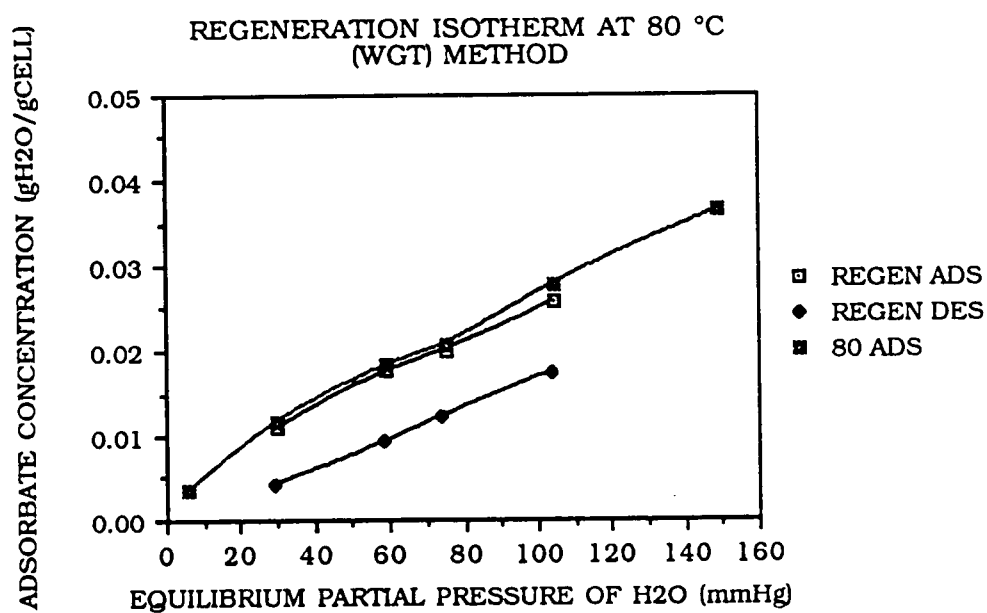
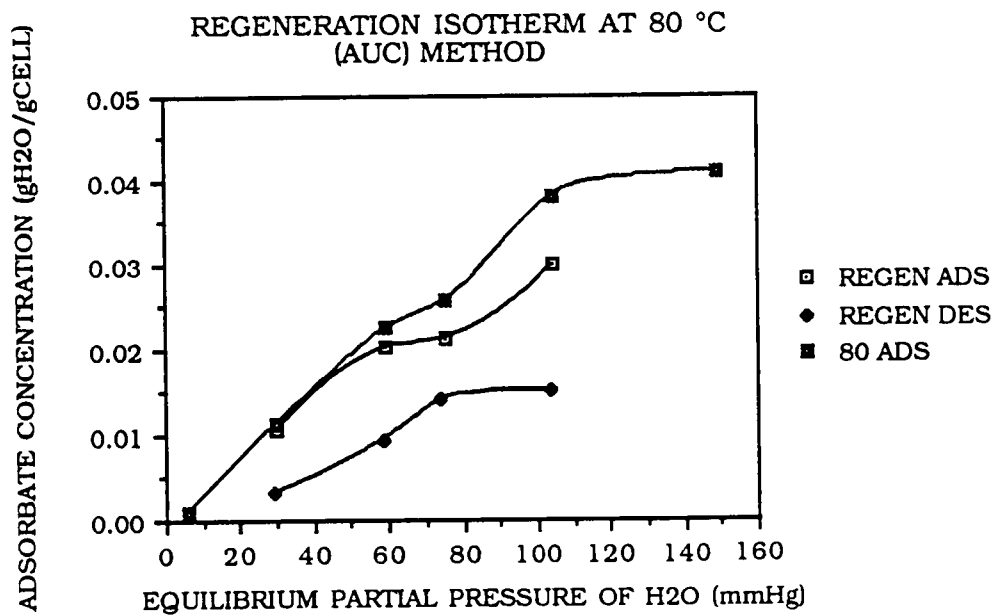


Figure 30. Adsorption/Desorption Isotherms for the Column
Regeneration Run.

desorption isotherm follows a path beneath the adsorption isotherm, i.e., less water is desorbed with a regenerating gas at 12 % humidity rather than a completely dry one. This is to be expected since equilibrium between the 12% Rh regenerating gas and cellulose would require some water to remain on the adsorbent.

Figure 15 showed the desorption profile using a completely dry regenerating gas. Figure 31 shows a plot of that data along with the data from the 12 % humidity desorption profile. For both cases, the adsorption conditions (temperature and humidity) were the same. The graph shows the 12% humidity stream profile lacking a plateau, which can be seen in the dry profile case. The decrease in slope is more gradual for the 12 % humid stream compared to the dry one, thus the desorption will take longer to reach a certain level of adsorbate concentration on the adsorbent, if at all. The tail, of course, shows the approach of the effluent to the influent.

From the graph, it appears that two-thirds of the total water is desorbed in the first 25 min. for both cases; however, the 0% Rh gas does continue to remove water until there is no more adsorbate in the column effluent. Overall, the graph would seem to indicate simply that the drier the regenerating gas, the more water removed.

COMPARISON OF DRY AND 12% RH REGENERATING DESORPTION PROFILES

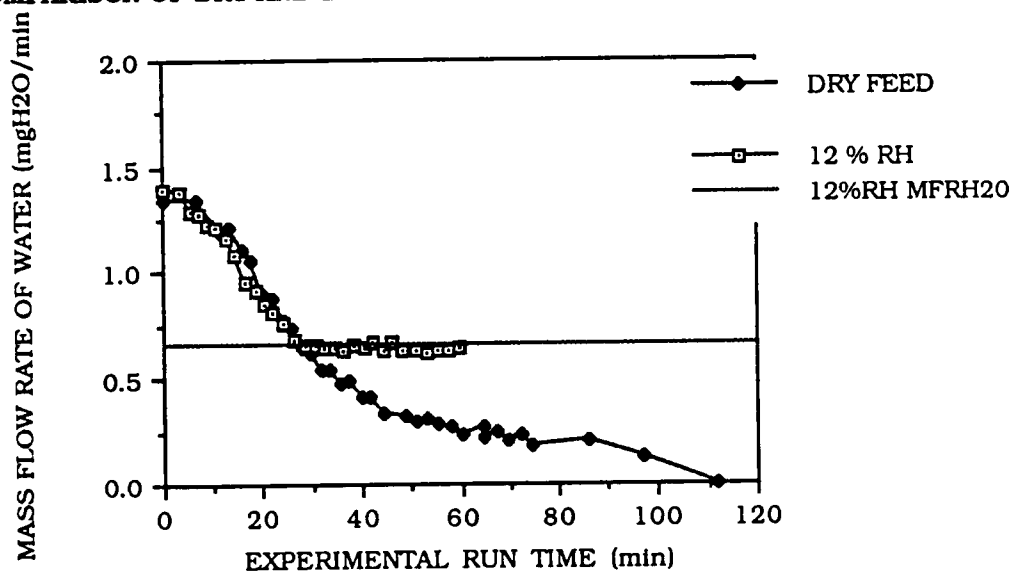


Figure 31. Comparison of Regenerating Gases of Varying Humidity.

V. CONCLUSIONS

The adsorption and desorption characteristics of the water vapor/cellulose system were studied at temperatures between 60 and 90°C. Cellulose was chosen as the adsorbent because of its abundance, low cost, and specific affinity for water. The mass transfer zone heights, heats of adsorption, mass transfer coefficients, and adsorption and desorption isotherms were the measured characteristics for this system.

Two independent methods were used to obtain the raw data for the calculations. The column weight difference procedure provided the most consistent and usable data. The area-under-the-curve method gave data that had more scatter in it, presumably due to poorer fit of the model breakthrough equation and estimation of the point of equilibrium on the breakthrough curve.

The heats of adsorption obtained, 11.6-14.8 kcal/mol, indicate that the adsorption process is a physical one. The isotherms are of the Type II variety, showing the typical s-shaped inflection points. The very thin mass transfer zone heights indicate that for a fixed bed adsorption column, with cellulose as the adsorbent, almost the entire bed length would be used for the removal of water. This, along with having a steep desorption profile, would indicate maximum use of the

bed and short cycle times, which are favorable process design criteria. The mass transfer coefficients were developed by a rigorous method; however, there are some simplifying assumptions used, so a completely formal description is lacking. The magnitude of the values are consistent with those found for other gas/solid adsorption systems in the literature, although no specific water vapor/cellulose data was found.

