Fractionation of Gas Mixtures in a Moving-bed Adsorber

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I. CORRELATION OF ADSORBER PERFORMANCE

The design and operation of a pilot-scale-moving bed adsorber to separate the various components of a gas mixture using activated carbon as the preferential adsorbent are described. A binary system, methane-acetylene, and a ternary system, methane-carbon dioxide-acetylene, were studied. The performance of the unit was analyzed by means of the transfer-unit-height (H.T.U.) concept based on the observed changes in gas composition during tower operation. For both the binary and ternary systems the transfer-unit height was independent of feed-gas composition but was found to vary linearly with the ratio of feed gas to carbon flow. The over-all transfer-unit-height values based on either the gas or the adsorbed phase were observed to vary from 6.5 in. at 1.39 std. cu. ft./lb. carbon to 36.9 in. at 4.81 std. cu. ft./lb. carbon.

The separation of acetylene from dilute gas mixtures containing methane and carbon dioxide, by selective adsorption on activated carbon in a pilot-scale moving-bed adsorber has been investigated experimentally as part of a more extensive program having as its objective the study of the production and recovery of various petrochemicals. Acetylene is of particular interest because of its potential extensive use if it can be recovered cheaply and conveniently from dilute mixtures with other hydrocarbon gases such as those obtained by cracking natural gas. A recent survey (*18*) has indicated that the use of a selective adsorption technique known commercially as hypersorption (*4* and *23*) is an economically attractive method for the purification of acetylene. Several general advantages of this method of separation over other more conventional methods in commercial use such as distillation, adsorption, or solvent extraction are (*a*) better selectivity, (*b*) relatively high capacity for low-boiling materials, (*c*) use of moderate temperatures and pressures, and (*d*) ability to recover with greater efficiency certain constituents present in small amounts in gas mixtures.

Chief industrial interest in gas adsorption until rather recently lay in processes to recover the last traces of condensible gases from relatively inert gases, as in the drying of gases, recovery of volatile solvents, and removal of odors and noxious gases from air (*27* and *28*). In the past few years, however, interest in the separation of gases having similar relative adsorbabilities has increased greatly. Equilibrium data for various binary and ternary hydrocarbon systems have been published (*24*), and equipment and processes for carrying out separations by selective adsorption in both fluidized and countercurrent moving adsorbent beds have been patented (*6* and *16*) and described in the literature (*3* and *21*). The most successful of these processes has been the hypersorption process of the Union Oil Company (*4* and *23*), under whose direction several large-scale adsorbers have been built. In spite of the intensive research now in progress, however, no design methods are generally available at the present time for determining the height of an adsorbent bed necessary to produce a desired separation. The present investigation, therefore, had as its chief objective the study of certain operating variables involved in the design of a moving-bed adsorber and the development of methods for the analysis of the performance of the pilot-plant unit based on the transfer-unit-height concept of Chilton and Colburn (*10* and *11*). Specifically, binary feed-gas mixtures of methane and acetylene, and later ternary feeds consisting of methane, carbon dioxide, and acetylene, were fractionated in a pilot moving-bed adsorber with the purpose of continuously separating and recovering the acetylene in higher concentrations.

Early work on this research program was carried on by Howard Kehde (*22*), who employed a simple countercurrent adsorption system. Binary gas mixtures of methane—ethylene and ethylene—propane were fed into the bottom of a 1-in. I.D. iron pipe down which was flowing a stream of activated charcoal. The change in vapor concentration between the feed and overhead was noted, and, by a method similar to that used for absorption or stripping, the transfer unit height (H.T.U.) or height equivalent to a theoretical stage (H.E.T.S.) could then be estimated. In the physical arrangement employed by Kehde the overhead stream becomes enriched in the more volatile component while the adsorbate on the carbon leaving the bottom of the tower is richer in the heavier component. It is obvious, however, that for such a system the maximum possible enrichment of the heavier component of the feed mixture corresponds to equilibrium with the feed gas. In order to obtain high purities of the heavy component it is necessary to employ a fractionation section below the feed point like that normally used in other cascade operations such as distillation. Operation in this manner was the next logical extension of the research program. The present investigation, therefore, was made on a tower containing both an adsorption (upper) and a stripping (lower) section, as shown in Figure 1, both binary and ternary gas systems being used, as mentioned above.

APPARATUS AND METHODS

The equipment used for carrying out these investigations is shown in Figures 1 to 6. The adsorber column proper was constructed of standard 1-in.-diam. steel pipe and had an over-all effective bed length of approximately 13 ft., measured from the overhead gas disengaging section, *O*, to the carbon flow-control valve, *V*. (*See* Figure 1.) The total height of the entire assembly including the two 55-gal. storage drums, *A* and *B*, was 21 ft. Because of height limitations imposed by the laboratory building, the bottom section of the tower located between the side product gas outlet, *S*, and the stripping has inlet, *P*, was inclined at an angle of 45 deg. to the vertical. No operating difficulties were experienced because of this construction, as the angle of repose of granular carbon is approximately 38 deg.

Carbon Flow

Activated Columbia HA carbon (10- to 28-mesh granules) was allowed to flow by gravity from the top storage reservoir, *A*, through the column and into the saturated carbon storage drum, *B*, at the base of the adsorber. The carbon flow was controlled accurately by a specially designed flow controller, *V*, which is shown in detail in Figure 3. It consisted essentially of a rotating element mounted between two stationary guide plates and was connected to a variable-speed transmission. Each revolution of the disk caused a fixed quantity of carbon to be transported through the valve. Thus controlling the speed of rotation of the disk, caused varying amounts of carbon to flow down the column. Pulsations in flow were observed to be negligible a few feet above the valve at ordinary operating speeds, and so flow through the column proper may be considered uniform. In order to further improve the flow characteristics and to prevent bridging of the carbon, a Syntron vibrator was also mounted on the column.