The single column regeneration run shows that the regenerating gas should be as dry as possible for the maximum unloading and the shortest cycle time between loading and unloading of the column. The absence or lack of hysteresis, due probably to the elevated (approaching the boiling point) temperatures used in the experiments, is noted.

The isotherms, when compared with others of biomass materials (Bienkowski, Hong, et al., page 26) show that cellulose does not have as large an adsorbate (water) loading capacity as some of the other materials, e.g., corn grits, and starches.

VI. RECOMMENDATIONS

The results of this work have lead to several recommendations for further study and development.

Instead of two columns of the same length and diameter, use several columns of varying diameter and length, to study these effects on mass transfer, flow patterns (axial or radial), etc. within the cellulose bed. This will also add more cellulose for adsorption, allowing more points to be taken along the breakthrough curve.

To study the temperature wave that accompanies the mass transfer wavefront, the columns should have thermocouples, with the associated equipment, placed along their length. The relation between the two waves can then be examined to determine their effect on one another.

A more in-depth study of the mass transfer coefficients would certainly add validity and accuracy to the values given in this paper. A more complex model taking into account the pore resistance, axial and radial diffusion, etc. could be used to more closely represent the physical phenomena.

A study of adiabatic operation, especially combined with the addition of thermocouples in the columns, might provide insight concerning the heat and mass transfer characteristics of cellulose. The addition of a third component (ethanol?) to the column influent to note the effects on bed capacity and mass transfer, as well as, a study of whether adsorption/desorption cycling, at these higher temperatures, effects the cellulose adversely would be useful.

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APPENDIXES

APPENDIX A : DRIERITE SATURATION DATA
SAMPLE LOOP CALIBRATION

DRIERITE SATURATION DATA

COL. WGT. (g)	-	42.76	42.76	42.77	42.75
COL. TOT. WGT. (g)	-	90.287	92.624	92.455	91.453
MFC-1 (cc/min)	-	50	5	50	5
Sat. Temp. (C)	-	60	60	60	60
Start Time	-	3:00pm	11:50am	10:00am	2:00pm
End Time	-	9:00pm	5:50pm	4:00pm	8:00pm
Patm (inHg)	-	30.24	30.16	30.09	30.38
Pout Sat. (inHg)	-	37.24	35.16	37.39	35.48
Final Col.Wgt (g)	-	93.424	92.952	95.653	91.764
Water Gain (g)	-	3.137	0.328	3.212	0.311
% Saturation	-	98	102	109	95

SMALL AND LARGE SAMPLE LOOP CALIBRATION DATA

<u>3.7% RH</u>		<u>20.1% RH</u>	
<u>Small</u>	<u>Large</u>	<u>Small</u>	<u>Large</u>
47033	47402	255670	307230
44920	50147	299070	289080
48288	50640	262270	294400
48651	44035	291100	305850
43767	41705	279390	306000
46494	43560	282260	288240
41774	44717	271120	297220
38768	41827	281470	269740
38958	43785	280390	291150
39453	42740	267230	290940
41755	41989		

<u>39.7% RH</u>		<u>50.0% RH</u>	
<u>Small</u>	<u>Large</u>	<u>Small</u>	<u>Large</u>
669010	689160	862690	876710
669490	689490	852460	881280
669080	696790	867330	869340
643640	652070	827770	886020
655940	662430	832060	876010
622210	668220	837550	874090
615460	662730	809670	839080
642300	657320	822250	843130
632850	665530	818540	850220

<u>69.9% RH</u>		<u>99.9% RH</u>	
<u>Small</u>	<u>Large</u>	<u>Small</u>	<u>Large</u>
1252900	1274200	1593900	1705100
1246400	1289700	1623100	1717900
1251100	1298900	1622100	1715600
1247200	1273800	1646600	1728700
1214800	1263100	1520400	1720600
1223900	1260200	1545100	1705500
1192200	1252100	1520300	1638900
1204300		1553300	1639800
		1510700	1613100
		1612900	1705200
		1619100	1710200
		1618600	1682700
		1623500	1671400
		1594600	1662900
		1598000	1760000
		1587000	1654800

APPENDIX B : COMPUTER PROGRAMS

```

C      THIS PROGRAM DETERMINES THE VAPOR PRESSURE OF WATER
C      BETWEEN THE TEMPERATURES OF 10 AND 70 DEG. C.
C      *****
C
C      VARIABLES:
C
C      T   = AMBIENT WATER TEMPERATURE, K
C      Tc  = CRITICAL TEMPERATURE, K
C      Pc  = CRITICAL PRESSURE, MPa
C      Tp  = TEMPERATURE CONSTANT, K
C      a   = EQUATION CONSTANT
C      Psat = CALCULATED SATURATION VAPOR PRESSURE, MPa
C      Psatc = CALCULATED SATURATION VAPOR PRESSURE, mmHg
C      *****
C
C      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
C      DIMENSION F (8)
C      T = 283.0
C      Tc = 647.286
C      Pc = 22.089
C      Tp = 338.15
C      a = 0.01
C
C      DO LOOPS TO READ IN CONSTANTS FOR VAPOR PRESSURE EQUATION
C      USED AND DO CALCULATIONS
C
C      OPEN (10,FILE='WATERVP.DAT',STATUS='OLD')
C      WRITE (10,5)
5      FORMAT (1X,'TEMP K',5X,'PSAT MPa',5X,'PSAT mmHg')
C
C      DO 20 I=1,900
C          DATA F/ -7.4192420d0,2.9721000d-1,-1.1552860d-1,
+          8.6856350d-3,1.0940980d-3,-4.3999300d-3,2.5206580d-3,
+          -5.2186840d-4/
C          E2 = 0.0
C          DO 10 J = 1,8
C              E1 = F(J)*(a*(T-Tp))**(J-1)
C              E2 = E1 + E2
10      CONTINUE
C          E3 = (Tc/T-1.0)*E2
C          Psat =(DEXP(E3))*Pc
C          Psatc = Psat*1000000/133.3
C          T = T+0.1
C          WRITE (10,30) T,Psat,Psatc
30      FORMAT (1X,F5.1,5X,F6.5,5X,F8.2)
20      CONTINUE
C      STOP
C      END

```

```

C
C THIS PROGRAM CALCULATES THE % RELATIVE HUMIDITY OF THE
C NITROGEN CARRIER STREAM FOR GIVEN OPERATING CONDITIONS OF
C THE DYNAMIC ADSORBER
C *****
C
C      IMPLICIT DOUBLE PRECISION (A-H,M-Z)
C      CHARACTER A

10      WRITE (*,10)
      FORMAT (1X,'INPUT THE SATURATOR TEMPERATURE IN DEG K')
      READ (*,*) STEMP

20      WRITE (*,20)
      FORMAT(1X,'INPUT THE COLUMN TEMPERATURE IN DEG K')
      READ (*,*) CTEMP

30      WRITE(*,30)
      FORMAT(1X,'INPUT SATURATOR PRESSURE IN mmHg ')
      READ (*,*) PIN

40      WRITE(*,40)
      FORMAT(1X,'INPUT COLUMN INLET PRESSURE IN mmHg ')
      READ (*,*) PINC

50      WRITE(*,50)
      FORMAT(1X,'INPUT WATER VAPOR PRESSURE AT SATURATOR TEMP.
      mmHg')
      READ (*,*) PSAT

C***** CALCULATION OF MOLE FRACTION OF H2O AND N2

      YH2O=PSAT/PIN
      YN2=1-YH2O

60      WRITE(*,60)
      FORMAT(1X,'INPUT MFC1 FLOW RATE cc/min')
      READ (*,*) MFC1

70      WRITE(*,70)
      FORMAT(1X,'INPUT MFC2 FLOW RATE cc/min')
      READ (*,*) MFC2

C***** CALCULATION OF MOLAR FLOW RATE OF N2 THROUGH THE
C CONTROLLERS DENSITY CALC. BY PM/RT AT 1 atm AND 21.1 C
C REFERENCE CONDS. OF MF-CONTROLLERS

      N2FC1 = MFC1*0.00116/28.0134
      N2FC2 = MFC2*0.00116/28.0134

C***** CALCULATION OF H2O MOLAR FLOW RATE AND OVERALL MOLE
C FRACTION

      H2OFR = (N2FC1/YN2)-N2FC1
      YH2OO = H2OFR/(N2FC1+N2FC2+H2OFR)
      PPH2O = YH2OO*PINC
      RHC = PPH2O/PSAT*100

90      WRITE (*,90)
      FORMAT(1X,'INPUT WATER VAPOR PRESSURE AT COLUMN

```

```

    TEMPERATURE mmHg')

    READ (*,*) VPCOL
    WRITE (*,100)
100  FORMAT(1X,'INPUT THE COLUMN OUTLET PRESSURE mmHg')
    READ (*,*) POUT

C***** CALCULATE H2O PARTIAL PRESSURE AT COLUMN CONDITIONS

    PPH2OC = YH2OO*((PINC+POUT)/2)

C***** CALCULATE %RH OF N2 STREAM AT COLUMN CONDITIONS

    RH = 100*PPH2OC/VPCOL

    WRITE (*,120) MFC1,MFC2
120  FORMAT(1X,'MFC1 = ',F4.1,' sccm', ' MFC2 = ',F4.1,' sccm')

    WRITE(*,130) STEMP,CTEMP
130  FORMAT(1X,'SATURATOR TEMP = ',F5.1,' K', ' COLUMN TEMP = ',
+    F5.1,' K')

    WRITE(*,140) RHC
140  FORMAT(1X,'% RELATIVE HUMIDITY OUT OF SATURATOR = ',F6.2)

    WRITE(*,150) RH
150  FORMAT(1X,'% RELATIVE HUMIDITY AT COLUMN CONDITIONS = ',F6.2)

    STOP
    END

```

```

C   THIS IS A PROGRAM TO CALL THE SUBROUTINE QAGS TO INTEGRATE
C   THE AREA UNDER THE MODEL BREAKTHROUGH EQUATIONS OBTAINED
C   FOR MY DATA, THE (AUC) METHOD
C *****

```

```

IMPLICIT DOUBLE PRECISION (A-H,O-Z)
EXTERNAL PMRAT

```

```

A = 0.0
B = 84.38
EPSABS = 0.000001
EPSREL = 0.000001

```

```

CALL QAGS(PMRAT,A,B,EPSABS,EPSREL,RESULT,ABSERR,IER)

```

```

WRITE (*,*) RESULT, ABSERR, IER
END

```

```

REAL*8 FUNCTION PMRAT(RTIME)
IMPLICIT DOUBLE PRECISION (A-H,O-Z)
PMRAT=5.8470*(0.2012*DEXP(-0.5114*(RTIME/60.))+0.7872*DEXP(-18.
+ 144*(RTIME/60.)**2))
RETURN
END

```

```

C      PROGRAM TO CALCULATE MASS TRANSFER COEFFICIENT FROM
C      PARTIAL DIFFERENTIAL OF BT EQUATION FOR SIMPLE RATE EQN.
C      .....
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      INTEGER RTIV

      WRITE (*,10)
10     FORMAT (1X,'ENTER THE FOUR CONSTANTS OF BT MODEL EQN. :')
      READ (*,*) B,B1,C,C1

      WRITE (*,15)
15     FORMAT (1X,'ENTER COL.FEED CONCEN. mol/cm3 : ')
      READ (*,*) CA

      WRITE (*,20)
20     FORMAT (1X,'ENTER STARTING RUN TIME :',' min')
      READ (*,*) RT

      DO 30 RTIV=1,10000
          X=1-(B*DEXP(-B1*RT/60))-(C*DEXP(-C1*((RT/60)**2)))
          IF (X.GE.0.500) THEN
              GOTO 40
          ENDIF
          RT=RT+0.1
30     CONTINUE

40     PC=CA*((B*B1/60*DEXP(-B1*RT/60))+(C*C1*RT/1800*DEXP(-C1*((RT
+ /60)**2))))

      WRITE (*,50) X
50     FORMAT (1X,'AVG ADSORBATE CONCENTRATION IN SOLID :',F6.2)
      WRITE (*,60) RT
60     FORMAT (1X,'RUN TIME FOR ADSORB.CON.TO REACH 50% OF FEED :',
+ F6.2)
      WRITE (*,70) PC
70     FORMAT (1X,'SLOPE OF TANGENT FOR BT CURVE AT 50% OF FEED :',
+ F6.4)

      STOP
      END

```

```

C      THIS IS A PROGRAM TO CALCULATE HEIGHT OF THE MASS TRANSFER
C      ZONE FROM THE MODEL BREAKTHROUGH EQUATIONS
C      *****
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      CHARACTER*13 ID
      INTEGER RTV

      READ (*,*) ID
      WRITE (*,5) ID
5      FORMAT (1X,'ENTER BT CURVE ID : ',A)

      READ (*,*) B, B1, C, C1
      WRITE (*,10) B, B1, C, C1
10     FORMAT (1X,'ENTER THE FOUR CONSTANTS OF MODEL EQUATIONS : '
+ ,F8.2,' ',F6.2,' ',F7.2,' ',F6.2)

      READ (*,*) RT
      WRITE (*,20) RT
20     FORMAT (1X,'ENTER STARTING RUN TIME : ',F6.1,' min')

      DO 30 RTV = 1,10000
          X=1-(B*DEXP(-B1*RT/60))-(C*DEXP(-C1*((RT/60)**2)))
          IF (X.LT.0.0501) VE=RT*50
          IF (X.GE.0.95) THEN
              VT=RT*50
              GOTO 40
          ENDIF
          RT=RT+0.1
30     CONTINUE

40     VZ=VT-VE
      HT=21.0
      HZ=HT*(VZ/(VT-(VZ/2)))
      VT1=VT/50
      VE1=VE/50

      WRITE (*,50) VE1
50     FORMAT (1X,'0.05 OF COL.FEED RUN TIME : ',F6.2,' min')
      WRITE (*,60) VT1
60     FORMAT (1X,'0.95 OF COL.FEED RUN TIME : ',F6.2,' min')
      WRITE (*,70) ID, HZ
70     FORMAT (1X,'HEIGHT OF MASS TRANSFER ZONE FOR ',A,'IS',F6.2,' cm')

      STOP
      END

```

A Fortran program to do a non linear regression on the breakthrough curve using SAS, and print out statistics and graphs.

```
FILENAME BT741A\PRB.CHAMPAGNE.DATA\BT741A.DAT;  
DATA BT741A AMRDATA; INFILE BT741A;  
TITLE ADSORPTION BT ANALYSIS 70-40-10';
```

```
INPUT AREA RTIME SLS;  
IF SLS=0 THEN RH=(AREA+15690)/1.6640E4;  
ELSE RH=(AREA+25640)/1.7610E4;  
IF RH<0 THEN RH=0;  
IF RH=0 THEN AREA=0;  
H20PP=RH*54.66/100;  
H20MF=H20PP/789.6;  
MOLRAT=H20MF/(1-H20MF);  
MRATEW=50*1.16*18.016/28.0134*MOLRAT;  
KEEP AREA MRATEW RTIME;  
OUTPUT AMRDATA;
```

```
LABEL AREA='GC INTEGRATOR RESPONSE '  
      MRATEW='MASS RATE H2O  mgH2O/min'  
      RTIME='EXPERIMENTAL RUN TIME (min)';  
PROC PRINT DATA=AMRDATA; VAR AREA MRATEW RTIME;  
PROC PLOT DATA=AMRDATA; PLOT AREA*RTIME='*' MRATEW*RTIME='*/HZERO;
```

```
DATA MRDATA; SET AMRDATA (DROP=AREA); RENAME MRATEW=PMRATEW;  
PROC SYNLIN DATA=MRDATA OUTMODEL=MTEST OUT=PTEST OUTPREDICT  
ITPRINT CONVERGE=0.001;  
  PARM B C B1 C1;  
  EXO RTIME;  
  ENDO PMRATEW;  
  PMRATEW=0.116*(1-B*EXP(-C*(RTIME/60))-B1*EXP(-C1*(RTIME/60)**2));  
  FIT PMRATEW START=(B 100 C 12 B1 -723 C1 9);
```

```
PROC SIMNLIN DATA=MRDATA MODEL=MTEST OUT=STEST STAT;
```

```
PROC PRINT DATA=PTEST;
```

```
DATA MATCH;  
  MERGE AMRDATA PTEST;  
  COLFED=0.116;  
PROC PLOT DATA=MATCH;  
  PLOT MRATEW*RTIME='*' PMRATEW*RTIME='1'  
  COLFED*RTIME='*/HZERO OVERLAY;
```