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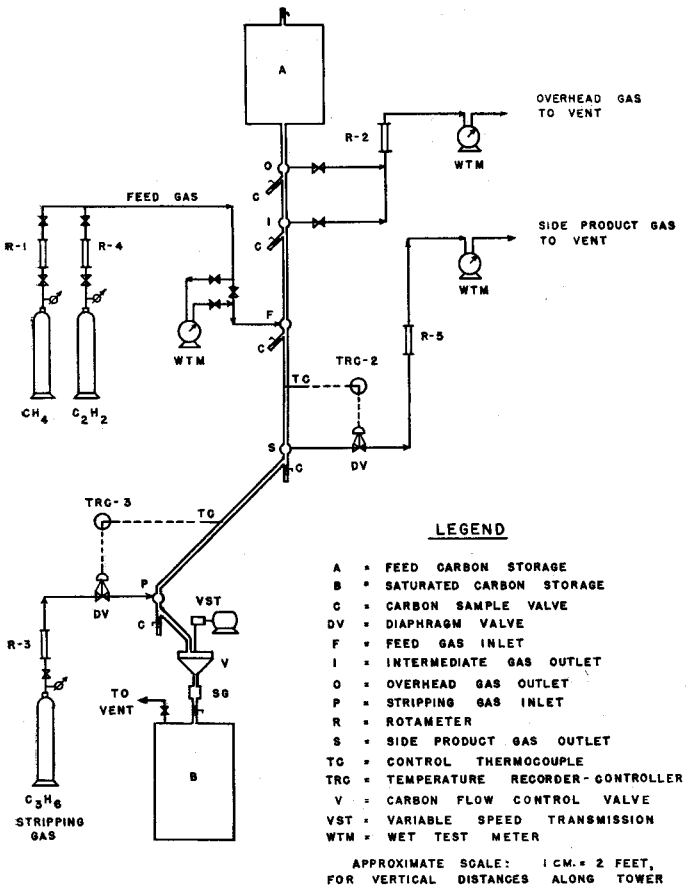


Fig. 1. Schematic diagram of hypersorber.

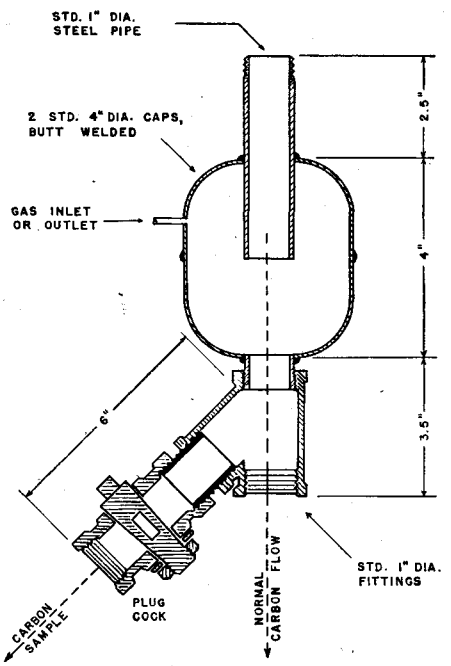


Fig. 2. Gas engaging or disengaging section.

Gas Flow

Feed gas, obtained from either high-pressure cylinders or brine-sealed atmospheric-pressure gas holders, was metered through rotameters, which were calibrated immediately prior to use with a wet-test meter and fed at substantially atmospheric pressure to the center of the column at the feed-gas engaging section, F. The gas flowed upward through the column, countercurrent to the descending carbon, and was withdrawn either at the disengaging section, O, to give the normal overhead gas product, or at section I, as the "intermediate" gas product. By contact with the carbon in this manner, the higher molecular weight constituents tended to be removed preferentially from the original feed-gas mixture by selective adsorption onto the surface of the activated carbon. Thus contact of a feed gas mixture consisting of methane and acetylene resulted in the removal of a portion of the acetylene from the gas and an accumulation of acetylene on the carbon to an extent depending on such factors as temperature, pressure, gas composition, flow rates, and carbon activity, as discussed elsewhere in this paper. The overhead gases, therefore, were enriched with respect to methane by this net removal of acetylene from the original gas stream.

The saturated carbon resulting from the above-mentioned gas contact continued to move down the column, and, if desired, it could be removed from the bottom of the tower without further treatment. The adsorbed gases, enriched in acetylene, could then be recovered by stripping the carbon in a separate vessel. The present apparatus, however, was designed to carry out this recovery operation continuously as an integral part of the over-all separation process, in order to simulate conditions obtained in modern industrial hypersorbers.

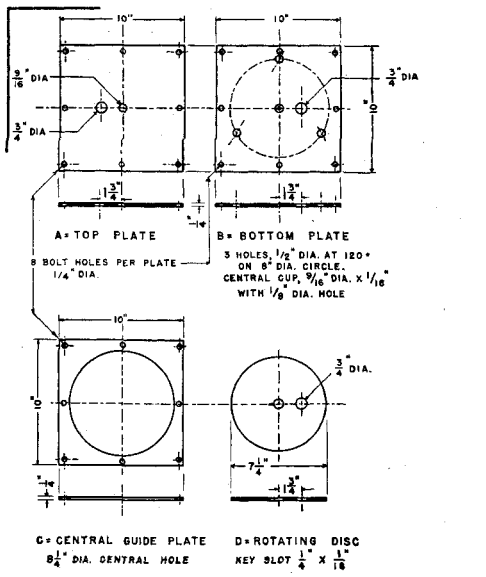
Although superheated steam is used in industrial hypersorbers as the stripping agent, it was not convenient to use this medium in the pilot adsorber, because of the difficulties which would be encountered by the condensation of water and the consequent wetting of the carbon at the operating temperatures and pressures employed. To achieve this purpose, therefore, a secondary feed of hydrocarbon gas was introduced at section P in the tower to act as a stripping agent for the gases adsorbed on the carbon in tne upper sections of the column. This secondary feed had to be a gas which was more strongly adsorbed by the carbon than the gases which were to be recovered from the main feed gas, and it had to be capable of displacing these gases from the carbon under the conditions existing in the tower. Thus, in the case under consideration, a secondary feed stream of propylene entering the tower at the gas-engaging section P displaced the acetylene-rich adsorbate from the carbon in the lower section of the column between points P and S. In general, it was observed that lower molecular-weight hydrocarbons were so displaced by higher molecular-weight hydrocarbons; that is a C-3 hydrocarbon would displace a C-2 hydrocarbon, or the latter a C-1 or hydrogen, and so forth. This tendency, however, was not true for all cases, for it was also observed than n-butane failed to displace propylene, and hence it could not be used for this purpose when it was desired to recover the propylene. It is apparent that the adsorption equilibria involved for specific systems and conditions must be carefully considered.