This program does a non-linear regression on the desorption profile using SAS and print out statistics and graphs.

```
FILENAME BT741D '[PRB.CHAMPAGNE.DATA]BT741D.DAT';
DATA BT741D AMRDATA; INFILE BT741D;
TITLE 'DESORPTION BT ANALYSIS 70-40-10';
```

```
INPUT AREA RTIME SLS;
IF SLS=0 THEN RH=(AREA+15690)/1.6640E4;
ELSE RH=(AREA+25640)/1.7610E4;
IF RH<0 THEN RH=0;
IF RH=0 THEN AREA=0;
H2OPP=RH*54.66/100;
H2OMF=H2OPP/790.4;
MOLRAT=H2OMF/(1-H2OMF);
MRATEW=50*1.16*18.016/28.0134*MOLRAT;
KEEP AREA MRATEW RTIME;
OUTPUT AMRDATA;
```

```
LABEL AREA='GC INTEGRATOR RESPONSE '
      MRATEW='MASS RATE H2O  mgH2O/min'
      RTIME='EXPERIMENTAL RUN TIME (min)';
PROC PRINT DATA=AMRDATA; VAR AREA MRATEW RTIME;
PROC PLOT DATA=AMRDATA; PLOT AREA*RTIME='*' MRATEW*RTIME='*'/HZERO;
```

```
DATA MRDATA; SET AMRDATA (DROP=AREA); RENAME MRATEW=PMRATEW;
PROC SYNLIN DATA=MRDATA OUTMODEL=MTEST OUT=PTEST OUTPREDICT
CONVERGE=0.001;
  PARM B C B1 C1;
  EXO RTIME;
  ENDO PMRATEW;
  PMRATEW=0.116*(B*EXP(-C*RTIME/60)+B1*EXP(-C1*((RTIME/60)**2)));
  FIT PMRATEW START=(B 10 C 1 B1 10 C1 1);
```

```
PROC PRINT DATA=PTEST;
```

```
DATA MATCH;
  MERGE AMRDATA PTEST;
  COLFED=0.116;
PROC PLOT DATA=MATCH;
  PLOT MRATEW*RTIME='*' PMRATEW*RTIME='1'
  COLFED*RTIME='-'/HZERO OVERLAY;
```

This is a Fortran program to regress the isothermal data to Henderson's equation to give the isotherms, as well as, give statistics and graphs.

```
FILENAME AD70WGT[PRB.CHAMPAGNE.ISODATA]AD70WGT.DAT';
DATA AD70WGT; INFILE AD70WGT;
TITLE'70 C ADSORPTION ISOTHERM  WEIGHT DIFFERENCE VALUES';

INPUT RH X;
IF RH=100 THEN RH=99.9;
LABEL RH = '% RELATIVE HUMIDITY'
      X = 'ADSORBATE CONCENTRATION gH2O/gCELL';
PROC PRINT DATA = AD70WGT; PROC PLOT DATA = AD70WGT;
PLOT X*RH='*/HZERO VZERO;

DATA CALC;SET AD70WGT;RENAME X=PREDX;
PROC SYSNLIN DATA=CALC OUTMODEL=MTEST OUT=PTEST OUTPREDICT;
  PARM A B ;
  EXO RH;
  ENDO PREDX;
  PREDX=0.01*((-LOG(1-(RH/100)))/(A*343))**(1/B));
  FIT PREDX START=(A 1 B 1 );

PROC PRINT DATA=PTEST;

DATA MATCH;
  MERGE AD70WGT PTEST;

PROC PLOT DATA=MATCH;
  PLOT X*RH='* PREDX*RH='P'/ HZERO VZERO OVERLAY;
```

APPENDIX C : EXPERIMENTAL BREAKTHROUGH DATA

RUN #	07-40-10	COLFEED	0.116 mg/min		
AVG. PATM	P SATmmHg.	Pin COL.	Pout COL.	MFC-1	MFC-2
766.6 mmHg	791.6 mmHg	789.6 mmHg	770.6 mmHg	5 cc/min	45 cc/min
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME		
0	40.70	66632	0.00		
15915	43.43	72022	2.05	WGT METHOD	
19843	46.83	74774	4.00	gGAIN/gCELL	0.023/4. 036
26451	49.76	69744	6.48	gLOSS/gCELL	0.028/4. 036
34253	52.36	69185	8.57		
34455	54.96	68354	10.55		
38808	57.10	71592	12.68		
43347	59.16	68622	14.60		
47199	61.76	66893	16.90		
46795	63.86	62696	19.28		
50825	65.78	63374	22.33		
53815	67.90	61777	24.32		
51964	70.06	61788	27.33		
49010	72.50	61136	29.77		
53375	74.38	62269	32.45		
57332	76.41	59402	35.52		
54374	78.48	62207	37.45		
56308	80.60	59402	35.52		
53845	82.66	62207	37.45		
57241	84.83	59230	39.77		
53826	88.25	53765	42.30		
55335	90.48	55932	44.70		
56689	92.45	55377	46.70		
54795	94.53	51496	48.60		
53202	96.95	52199	50.52		
54484	98.96	50001	52.55		
58373	101.13	47808	54.68		
61172	103.18	48058	57.28		
58032	105.18	47885	59.32		
56812	107.28	43209	61.78		
61294	109.26	40107	64.10		
55211	111.33	42163	66.30		
50545	116.63	34635	68.78		
56533	118.63	37240	71.85		
56505	121.01	38777	74.25		
		35373	76.58		
		31602	79.42		
		29862	83.93		
		27879	86.18		
		27136	88.43		
		26554	90.75		
		25402	92.88		
		25146	96.10		
		23454	98.50		
		23775	100.98		
		21764	103.67		
		21166	106.17		
		21861	108.98		
		21305	111.52		
		22528	114.13		
		14132	117.15		
		14468	119.43	15428	125.27
		13069	122.83	0	137.7

RUN #	70-60-20	COL.FEED mgH2O/min	1.3102
AVG.PATM mmHg	PSAT mmHg	PinCOL mmHg	Pout COL mmHg
762.5	788.3	784.9	767.5
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME
0	26.70	293640	0.00
47567	41.70	300420	1.90
100290	43.91	302970	3.90
166430	45.75	290980	5.87
200280	47.65	298300	7.82
229740	49.46	288860	9.58
240390	51.25	294900	11.40
255730	53.35	280650	13.20
253720	55.30	268080	15.57
270700	57.08	250840	17.28
256820	59.10	243440	19.15
271200	60.89	213570	21.18
263400	62.80	208290	22.98
272240	64.58	181370	24.85
268190	66.30	163160	27.43
274730	68.16	151050	29.25
269360	69.88	125490	33.03
281550	71.70	121930	34.87
269410	73.50	117320	36.85
270660	76.08	105790	38.63
272430	77.81	99506	40.47
283980	79.61	92678	42.35
277260	81.35	86736	44.57
285230	83.20	84109	46.37
280950	85.10	76762	48.42
291370	86.86	68044	50.55
277560	88.76	65346	53.50
290620	90.56	61898	55.58
277560	92.41	60243	57.53
286130	94.21	55399	59.60
273250	96.36	55168	61.63
289670	98.23	55058	63.65
280440	100.11	49099	65.80
267950	106.70	37923	73.22
259210	112.10	32519	85.20
269280	116.70	25557	94.25
254170	126.71	24455	100.27
258970	136.91	16231	106.25
253960	146.80	20498	111.65
262730	156.71	19091	117.22
254110	166.71	12600	122.22
276600	177.58	14998	127.32
264640	188.76	13671	132.65
257030	248.51	12879	137.40
280900	250.30	13333	140.77