Reflux

As seen in Figure 1, the descending carbon with its adsorbate containing the heavier components of the main feed gas flowed past the feed point, F, and into the lower or enriching section of the adsorber, where it came in contact with the stripping agent, propylene. The introduction of the stripping agent and the consequent displacement of the lighter components from the carbon, e.g., acetylene and methane, created a gas stream which originated in the area of displacement between tower sections P and S and moved up the column as a reflux stream.

All or part of this ascending gas stream could be removed as a side product at the gas disengaging section S. If all this gas was removed at S, then a condition analogous to a state of no reflux existed in the section of the tower between S and F, and the lower section of the column between points P and S acted only as a carbon-stripping section. If only a part of the desorbed gas was removed as a side stream at section S, by regulating the outlet valve, then the remainder of the gas continued to ascend between sections S and F as reflux. Because this reflux contained the desorbed heavier components of the main feed gas, it tended to displace the less strongly adsorbed components from the descending carbon, thus giving a side-product gas richer in the heavier components. Such a desorption process is analogous to that used in a continuous reboiled absorption unit, in which the rich solvent is completely stripped of absorbed components, a portion of the desorbed stream being returned to the system as reflux while the remainder is taken off as a bottoms product.

If none of the gas was removed as a side product at section S, corresponding to a type of total reflux, the total feed input was eventually recovered at the overhead gas



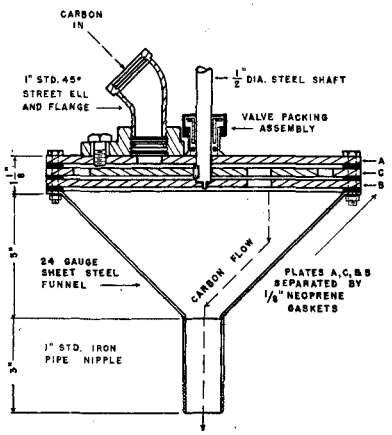


Fig. 3. Carbon flow control valve.

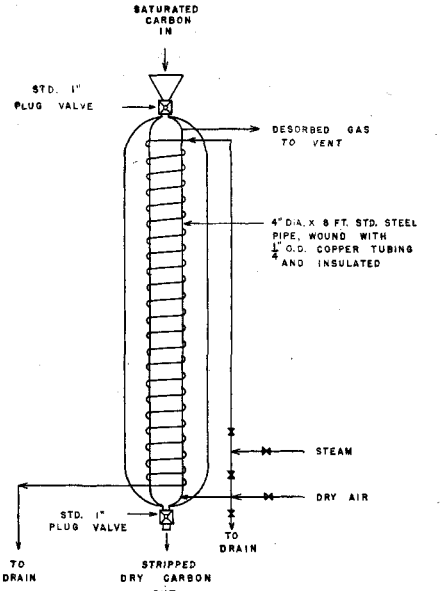


Fig. 4. Carbon regenerator.

outlet, O, and the adsorber behaved similarly to a fixed bed which became progressively saturated and finally reached a state of equilibrium with the feed gas such that no net change in gas composition occurred as it passed through the bed. Under these conditions continuous separation was not possible. To achieve maximum over-all separation of a particular gas mixture, therefore, there must be an optimum amount of reflux.

Temperature Control

The adsorption of propylene by activated carbon occurred in a narrow band, which moved up the tower from point P. Accompanying this adsorption wave was a sharp temperature rise owing to the release of energy upon adsorption. This rise formed the basis for the control of the propylene flow to the tower. Thus, when the propylene band reached the control thermocouple, the temperature effect was transmitted to TRC-3, a Brown temperature-recorder controller of the proportional plus reset type, which actuated a diaphragm valve on the propylene-supply line. This valve was then throttled sufficiently until the ascending propylene-adsorption band was transported down below the control thermocouple by the descending flow of carbon. As soon as the temperature at this point fell below the set point, the controller TRC-3 acted to increase the propylene flow, thus maintaining the system in proper balance without contaminating the side-product stream with propylene.

Similarly another Brown temperature-recorder controller, TRC-2, actuated by the temperature rise produced by the ascending reflux stream in the tower section between points S and F, operated a second diaphragm valve on the side-product outlet line, limiting the flow of side product from the system and thus regulating the level of reflux as described above. Control of the reflux level in this fashion, however, was not entirely satisfactory, as the relatively small amounts of available gas tended to produce a cyclic disturbance which prevented true steady state operation of the tower in some cases. In most runs, therefore, very little reflux was used, because best over-all stability was obtained under these conditions.

The column was drilled and tapped at strategic points for installation of 1/8-in.-diam. pencil-type iron-constantan thermocouples, fitted with compression-type sleeves, for measurement of bed temperatures. The thermocouples were connected to a twelve-point Brown potentiometer or to the temperature-recorder controllers.

The gas-engaging and -disengaging sections were identical and, as shown in Figure 2, were constructed by welding together two standard 4-in.-steel welding caps. A 1-in.-diam. pipe nipple was welded into the top half of each section as shown, thus providing a gas space from which a carbon-free gas stream could be removed or into which a feed-gas stream could be introduced via a 1/4-in. O.D. tubing connection. The bottom of each unit was fitted with a close nipple and a standard Y connection, to which was attached a plug valve to permit withdrawal of a carbon sample just below the section.

The saturated carbon was removed periodically from the storage drum (B, Figure 1) and sent to a batch steam stripper illustrated in Figure 4. Saturated or slightly superheated steam was admitted to the bottom of this vessel and allowed to pass upward through the carbon charge until all the adsorbed gases were removed. The steaming was then discontinued, and hot, dry air was admitted. When the carbon was dry, it was drained from the bottom of the unit and recharged to the carbon-feed-storage reservoir (A, Figure 1) of the adsorber to complete the cycle. Industrially the carbon is stripped continuously and returned via a gas lift to the top of the hypersorber, a portion of the carbon recycle being sent to a high-temperature reactivator to remove very strongly adsorbed or polymerizable materials which tend to reduce the activity of the carbon. This type of reactivation was unnecessary in the present investigation because high-purity reagent gases were used.

Materials

The gases used in this investigation were all of high purity (approximately 99%) and were obtained from the Matheson Company in standard high-pressure cylinders. Acetylene was bubbled through water and then passed through a calcium chloride drying chamber before entering the system. The gases were metered through calibrated rotameters at 5 lb./sq. in. gauge and sent to the tower feed line, which entered at section (F, Figure 1). The overhead- and side-product gases, which were withdrawn from the column at sections O and S respectively, were passed through rotameters or through wet-test meters to be measured before being vented to the atmosphere.

The carbon used for this investigation was Columbia grade HA activated cocoanut-shell charcoal, supplied by Carbide and Carbon Chemicals Corporation in the form of 10- to 28-mesh granules. The carbon activity was determined by a standard n-butane–adsorption technique.

Sampling Techniques

Gas-sampling connections were installed on all gas lines leading to and from the adsorber, thus making it possible to obtain gas samples simultaneously at the overhead-, intermediate-, feed-, and side-product locations. To obtain a gas sample, a 250-ml. gas-sample bulb, filled with a slightly acid saturated aqueous solution of sodium chloride in which the gases used were essentially insoluble, was attached to the sample line through an upper stopcock, and the salt was allowed to drain slowly from the lower stopcock of the bulb. In this way a representative gas sample was collected over a controlled period of time by displacement of the liquid. Although the samples could be stored indefinitely, they were usually analyzed within 24 hr. or less by means of an Orsat apparatus. While a run was in progress provision was also made to sample the various gas streams directly for chemical analysis by an Orsat apparatus mounted on the control panel. In this manner an instantaneous check on gas compositions could be obtained.

Carbon was sampled at the overhead-, intermediate-, and side-product outlet points, as well as the main and secondary feed-gas inlet points by means of the carbon-

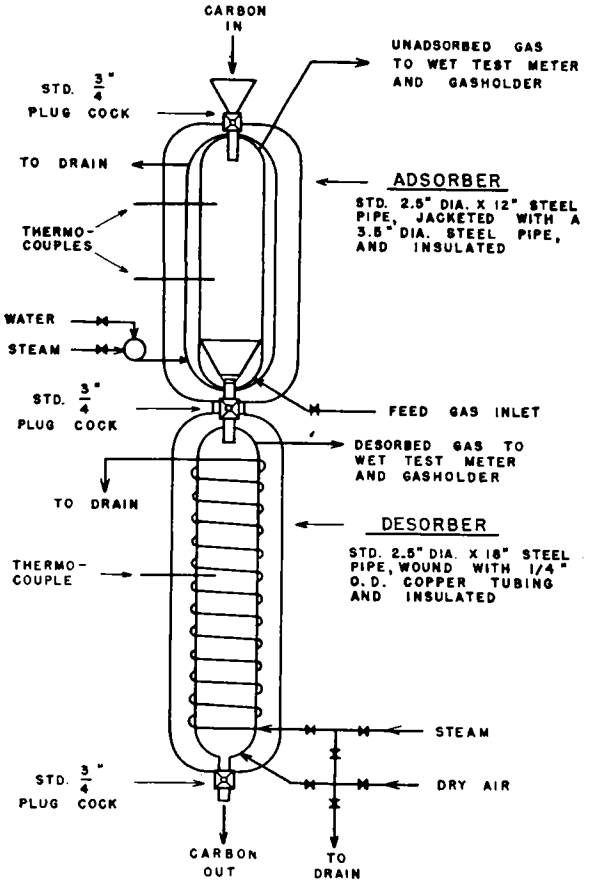


Fig. 5. Carbon activity—equilibrium apparatus.

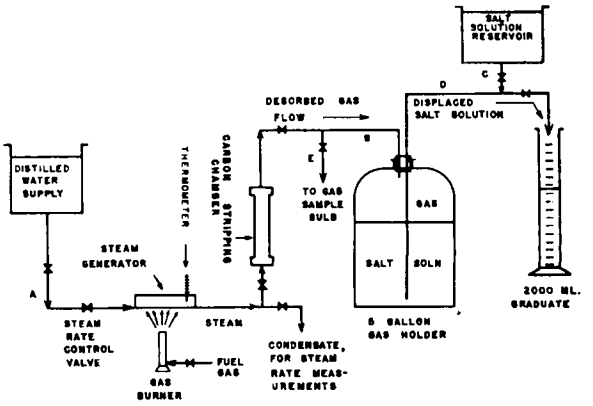


Fig. 6. Carbon sample-stripping apparatus.

sampling valves attached to the gas engaging and disengaging sections. (*See* Figures 1 and 2.) The carbon samples were collected and stored in 250-ml.-capacity screw-cap jars and then transferred to the small-scale carbon stripper shown in Figure 6. In this apparatus a known weight of saturated carbon was stripped with steam, which was freshly generated from boiled, distilled water, the desorbed gases being collected over a saturated salt solution in a 5-gal. reservoir. The gases thus collected were forced by liquid displacement into a standard glass sampling bulb in a manner similar to that used to collect the primary gas samples from the moving-bed adsorber.

The chemical analysis of feed and product gases from the column, as well as the gas desorbed from the various carbon samples, was carried out in an Orsat apparatus which was equipped with a pressure-compensated, high-precision measuring tube, with which it was possible to measure gas volumes to 0.01 ml. Mercury was used as the confining liquid, and contact pipettes were attached to the capillary manifold by spherical ball-and-socket points. The particular combinations of gases which were used to study the performance of the moving-bed adsorber were such that a complete analysis by Orsat technique was feasible. A typical combination included methane, acetylene, propylene, and carbon dioxide, along with nitrogen and oxygen from air leakage. In this case a sample in the Orsat apparatus was passed through the following solutions: (*a*) 50% aqueous potassium hydroxide, to absorb carbon dioxide; (*b*) alkaline potassium iodomercurate solution (*18*), to absorb acetylene; (*c*) acid mercuric sulfate solution (*18*), to absorb propylene; and (*d*) alkaline potassium pyrogallate solution to absorb oxygen. As all oxygen and nitrogen originated from the air, it was possible to calculate the nitrogen content from a knowledge of the oxygen present. The residual methane content was then calculated by difference from 100 volume %.