MFC-1 MFC-2
 cc/min cc/min
 8.5 41.5

WGT METHOD
 gGAIN/gCELL 0.065/4. 036
 gLOSS/gCELL 0.065/4. 036

RUN #	70-60-40	COL.FEED mgH2O/min	3.0364
AVG.PATM mmHg 762	PSAT mmHg 788.8	PinCOL mmHg 785.8	Pout COL mmHg 767
AD. AREA 0	AD.RUN TIME 25.75	DE.AREA 642940	DE.RUN TIME 0
259320	35.75	662670	4.2
410600	37.6	635490	6.25
469040	39.43	631870	8.68
544220	41.37	585940	10.7
559850	43.22	566700	12.68
599930	49.98	510070	14.57
598680	46.77	456090	17.33
620760	48.97	349000	21.43
606160	51.37	343010	23.45
645860	53.25	295540	25.47
621780	55.25	276610	27.67
648770	57.07	230400	30.27
629190	58.88	231880	32.27
646330	61.15	197210	34.48
631780	63	186920	36.45
654620	64.87	162630	38.75
633730	66.82	159460	41.02
645330	69.83	135710	43.1
630880	72	132410	44.98
656860	73.92	117750	46.93
627710	76.07	105920	49.62
659580	78.05	96172	52.28
628000	81.28	98524	54.18
641070	85.35	85855	56.12
611170	90.75	84193	58.23
658120	93.35	77175	60.78
612270	99.45	71627	62.83
		63399	64.93
		67158	67.08
		60091	69.08
		61129	70.98
		53898	72.97
		54047	74.93
		51299	76.97
		47482	79.13
		49764	81.4
		46878	83.9
		39122	86.07
		36749	88.62
		36734	90.73
		35121	92.95
		34281	95.07
		31027	100.98
		28028	109.1
		21021	118.88
		18040	126.55

WGT METHOD
gGAIN/gCELL 0.115/4. 032
gLOSS/gCELL 0.110/4. 032

RUN #	70-60-50	COL.FEED mgH2O/min	4.0746
AVG.PATM mmHg	PSAT mmHg	PinCOL mmHg	Pout COL mmHg
762.5	789.3	786.3	767.5
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME
0	28.30	884030	0.00
371630	32.18	915980	4.37
617130	34.85	831990	7.05
737130	37.38	824400	8.98
756210	40.62	735480	10.80
816930	42.42	695730	12.82
791200	44.25	608780	14.68
824090	46.67	573540	16.68
807910	48.50	504900	18.67
839200	50.42	461160	20.90
808840	52.72	417170	22.67
837210	55.28	398200	24.50
800580	60.08	341630	26.63
848490	62.20	324050	28.50
822120	64.18	271970	31.37
854620	66.45	259690	33.30
803770	70.07	234760	35.13
841160	73.23	223860	36.87
808480	77.35	186960	39.37
860710	79.23	184440	41.48
791870	87.25	161500	43.28
837570	92.73	157810	45.37
796780	100.12	137190	47.62
827060	108.47	118350	52.30
		113520	53.85
		103880	55.67
		93817	58.60
		84310	60.82
		84808	63.12
		79117	65.17
		69873	68.28
		65134	70.58
		66019	72.98
		62439	75.37
		60602	77.50
		53326	79.93
		52536	82.00
		51802	84.03
		45337	86.85
		45468	88.85
		40797	91.48
		33223	96.85
		39210	98.98
		29304	105.63
		26068	112.82
		26198	121.22
		16675	132.45
		14628	140.63
		14382	146.42

WGT METHOD
gGAIN/gCELL 0.126/4. 032
gLOSS/gCELL 0.126/4. 032

RUN #	70-60-70	COL.FEED mgH2O/min	6.0453
AVG.PATM mmHg	PSAT mmHg	PinCOL mmHg	Pout COL mmHg
762.8	791.6	790.6	767.8
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME
0	24.9	1169100	0
337610	27.57	1227500	3.55
600340	29.52	1180600	5.52
788190	31.3	1168300	7.72
878360	33.15	1058000	9.7
1003900	35.15	997140	11.77
1024500	37	852490	14.18
1104400	38.92	806790	16.17
1095700	40.85	711260	18.12
1158200	42.85	639140	20.73
1139400	44.9	564200	22.62
1189900	46.88	513720	24.9
1159400	48.77	417900	27.95
1128100	49.08	381170	30.33
1154600	50.95	334380	32.37
1194800	53.25	314130	34.22
1159300	55.68	273820	36.05
1196600	58	230770	39.32
1161500	60.68	186840	42.53
1200900	63.32	182140	44.77
1178400	65.77	158560	46.98
1224800	67.68	131350	50.92
1187600	69.62	117960	53.6
1229400	71.57	108640	55.82
1192900	73.47	96411	58.55
1227800	75.58	83208	61.93
1187700	77.85	89350	63.95
1225900	80.33	75730	66.42
1187700	82.55	73002	68.63
1233800	84.53	65242	70.67
1177300	87.37	67993	72.95
1233700	89.33	62111	75.38
1183100	91.83	56457	77.88
1234300	93.88	51222	80.1
		50006	82.68
		44919	84.68
		39893	88.02
		42834	90.15
		40272	92.42
		37911	94.88
		40538	97.12
		38078	99.47
		28025	108.4
		17546	117.17
		21301	127.18
		20385	137.18
		13927	143.7

WGT METHOD
gGAIN/gCELL 0.167/4. 036
gLOSS/gCELL 0.164/4. 036

RUN #	70-60-100	COL.FEED mgH2O/min	8.4247
AVG.PATM mmHg	PSAT mmHg	PinCOL mmHg	Pout COL mmHg
766.6	795.4	795.4	771.6
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME
0	20.77	1502000	0
456950	23.6	1633000	4.43
796180	25.45	1548900	6.43
1063200	27.25	1539800	10.6
1203500	29.13	1332200	15.67
1375700	31.05	734710	24.58
1435800	33.07	656690	26.52
1550500	34.98	592800	28.52
1466600	36.98	487450	30.95
1586800	38.97	427410	33.47
1520100	40.9	357220	35.87
1605200	43.37	333910	37.78
1501600	46.18	281410	39.98
1628000	48.1	240450	42.95
1541000	50.12	213370	45.12
1613600	52.37	202360	46.98
1600800	54.42	175350	48.97
1648000	56.77	165070	50.97
1555200	58.73	143250	52.98
1664300	61.42	142110	54.82
1618200	63.58	123660	56.85
1711700	65.6	112710	59.38
1549500	68.52	101960	61.61
1638200	70.77	93433	64.23
1666500	73.08	87191	66.37
1719000	75.07	77906	69.93
1580200	77.27	71572	72.05
1983100	79.77	72210	74.08
1523500	81.75	64416	76.15
1617700	83.83	59837	79.47
1557000	85.78	55948	81.63
1602000	87.8	58079	83.9
1513700	89.82	50584	86.3
1623200	91.77	51268	88.37
		38387	95.42
		39248	100.42
		35862	105.47
		31357	111.72
		29979	120.62
		23736	124.95

MFC-1 MFC-2
 cc/min cc/min
 50 0

WGT METHOD
 gGAIN/gCELL 0.233/4. 032
 gLOSS/gCELL 0.226/4. 032

RUN #	80.40-10	COL.FEED mgH2O/min	0.0971
AVG.PATM mmHg	PSAT mmHg	PInCOL mmHg	Pout COL mmHg
759.7	778.2	774.5	763.4
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME
0	31.25	43683	0
13866	34.33	45289	2.93
14785	37.27	44471	5.08
16054	40.25	46871	7.22
17563	42.77	39008	9.72
24847	45.37	41921	11.78
27626	47.88	38224	13.88
30583	50.23	39323	16
37953	52.55	37179	18.13
36258	55	38138	20.48
36432	57.2	35501	22.73
34811	59.33	33290	25.03
42112	61.4	27842	27.72
39213	63.52	29931	30
44464	65.68	27346	32.45
43810	67.88	25075	34.77
45792	69.95	22033	37.13
43798	72.17	14225	39.92
44403	74.23	22055	42.33
43378	80.62	22919	44.98
42759	85.62	19266	50.92
42320	90.62	13714	57.5
		0	63.05