RESULTS AND DISCUSSION

The transfer-unit-height concept of Chilton and Colburn (*10* and *11*) provides a convenient method of comparing the efficiency under different operating conditions of various types of mass transfer equipment, as it expresses the performance quite simply in terms of a single number which has the dimension of length and a numerical magnitude which is a direct measure of the relative difficulty of effecting a particular separation. It was decided, therefore, to use this approach in the case of the moving-bed adsorber. Although the actual procedure adopted to estimate the transfer-unit height differed somewhat for the case of the binary system, methane–acetylene, as compared with the ternary system, methane–carbon dioxide–acetylene, the calculations in both cases were made from experimental adsorber-operating data such as those listed in Table 1 and the adsorption-equilibrium data which were predicted by one of the two correlation methods developed during this investigation and which will be described in Part II of this article. The experimental determination of adsorption-equilibrium data in all ranges which were required was considered beyond the scope of this investigation. It would be highly desirable, however, for such determinations to be undertaken in future studies.

Binary System

By use of the apparatus and techniques described above, eleven adsorber runs were made at substantially atmospheric pressure and at temperatures between 75° and 100° F. on binary feed mixtures of methane and acetylene which ranged in composition from 5 to 50 volume % acetylene. Total gas throughputs were controlled from approximately 5 to 20 std. cu. ft./hr., measured at 60° F. and 1 atm., and carbon flow rates varied from 2 to 4 lb./hr., these limits being imposed by the construction and satisfactory operation of the test equipment. More emphasis was placed on feed mixtures dilute in acetylene, viz.: 5 to 15 volume %, as these concentrations would be the ones most likely to be encountered in the commercial production of acetylene by pyrolysis or partial oxidation of hydrocarbons. It has been pointed out (*18*) that in cases of this type the use of hypersorption to increase the acetylene concentrations in the furnace effluents possesses economic advantages over other methods of enrichment. Typical adsorber data obtained for the binary system are listed in Table 1. By suitable control of the gas and carbon flow rates it was found possible in exploratory runs to reduce the overhead loss of acetylene to zero and at the same time to increase its concentration in the side product to as high as 96 volume % acetylene, starting with 30% acetylene in the feed. For analytical purposes in the present study it was desirable to obtain reasonable concentration changes and to avoid those operating conditions which reduced the concentration of one component to zero in either of the product streams. For this

reason the concentration changes were proportionately much greater in certain cases than in others. The optimum flow rates and concentrations to be used in commercial practice would be determined by appropriate economic balances.

For analysis of the binary system, a material balance was first made on the top section of the moving-bed adsorber, between points O and F in Figure 1, by use of the observed gas rates and compositions and the experimentally determined adsorbate on the carbon at the overhead gas outlet to determine the amount and composition of the adsorbate on the carbon at the main feed inlet. This procedure was followed because it was a relatively simple matter to collect representative gas samples continuously while the adsorber was operating at steady state, but it was a much more difficult task to sample the carbon accurately. It was found impractical to attempt to collect carbon samples before or during gas sampling because of the serious disturbances to the tower equilibrium which occurred whenever a carbon valve was opened. The procedure finally adopted, therefore, was first to sample all the gas streams slowly and simultaneously over a 15- to 20-min. interval of steady state operation without collecting any carbon. When the gas sampling was complete, carbon samples were withdrawn rapidly, starting at the top of the column, by opening in turn each plug valve to allow flow into a screw-cap bottle. Using this sampling technique, the authors concluded that all the gas samples were representative and that the carbon sample collected first (i.e., at the overhead gas outlet) was the most reliable. With the exception of the carbon sample withdrawn from the bottom of the column, where the disturbing effects of sampling were negligible, all other carbon samples were subject to greater error and were generally observed to give low total amounts of adsorbate when steam stripped as compared with those predicted and required by material-balance considerations. As the over-all material balances checked to within 5% in most cases, it was decided to calculate the amount and composition of the adsorbate at the main feed section, F, as mentioned above, in order to provide a consistent basis for the calculations.

Table 1. Typical Experimental-adsorber Data**

	I-A Binary system		I-B Ternary system	
Run	1		16	
	Rate	%	Rate	%
Feed gas*				
Methane	4.32	70.0	2.99	41.7
Carbon dioxide	....	....	2.39	33.3
Acetylene	1.85	30.0	1.80	25.0
Total	6.17	....	7.18	....
Overhead gas				
Methane	3.21	90.4	2.81	51.0
Carbon dioxide	....	....	1.91	34.2
Acetylene	0.34	9.6	0.81	14.8
Total	3.55	....	5.53	....
Side-cut gas				
Methane	0.59	30.9	0.22	13.5
Carbon dioxide	....	....	0.45	27.0
Acetylene	1.32	69.1	0.99	59.5
Total	1.91	....	1.66	....
Entering carbon				
Methane	0.33	55.2	0.23	92.0
Carbon dioxide	....	....	0.01	4.0
Acetylene	0.27	44.8	0.01	4.0
Total	0.60	....	0.25	....
Bottoms carbon				
Methane	0.0	0.0	0.0	0.0
Carbon dioxide	....	....	0.02	50.0
Acetylene	0.10	3.9	0.02	50.0
Propylene	2.52	96.1	....	....
Total	2.62	....	0.04‡	....
Avg. temp., °F.	94		93	
Bed height, in.	48		26	
N_{OG}	2.6		1.9	
H_{OG}, in.	18.4		13.7	
N_{OA}	2.8		1.9	
H_{OA}, in.	18.4		13.7	
Lb. carbon/hr.	2.0		2.2	
Std. cu. ft. gas/lb. carbon†	2.57		2.72	

*All gas and adsorbate rates are expressed as gram-moles per hour. Compositions are mole %.
†Standard cubic feet of gas measured at 60°F. and 1 atm.
‡Propylene-free basis.
**Complete tabular material has been deposited as document 4965 with the American Documentation Institute, Photoduplication Service, Library of Comgress, Washington 25, D. C., and may be obtained for 1.25 for photoprints or 35-mm. microfilm.

With the input and output quantities for each component over the adsorber section between points O and F (Figure 1) known, the molal flow rates of the gas in this portion of the tower were assumed to change uniformly, a change which was equivalent to the assumption of a straight operating line when the data were plotted as mole fraction of acetylene in the gas phase vs. gram moles of acetylene per gram mole of carbon. Adsorption-equilibrium data for the methane-acetylene binary were then calculated for gas compositions in the required ranges by Method I, binary adsorption equilibria, which was based on a modification of the Polanyi adsorption potential theory as described in Part II of this paper. The calculated equilibrium data were then plotted on the same diagram as the operating data, and the number of over-all gas-phase and adsorbed-phase transfer units, H_{OG} and H_{OA}, based on acetylene concentration changes between the main feed and the overhead gas outlet were evaluated graphically, by means of the "half-line" method of Baker (*1*).