MFC-1 MFC-2
 cc/min cc/min
 5 45

WGT METHOD
 gGAIN/gCELL 0.014/4. 032
 gLOSS/gCELL 0.017/4. 032

RUN #	80-60-20	COL.FEED mgH2O/min	1.2846
AVG.PATM mmHg 767.8	PSAT mmHg 790.7	PinCOL mmHg 788.4	Pout COL mmHg 772.2
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME
0	18.72	291100	0
15829	21.83	300740	6.74
14801	24.55	257160	11.59
15935	27.17	271080	13.42
28533	29.92	240680	15.65
63431	32.52	233260	17.45
125300	34.92	194600	19.82
173870	36.95	190030	21.79
213550	38.72	163610	23.89
227310	40.52	156960	25.65
252270	43.2	135730	27.79
254290	45.32	128130	29.72
263070	48.28	112050	31.62
263820	50.12	107780	33.47
273640	52.13	96123	35.45
267150	54.12	96578	37.42
283180	55.83	81532	39.77
262190	58.48	76373	41.85
281930	60.53	63247	44.19
268150	62.65	53589	49.04
280080	64.6	54146	51.09
270290	66.5	51277	53.14
281770	68.43	51278	55.32
273720	70.3	43609	57.9
283160	72.18	40200	60.32
		40910	64.69
		36871	64.69
		34730	67.17
		34258	69.4
		32601	72.3
		27873	74.79
		25044	86.09
		15525	97.75
		0	111.82

MFC-1 MFC-2
cc/min cc/min
8.5 41.5

WGT METHOD
gGAIN/gCELL 0.047/4. 032
gLOSS/gCELL 0.052/4. 032

RUN #	80-60-40	COL.FEED mgH2O/min	2.9297
AVG.PATM	PSAT	PinCOL	Pout COL
mmHg	mmHg	mmHg	mmHg
766.3	793.9	791.2	770.9
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME
0	21.35	612380	0
84322	24.27	545130	9.38
274030	26.17	442970	12.63
430610	27.99	285610	18.78
497720	29.99	258460	20.82
562740	32.73	233790	22.92
562520	35.45	205480	24.78
605930	37.23	191670	26.65
583740	39.75	169450	28.37
619050	41.67	158780	30.17
600700	43.43	133560	32.4
622880	45.37	117380	34.87
601470	47.25	100430	37.58
626710	49.2	100480	39.45
596960	52.15	86053	41.57
619450	54.92	81371	43.55
593480	58.67	74381	45.42
618700	61.55	71665	47.72
611110	63.45	62772	49.88
622770	66.95	56138	52.45
591600	71.13	51107	54.43
634120	73.25	48283	57.17
607600	75.52	43021	59.93
627450	77.82	40550	62.1
611830	79.7	39309	65.25
579650	165.75	34683	67.57
579200	174.67	32693	69.93
631320	176.67	30494	72.17
611710	178.67	29416	75.17
		25024	77.8
		23974	80.82
		23771	83.67
		16554	89.13
		15665	94.05
		14453	100.9
		13401	104.83
		0	109.43

WGT METHOD
gGAIN/gCELL 0.074/4. 036
gLOSS/gCELL 0.076/4. 036

RUN #	80-60-50	COL.FEED mgH2O/min	3.9635
AVG.PATM mmHg	PSAT mmHg	PinCOL mmHg	Pout COL mmHg
756.2	782.9	781.9	760.8
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME
0	15.05	786630	0
27057	20.05	835000	4.45
329870	22.63	752130	6.92
578500	24.47	722410	8.95
706530	26.3	588510	11.02
735300	28.1	520780	13.2
789000	29.95	431750	15.07
778500	31.8	378400	17.32
808850	33.65	313970	19.43
787050	35.48	270480	21.93
823130	37.32	239870	23.87
794670	39.2	221150	25.6
826920	41.08	188330	27.5
790480	43.45	175710	29.35
827280	45.28	153590	31.22
798880	47.32	140950	33.12
828750	49.27	122390	35.03
799950	51.35	108200	37.07
830010	53.32	95039	39.1
804700	55.22	88167	41.07
825450	57.1	83571	43.02
793460	59.42	76971	45.3
835700	61.5	67877	47.3
803900	63.72	65953	49.28
827210	65.88	59394	51.42
805570	67.88	57533	53.58
831590	69.87	53553	56.08
806640	71.93	45313	58.25
834440	74.05	41859	60.35
803950	75.98	37494	63.23
790980	88.78	39766	65.48
780410	94.7	35334	68.2
		28219	76.73
		22835	84.23
		16973	89.8
		14574	95.87
		15780	101.02
		0	111.25

MFC-1 MFC-2
 cc/min cc/min
 22.5 27.5

WGT METHOD
 gGAIN/gCELL 0.084/4. 036
 gLOSS/gCELL 0.087/4. 036

RUN #	80-60-70	COL.FEED mgH2O/min	6.2029
AVG.PATM mmHg	PSAT mmHg	PinCOL mmHg	Pout COL mmHg
756.9	782.7	781.3	761.5
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME
0	15.58	1197600	0
338170	18.4	1159600	4.08
764800	20.57	1096100	6.35
919150	22.42	931810	8.32
1046400	24.33	820470	10.3
1055200	26.5	688120	12.23
1127800	28.45	598040	14
1110800	30.47	508930	16.1
1176400	32.45	446320	18.13
1147300	34.55	366140	20.12
1188200	36.75	339510	21.95
1153400	38.9	279270	23.98
1201200	41.15	262420	25.73
1149300	43.68	215680	27.63
1200500	45.85	197460	29.78
1161800	47.78	166170	31.68
1201300	49.77	151670	33.5
1169300	51.72	135590	35.23
1205800	53.92	125440	37.08
1146300	56.92	107150	38.87
1189700	59.27	94443	40.97
1157300	61.35	87583	42.9
1209600	63.48	83983	44.72
1168600	65.6	73042	46.7
1194900	68.42	65614	49.05
1169000	70.33	55838	51.5
1211600	72.3	53299	54.87
		52188	60.63
		37408	65.85
		29470	70.7
		16725	76.18
		17203	80.33
		17873	86.25
		15244	91.3

MFC-1 MFC-2
cc/min cc/min
32.7 17.3

WGT METHOD
gGAIN/gCELL 0.112/4. 032
gLOSS/gCELL 0.110/4. 032

RUN #	80-60-100	COL.FEED mgH2O/min		7.9244
AVG.PATM	PSAT	PinCOL	Pout COL	MFC-1 MFC-2
mmHg	mmHg	mmHg	mmHg	cc/min cc/min
760.7	794.8	793.8	766.7	50 0
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME	
0	12.92	1394400	0	
90693	16.23	1526100	2.68	WGT METHOD
970300	18.18	1489500	5.1	gGAIN/gCELL 0.147/4. 036
1323600	20.17	1417500	7.45	gLOSS/gCELL 0.147/4. 036
1486000	22.12	1226600	10.08	
1427000	24.13	1149900	12.25	
1505100	26.27	746120	14.62	
1426000	28.8	561170	17.2	
1512100	30.82	475590	19.08	
1476400	32.92	423820	20.93	
1552100	35.62	363820	22.82	
1506100	37.68	323370	24.65	
1569500	39.98	275310	26.55	
1507700	42.07	257310	28.42	
1549900	44.1	213150	30.27	
1465500	46.13	187120	32.68	
1534200	48.47	165000	34.65	
1471800	50.68	156450	36.42	
1558700	52.9	139550	38.23	
1483100	55.02	128300	40.03	
1589200	57.08	111410	42.43	
1489300	59.18	104600	44.37	
1579000	61.55	86619	47.07	
1576300	63.68	76980	51.75	
1623100	65.97	58749	55.5	
1494800	68.48	61818	57.57	
1552300	70.47	56878	59.62	
1504200	72.48	48193	62.93	
1617900	74.47	50975	65.15	
1509200	76.82	46185	67.6	
1536600	78.9	36628	73.17	
		36005	79.17	
		29786	82.88	
		17467	87.78	
		24773	92.8	
		24284	97.85	
		13264	103.55	
		19059	107.87	
		15014	112.93	
		13227	117.83	
		0	123.27	

RUN #	90-40-10	COL.FEED mgH2O/min	0.0908
AVG.PATM	PSAT	PinCOL	Pout COL
mmHg	mmHg	mmHg	mmHg
762.8	793.2	790.5	768.3
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME
0	34.7	51803	0
17617	37.5	56422	3
20488	41.17	52868	5.42
26332	44.33	47035	7.52
29090	46.98	45377	9.53
30664	49.52	41625	11.57
35546	51.77	44535	13.75
38361	54.22	45922	15.88
36882	56.62	39797	18.57
38699	58.82	42485	20.67
37638	61.05	43826	23.1
39676	64.38	39441	25.57
38227	67.05	38734	27.65
39170	69.27	36335	29.95
38119	71.72	35926	32.1
37262	74.47	35279	34.88
35661	76.7	30906	36.63
37998	79.2	32798	38.92
38173	81.43	24996	41.48
37500	83.78	27336	43.95
41090	85.98	21194	46.67
		20170	49.37
		13995	52.32
		12962	55.18
		14258	57.75
		0	61.02

MFC-1 MFC-2	
cc/min	cc/min
5	45

WGT METHOD	
gGAIN/gCELL	0.006/4. 036
gLOSS/gCELL	0.008/4. 036

RUN #	90-60-20	COL.FEED mgH2O/min	1.2982
AVG.PATM	PSAT	PInCOL	MFC-1 MFC-2
mmHg	mmHg	mmHg	cc/min cc/min
762.3	784.4	782.6	8.5 41.5
AD. AREA	AD.RUN TIME	DE.AREA	
0	19.17	272540	0
27795	21.88	308130	4.03
78702	24.6	288160	5.87
154240	26.55	292420	7.92
199070	28.35	272000	9.85
232630	30.27	261670	11.65
239870	32.18	235720	13.45
258960	34.25	211130	15.3
254210	36.05	170460	17.42
268600	37.82	156680	19.23
263170	40.03	130230	21.15
267240	42.8	110500	23.98
261990	45.23	100550	25.35
276470	47.45	87628	27.32
268360	49.38	73472	29.2
280830	51.23	65495	31.83
267530	53.45	59638	34.03
282270	55.22	56634	36.02
270970	57.02	44078	38.1
276920	59.12	45239	40.43
271490	61.07	38894	42.63
287890	62.82	37236	44.8
271940	64.62	33322	46.97
284860	66.45	28685	49.15
		29057	51.5
		26490	54.3
		22620	57.1
		21877	59.87
		20932	62.93
		14417	65.92
		13269	68.58
		0	71.52

WGT METHOD
gGAIN/gCELL 0.032/4. 036
gLOSS/gCELL 0.035/4. 036

RUN #	90-60-40	COL.FEED mgH2O/min	2.9566
AVG.PATM mmHg	PSAT mmHg	PinCOL mmHg	Pout COL mmHg
762.3	785.4	783.1	766.9
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME
0	10.82	301420	0
17242	15.92	264670	1.85
232550	18.77	209340	4.05
434810	20.9	177740	6.2
544160	22.72	150420	8.02
556360	24.53	106290	11.57
601800	26.42	97687	13.43
592640	28.29	91026	15.3
616480	30.43	75640	17.43
604450	32.38	67630	19.4
625460	34.88	60084	22.08
607980	37.58	53634	24.1
629470	40.1	50970	26.15
625390	41.87	40625	28.22
651540	43.77	41153	30.28
625890	46.13	37587	32.57
650450	48.65	29727	36.85
626110	50.77	29290	39.3
654070	52.55	25393	42.6
614780	54.5	16807	48.43
643380	56.4	15741	51.15
613430	58.57	13582	57.3
636300	60.4	0	62.02
600220	62.98		
611000	66.05		
605940	68.05		
616830	70.15		
587030	72.52		

WGT METHOD
gGAIN/gCELL 0.05/4.032
gLOSS/gCELL 0.053/4.032

RUN #	90-60-50	COL.FEED mgH2O/min	3.8176
AVG.PATM	PSAT	PinCOL	Pout COL
mmHg	mmHg	mmHg	mmHg
764.5	794.9	794.1	769.2
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME
0	10.13	781660	0
110700	15.35	770370	2.05
547720	18	727730	4
675010	19.82	577280	6.42
739680	21.7	487220	8.47
751410	23.82	364970	10.87
784530	25.93	316670	12.43
764860	28	264240	14.48
796520	29.98	222510	16.48
771900	32.2	183760	18.5
801230	34.03	162170	20.33
770360	35.88	122830	22.75
794210	37.85	109460	24.98
778760	40.22	89549	27.32
787600	43	71193	30.22
766930	45.62	64035	32.47
800280	47.6	57723	34.38
776160	49.68	57141	36.45
810330	51.58	46849	38.6
778610	53.52	34022	39.27
802430	55.75	36152	46.55
778940	57.87	31314	48.87
799910	59.83	26274	51.43
778180	62.15	26831	54.32
799130	64.12	16103	61.8
		0	67.82

MFC-1	MFC-2
cc/min	cc/min
22.5	27.5

WGT METHOD	
gGAIN/gCELL	0.060/4. 032
gLOSS/gCELL	0.062/4. 032

RUN #	90-60-70	COL.FEED mgH2O/min	5.6609
AVG.PATM mmHg	PSAT mmHg	PInCOL mmHg	Pout COL mmHg
762	792.4	791.5	767.5
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME
0	10.55	1127900	0
18716	13.2	1086700	2.3
706530	16.82	989930	4.75
973330	18.87	810700	6.65
1028300	20.83	638100	9.13
1099600	22.72	513330	11.12
1086600	24.68	428700	13.08
1130900	26.75	345480	15.03
1092500	28.72	296410	17.1
1112700	30.62	229670	19.37
1091200	32.52	190950	21.85
1120900	34.45	160190	23.77
1092500	36.47	139590	25.57
1133400	38.55	118540	27.47
1107300	40.58	107280	29.45
1154000	42.48	86478	31.38
1112600	44.47	79486	33.28
1140800	46.55	72061	35.27
1080900	48.7	58270	38.32
1111000	50.85	57656	40.43
1088900	52.73	47808	42.65
1125700	55.25	45675	45.75
1102900	57.25	36749	48.23
1136300	59.23	34356	50.68
1096100	61.17	31751	53.07
1141700	63.13	29615	55.58
		26706	58.28
		15975	61.35
		21211	63.8
		17964	66.88
		14479	69.88
		12370	73.12
		0	75.92

WGT METHOD
gGAIN/gCELL 0.079/4. 036
gLOSS/gCELL 0.080/4. 036

RUN #	90-60-100	COL.FEED mgH ₂ O/min	8.6248
AVG.PATM	PSAT	PinCOL	Pout COL
mmHg	mmHg	mmHg	mmHg
762.3	792.7	789.9	767.8
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME
0	10.07	1600500	0
1337800	13.38	1332600	4.27
1449900	15.33	932130	6.75
1549600	17.35	724130	8.68
1477100	19.43	598980	10.65
1568000	21.58	471630	12.55
1472500	24	394850	14.48
1558800	26.48	309020	16.55
1483900	28.92	265070	18.37
1571500	30.97	177440	21.75
1482600	33.22	159280	23.58
1570100	35.28	135830	25.43
1556500	37.32	116570	27.53
1603600	39.3	92622	29.38
1521200	41.3	88420	31.27
1923700	43.92	78563	33.23
1515800	45.95	70227	35.28
1589500	48.15	59560	37.33
1505600	50.23	52914	39.65
1595200	52.42	49645	41.73
1493800	54.6	38537	44.18
1558900	56.87	40130	46.32
1957200	58.97	33781	48.62
1573800	61.12	31011	50.93
1502700	63.13	31295	53.3
1574200	65.68	26887	55.93
		19654	58.82
		23240	61.88
		15707	64.67
		16350	67.4
		14487	70.18
		0	73.17

WGT METHOD
gGAIN/gCELL 0.101/4. 032
gLOSS/gCELL 0.101/4. 032

RUN #	80-60-20-12	COL.FEED mgH2O/min			
		1.2087	0.6266		
AVG.PATM	PSAT	PinCOL	Pout COL	MFC-1	MFC-2
mmHg	mmHg	mmHg	mmHg	cc/min	cc/min
766.8	788.9	786.2	772.4	8.5	41.5
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME	5	45
0	26.85	302310	0		
24722	29.83	308140	3.28		
98027	32.73	279010	5.23	WGT METHOD	
169260	34.87	282730	7.03	gGAIN/gCELL	0.044/4. 032
204130	37.55	265320	8.77	gLOSS/gCELL	0.017/4. 032
228460	39.63	269340	10.52		
232170	42.1	250310	12.47		
255680	43.82	239530	14.4		
144510	46.18	206010	16.47		
258930	47.92	199830	18.5		
249570	49.9	180490	20.32		
258930	51.78	173370	22.17		
252370	53.6	160400	23.93		
261070	55.88	143650	26.22		
255480	57.88	137120	28.3		
261730	60.03	134940	30.62		
256140	62.27	134580	32.47		
		134420	34.6		
		131040	36.43		
		136300	38.52		
		132980	40.35		
		140880	42.12		
		130740	44.2		
		138080	46.28		
		130820	48.3		
		130120	51.05		
		129840	53.03		
		131620	55.43		
		132340	57.43		
		134730	59.48		