Ternary System

In the calculation of the height of an over-all transfer unit for the ternary system, material balances were first obtained around the entire adsorption column and the section of the column under consideration. In all the runs made on the ternary system, both adsorption and enriching runs, the top or adsorption section of the column was used, and so sectional material balances were always made from the top of the column to the feed-gas entry point. For the ternary work the overhead gas was all taken off at gas-outlet point I in Figure 1 instead of point O, as in the binary work. This was done to increase the head of carbon above the gas outlet, thus increasing the resistance to gas channeling into the reservoir, A. The actual bed length for the ternary runs, therefore, was only 26 in., as compared with 48 in. for the binary runs. As stated earlier, carbon samples taken during tower operation through 1-in. diam. plug valves served to upset the tower equilibrium. Therefore all material balances were based on changes in gas flow and composition. Thus, by analysis of the overhead- and feed-gas streams at steady state, the entering carbon composition in the reservoir having been ascertained previously, it was possible to determine by a material balance the composition and quantity of the adsorbate on the carbon passing point F.

Since no experimental data were obtained on the variation of gas composition with distance up the column, it was necessary to approximate this relationship in order to plot the equilibrium curve and the operating line for the determination of the over-all transfer-unit height. In the case of the binary system a straight-line relationship was observed

for the operating lines. This relationship was established for each run by making a series of internal material balances between one end of the section (e.g., at the feed or overhead), where compositions were known, and several intermediate points by assuming that the quantities of gas and adsorbate flowing through the particular section varied uniformly over the section in question. For the ternary work it was decided that the use of the theoretical-stage method employed in multicomponent distillation calculations would be more suitable for the present purpose. With this method the assumption is that over each theoretical stage the adsorbate leaving is in equilibrium with the gas leaving the same stage. Thus, starting at the top of the tower the composition and quantity of the adsorbate on the carbon leaving the first stage was computed by assuming it to be in equilibrium with the overhead gas. This calculation was made by use of the adsorption-equilibrium equations of Lewis et al. (*24*) discussed later. Then, with the composition and quantity of the overhead gas, the entering carbon, and the carbon leaving the first stage known, the gas entering the first stage was obtained by a material balance. This process was repeated from stage to stage down the tower until the feed-gas and adsorbate compositions were reached. The number of theoretical stages required to effect the change in gas composition from the feed to the overhead was thus obtained, and the height equivalent to a theoretical stage (H.E.T.S.) was then the height of the section divided by the number of theoretical stages. For calculation of the over-all transfer-unit height, however, the equilibrium and operating data obtained in the H.E.T.S. calculation was plotted as mole fraction in the vapor vs. milligram moles of adsorbate per gram of carbon, and the number of transfer units based on both the gas phase and the solid phase was evaluated either by graphical integration or by the "half-line" method of Baker (*1*), in the same manner as used in the case of the binary-system data. Actually the use of this method is based on the assumption that the efficiency of mass transfer of each component is the same, that is, that the approach to equilibrium is the same for each component. Such an assumption is usually made for calculating multicomponent distillation operations because of the complexity of any other approach. In the present case this assumption appears justified by the fact that in most instances each of the components shows approximately the same approach to equilibrium on the feed carbon. In a typical run, for instance, the approach to equilibrium at the feed for methane, carbon dioxide, and acetylene is 94.7, 90.5 and 88.3% respectively.

Eleven adsorber runs were made on the ternary system methane–carbon dioxide–acetylene. Six of the runs were designated as acetylene-enriching runs. As previously mentioned, it was the purpose of this research to study the performance of both the upper, or adsorption, section of the column and the lower, or enriching, section. Work on the binary system indicated that operation of the lower section of the column as originally planned, that is, stripping the descending carbon with propylene and dividing the desorbed gas between side-product gas and reflux, did not yield significant transfer-unit data for the section, because the quantity of desorbed gases was insufficient to provide both reasonable enrichment in the downflowing carbon and adequate samples. In order to obtain more reliable data on enriching-section performance, therefore, the upper section of the tower (between points F and I, Figure 1) was used for the enriching runs. In these enriching runs the carbon entering from the reservoir, A, was first pretreated with a relatively dilute mixture of the ternary gases in order to produce an adsorbate simulating that which would be present normally at the top of the enriching zone. This presaturated carbon then descended the tower countercurrent to a feed gas the composition of which approximated that of the normal side-cut gas. By operating in this fashion, the enriching data were obtained over the same section of the tower as the adsorption data, and thus the effect of any construction variables was eliminated and direct comparison of the two processes permitted.

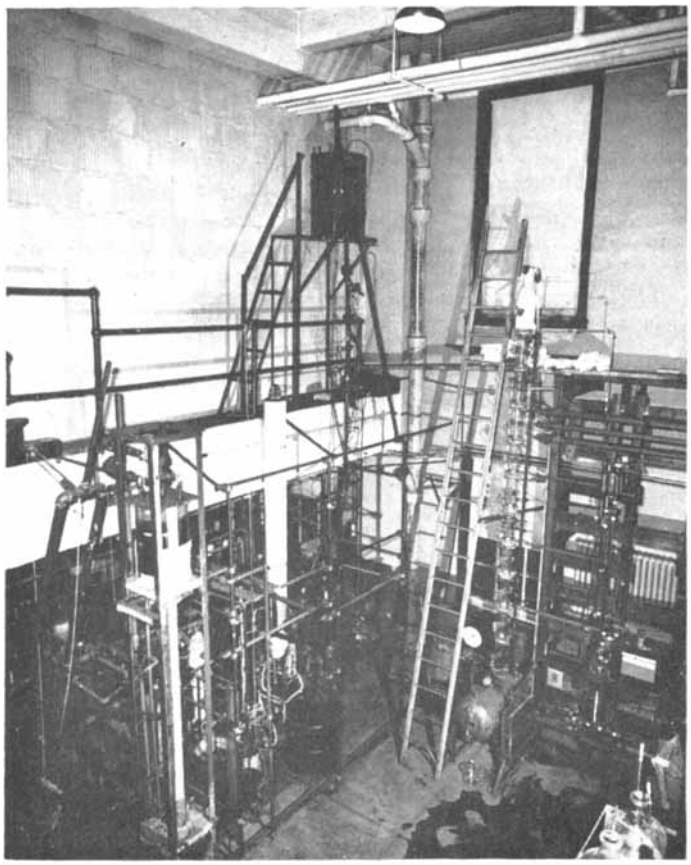


Fig. 7. Fractionation of gas mixtures in a moving-bed adsorber.

Three runs were made to study the effect of gas rate and composition on the height of an over-all transfer unit, without bottoms reflux. In these runs essentially all the desorbed gas was removed as side product. In two other runs the ratios of reflux to side-product rate were 2/3 and 1/1 respectively with the same feed gas. Under these conditions the percentage of acetylene in the side-product gas was increased from 42.7 to 55.2%. Another run was made to observe the effect of increase in the carbon flow rate on the height of an over-all transfer unit. In this run the carbon rate was increased to 3.2 lb./hr. as compared with the 2.2 lb./hr. normally used for the ternary-system runs. As seen in Figure 8, no effect of increased carbon rate on the adsorbed-phase over-all transfer-unit height, H_{OA}, is indicated when plotted vs. the gas-to-carbon–rate ratio. This result agrees with the data on the binary system in which the over-all transfer-unit height was found to be independent of the carbon rate in the range from 2.0 to 4.0 lb. of carbon/hr.

Correlation of Data

The data on the binary adsorption system, as well as the ternary adsorption and enriching systems, were correlated by plotting the over-all transfer-unit

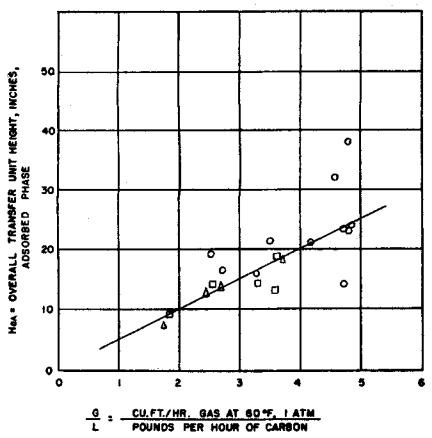


Fig. 8. Transfer unit height correlation—I-adsorption of acetylene, methane, and carbon dioxide on columbia—HA carbon in a moving bed adsorber; O = binary system: methane—acetylene—adsorption, □ = ternary system: methane—carbon dioxide—acetylene—enriching, Δ = ternary system: methane—carbon dioxide—acetylene—adsorption.

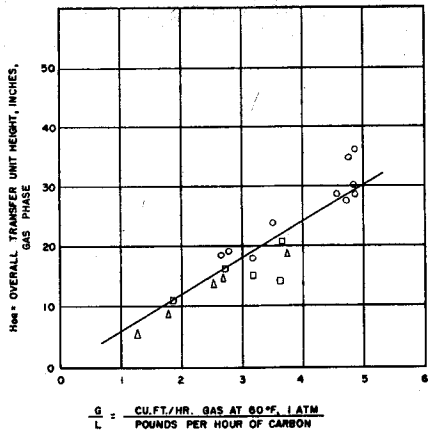


Fig. 9. Transfer unit height correlation—II-adsorption of acetylene, methane, and carbon dioxide on columbia—HA carbon in a moving bed adsorber; O = binary system: methane—acetylene—adsorption, □ = ternary system: methane—carbon dioxide—acetylene—enriching, Δ = ternary system: methane—carbon dioxide—acetylene—adsorption.

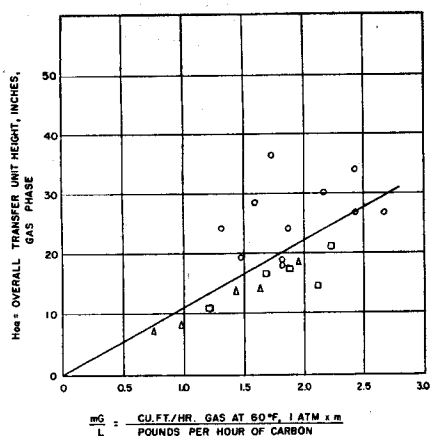


Fig. 10. Transfer unit height correlation—III-adsorption of acetylene, methane, and carbon dioxide on columbia—HA carbon in a moving bed adsorber; O = binary system: methane—acetylene—adsorption, □ = ternary system: methane—carbon dioxide—acetylene—enriching, Δ = ternary system: methane—carbon dioxide—acetylene—adsorption.

heights, H_{OA} and H_{OG}, vs. the ratio of gas to carbon rate. Thus the over-all transfer unit height in inches, based on the adsorbed phase, H_{OA}, is plotted in Figure 8 as a function of the standard cubic feet of gas at 60° F. and 1 atm., G, divided by the carbon rate in pounds per hour, L. A straight-line relationship was observed for the three sets of data, which may be stated analytically as

$$H_{OA} = 5\left(\frac{G}{L}\right) \tag{1}$$

Figure 9 shows the corresponding relationship obtained by plotting H_{OG}, the over-all height of a transfer unit in inches based on the gas phase vs. G/L in the same units as above, which is also expressed by the equation

$$H_{OG} = 6\left(\frac{G}{L}\right) \tag{2}$$

From the fact that in each case above a single straight line was obtained for the three independent sets of data on the two systems it may be concluded that the height of an over-all transfer unit is a linear function of the ratio of the gas to carbon rate and is independent of the feed-gas composition.

It is also of interest to attempt to interpret the results of this investigation on the basis of the rate mechanisms involved in the adsorption process. As discussed earlier, the successive steps involved in the adsorption of a vapor from a gas mixture are as follows: (1) transfer of the vapor from the main gas stream to the external surface of the particle; (2) transfer of the component within the pores of the adsorbent. (such transfer taking place either by diffusion in the gas phase in the pores or by adsorption at the mouth of the pores and diffusion of the adsorbed phase to the interior of the pore and both mechanisms probably occurring simultaneously, the greater the width of the pores the greater the percentages of transfer occurring by gas diffusion); and (3) physical adsorption of the vapor on the adsorbent surface.