RUN #	80-60-40-12	COL.FEED mgH2O/min			
		2.8814	0.6638		
AVG.PATM	PSAT	PinCOL	Pout COL	MFC-1	MFC-2
mmHg	mmHg	mmHg	mmHg	cc/min	cc/min
766.1	795.6	793.3	771.6	17.5	32.5
AD.AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME	5	45
0	21.03	737830	0		
121180	23.78	697560	2.57	WGT METHOD	
323810	25.6	647990	4.37	GAIN/gCELL	0.071/4. 036
458290	27.58	633860	6.23	LOSS/gCELL	0.037/4. 036
508710	29.6	577300	8.25		
560110	31.37	547070	10.22		
553880	33.43	452110	12.58		
585370	35.53	398520	14.85		
577390	37.33	341920	16.63		
593720	39.65	312220	18.45		
580090	41.95	249930	21.07		
606330	43.98	241690	22.88		
580090	46.75	203260	24.82		
610780	48.72	195710	26.95		
585180	51.17	173130	29.23		
610420	53.47	169600	31.13		
595350	55.4	159860	32.93		
612450	57.4	155840	34.83		
593670	59.37	150970	36.83		
609960	61.75	156570	38.6		
		139800	41.48		
		148140	43.53		
		144150	46.05		
		149460	47.87		
		140930	50.05		
		149030	52.17		
		142120	54.28		

RUN #	80-60-50-12	COL.FEED mgH2O/min		
		3.8517	0.6649	
AVG.PATM	PSAT	PinCOL	Pout COL	MFC-1 MFC-2
mmHg	mmHg	mmHg	mmHg	cc/min cc/min
766.3	788.5	786.6	770.9	22.5 27.5
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME	5 45
0	13.48	1007200	0	
33519	16.16	865900	2.85	WGT METHOD
207160	18.55	847780	4.95	gGAIN/gCELL 0.081/4. 032
503950	20.53	763270	7.12	gLOSS/gCELL 0.049/4. 032
641310	22.43	709250	9	
740090	24.43	576240	11.25	
759210	26.43	527720	13.17	
800440	28.51	429360	15.45	
788250	30.8	374240	17.92	
817490	33.11	317530	20.25	
802530	34.95	287990	22.57	
823700	37.18	261310	24.58	
793330	40.41	250110	26.42	
828640	42.31	212780	28.78	
803800	44.46	209790	30.62	
832700	46.4	190390	32.55	
802310	48.9	190960	34.38	
793610	56.95	178270	36.42	
784770	62.03	180300	38.27	
790370	74.21	158220	41.35	
777510	80.3	168790	43.55	
		153930	46.55	
		166050	48.62	
		155290	50.87	
		150070	53.87	
		162180	55.62	
		153660	58.17	
		146240	61.47	
		151960	64.2	
		154040	66.37	
		154520	68.8	
		150870	71.15	
		154270	73.42	
		150320	75.92	
		145760	80.2	
		142220	84.48	
		148710	89.75	
		132160	102.1	
		152070	104.22	

RUN #	80-60-70-12	COL.FEED mgH ₂ O/min		
		5.847	0.673	
AVG.PATM	PSAT	PinCOL	Pout COL	MFC-1 MFC-2
mmHg	mmHg	mmHg	mmHg	cc/min cc/min
764.5	785.8	784.8	770.1	32.7 17.3
AD. AREA	AD.RUN TIME	DE.AREA	DE.RUN TIME	5 45
0	11.8	1205800	0	
23309	15.05	1146100	3.6	
354000	18.48	1100500	5.93	WGT METHOD
875150	20.93	867110	8.8	gGAIN/gCELL 0.104/4.032
1069700	22.9	771840	10.77	gLOSS/gCELL 0.0704.032
1093200	25.02	583350	13.65	
1159500	27.2	501340	16.03	
1134300	29.25	433970	17.92	
1168300	32.83	385190	19.95	
1157000	34.77	331030	21.82	
1184600	36.88	300790	23.75	
1151500	39.08	260750	25.98	
1183600	41.92	233160	28.1	
1144500	45.25	200530	30.77	
1195600	47.17	184210	34.07	
1161800	49.17	169320	36.82	
1192300	51.38	177000	38.6	
1154700	53.87	160200	40.72	
1197300	56.23	164620	42.58	
1161200	58.18	154470	44.43	
1197400	60.2	158200	46.27	
1154600	62.68	151100	48.22	
		147770	50.77	
		146990	52.93	
		151810	55.22	
		145360	57.17	
		146180	59.48	
		147020	61.4	
		146270	63.33	
		141010	65.43	
		151200	67.65	
		144730	69.6	
		147210	71.77	
		128400	79.82	
		136290	84.38	

APPENDIX D : OPERATIONAL CALCULATIONS

Operational Calculations

Calculation of the % relative humidities and flow rates through MFCs 1&2 had to be done before any experimental work could begin. The % relative humidities were calculated for the column inlet at saturator conditions (T, P) and column conditions (T, P).

The basic definition of relative humidity can be manipulated to become :

$$Rh = PP_{H_2O} / VP_{H_2O} \quad (35)$$

$$PP_{H_2O} = y_{H_2O} * P_{sat} \quad (36)$$

$$VP_{H_2O} = y_{satH_2O} * P_{sat} \quad (37)$$

$$\therefore Rh = PP_{H_2O} / VP_{H_2O} = y_{H_2O} * P_{sat} / y_{satH_2O} * P_{sat} = y_{H_2O} / y_{satH_2O} \quad (38)$$

The mole fraction of H₂O and N₂ is calculated at the saturator temperature, assuming 100% saturation :

$$y_{H_2O} = P_{sat} / P_{ins} \quad (39)$$

and
$$y_{N_2} = 1 - y_{H_2O} \quad (40)$$

Now the molar flow rate of N₂ through the controllers at the reference conditions is calculated :

$$N_2FC1 = MFC1 * \rho_{N2} / M_{N2} \quad (41)$$

$$N_2FC1 = MFC2 * \rho_{N2} / M_{N2} \quad (42)$$

Then calculate the molar flow rate and overall mole fraction of the water in the combined streams :

$$H_2OFR = (N_2FC1 / y_{N2}) - N_2FC1 \quad (43)$$

$$Y_{H2O} = H_2OFR / (N_2FC1 + N_2FC2 + H_2OFR) \quad (44)$$

The partial pressure of the water at the column inlet and within the column is :

$$PP_{H2O} = Y_{H2O} * P_{inc} \quad (45)$$

$$PP_{H2OC} = Y_{H2O} * ((P_{inc} + P_{out}) / 2) \quad (46)$$

Therefore, the % relative humidity out of the saturators and within the column is :

$$Rhsat = PP_{H2O} / P_{sat} * 100 \quad (47)$$

$$Rh = PP_{H2OC} / P_{satc} * 100 \quad (48)$$

where Rh is the relative humidity that the cellulose "sees" in the column.

This calculation is an iterative process; guess an initial N₂ flow rate for both controllers, so the combined flows equal 50 sccm, then calculation of the resulting % Rhs until the desired relative humidities are achieved. The flow rates must then be checked to be sure that the are not too high or too low for the reasons mentioned in the previous section. Two Fortran programs were written to accomplish this set of calculations. See Appendix B.

The data points for Figures 9 and 10, the saturation assumption graphs, are listed in Appendix A. The points are the arithmetic average of all the data obtained for the specific flow and temperature conditions of the experimental run and were obtained as mentioned in the section on calibration.

Once the flow rates and relative humidities were determined, the assumption of saturation validated, and all the minor problems mentioned previously corrected, calibration of the GC could be accomplished. The procedure for doing the calibration was done as mentioned previously. Once the data points were obtained, they were divided into two sets corresponding to either large or small sample loop size. The average of all the points at each flow, temperature, and associated sample loop size was taken as the calibration point. See Appendix A and Figure 11.

VITA

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