If the replacement of one gas on the carbon by a second gas is occurring, then the above mentioned three steps in reverse order must be considered for the desorbed gas.

Step (1) of the foregoing process, diffusion of vapors from a gas stream to the surface of a particle, has been carefully investigated by Gamson, Thodos and Hougen (*15*) and by Wilke and Hougen (*32*). They found that the mass transfer rate could be correlated as a function of the modified Reynolds number, D_pG'/μ, with a transition occurring at $D_pG'/\mu = 350$. The results were expressed in terms of the j factor or the height of a gas-film mass transfer unit, H_G, as follows:

$$\frac{D_pG'}{\mu} < 350$$

$$j_M = \frac{k_G'}{G_M'}\left[\frac{\mu}{\rho D}\right]^{2/3} = 1.82\left[\frac{D_pG'}{\mu}\right]^{-0.51} \tag{3}$$

$$sH_G = \frac{G_M'}{k_G'} = 0.55\left[\frac{D_pG}{\mu}\right]^{0.51}\left[\frac{\mu}{\rho D}\right]_g^{-2/3} = \frac{1}{j_M}\left[\frac{\mu}{\rho D}\right]_g^{2/3} \tag{4}$$

$$\frac{D_pG'}{\mu} > 350$$

$$j_M = \frac{k_G'}{G_M'}\left[\frac{\mu}{\rho D}\right]^{2/3} = 0.989\left[\frac{D_pG'}{\mu}\right]^{-0.41} \tag{5}$$

$$sH_G = \frac{G_M'}{k_G'} = 1.011\left[\frac{D_pG'}{\mu}\right]^{0.41}\left[\frac{\mu}{\rho D}\right]_g^{-2/3} = \frac{1}{j_M}\left[\frac{\mu}{\rho D}\right]_g^{2/3} \tag{6}$$

Values of s for various sized particles at a number of different void volumes are presented by Wilke and Hougen (*32*).

By use of the foregoing equations and other data (*13* and *26*) to calculate values of H_G, individual transfer-unit heights in the order of 0.1 to 1.0 in. are obtained. Since the experimental over-all transfer-unit heights were found to be about 6.5 to 36.9 in., it is apparent that the external gas-film resistance is not the controlling resistance in the adsorption process. It should be further noted that according to the gas-film individual-transfer-unit equations (4) and (5), H_G varies as G' raised to the exponent 0.41 to 0.51. Were this the controlling resistance, the plot of over-all transfer-unit heights vs. the gas-carbon-rate ratio shown in Figures 8 and 9 would be expected to yield exponential curves rather than straight lines.

Step (1) having been eliminated as the rate-controlling step, it is apparent that either diffusion within the pores or physical adsorption must control. Although accurate direct measurement of

the rate of physical adsorption is very difficult to obtain, as is pointed out by Brunauer (*8*), because of the difficulty of eliminating pore resistance and thermal effects which accompany adsorption, it is generally assumed that this process occurs with extreme rapidity and that the resistance involved is negligible compared with the other diffusional resistances involved. Such an assumption appears reasonable also from the quantity of heat involved in physical adsorption as compared with the much slower chemisorption process. The heat of physical adsorption is equal to or only slightly greater than that involved in condensation, which is assumed to occur instantaneously, while the heat evolved in chemisorption is about ten times that for physical adsorption. Eliminating gas-phase diffusion and physical adsorption as rate-controlling steps, we are left with only internal pore diffusion as the possible rate-determining step.

Other investigators have also reached the same conclusion. Foster and Daniels (*14*) concluded that for adsorption of nitrogen dioxide from air on silica gel the rate-determining step is the diffusion of the solute inside the particles. Eagleton and Bliss (*13*) also reported that diffusion inside the particles was controlling for the adsorption of water vapor on alumina.

That the resistance to mass transfer through the gas phase is negligibly small as compared with the adsorbed phase is also demonstrated by use of the present data by plotting the over-all transfer-unit height based on the gas phase, H_{OG}, vs. mG/L, the ratio of gas to carbon rates multiplied by the average slope of the equilibrium curve as shown in Figure 10. This plot expresses the usual relationship between the over-all and individual mass transfer unit heights, which is given by the equation

$$H_{OG} = H_G + \frac{mG}{L} H_A \qquad (7)$$

In the plot of H_{OG} vs. mG/L the slope of the line is equivalent to the value of H_A, and the y intercept is the value of H_G. Figure 10 shows H_G to be essentially zero, thus pointing to the negligible resistance to diffusion in the gas film. Allowing for scatter in the experimental data, the average value of the individual transfer-unit height based on the adsorbed phase, H_A, is observed to be about 11 in.

CONCLUSIONS

The performance of a pilot-scale moving-bed adsorber has been studied by means of a binary system of methane-acetylene, and a ternary system of methane–carbon dioxide–acetylene, with Columbia grade-HA activated carbon as the adsorbent. The data were correlated by plotting the over-all transfer unit height values against the ratio of the gas-to-carbon rate. A straight-line relationship was found to exist for both adsorption and enriching operations with over-all-transfer-unit-height values based either on the gas phase or the adsorbed phase ranging from 6.5 to 36.9 in., for ratios of gas-to-carbon rate of from 1.39 to 4.84 cu. ft. of gas (60 °F., 1 atm.)/lb. of carbon. The individual transfer-unit height for the gas phase, H_G, was observed to be essentially zero, an indication that the resistance to mass transfer occurred mostly in the adsorbed phase. The individual transfer-unit height based on the adsorbed phase, H_A, was estimated from the experimental data to be approximately 11 in.

II. EQUILIBRIUM CONSIDERATIONS

A method for estimating adsorption equilibria based on a modification of the Polanyi adsorption-potential theory was developed for use in the investigation described in Part I of this article. In addition, the recently published correlation method of Lewis, Gilliland, Chertow, and Cadogan, suitably modified for the present application, was successfully employed in the correlation and extrapolation of the ternary equilibrium data.

The ability of certain highly porous solids such as activated charcoal, silica gel, and alumina to adsorb large volumes of gases has been recognized and used industrially for over one hundred and fifty years. A large amount of experimental work has been carried out on the equilibrium relations of various individual gases on different adsorbents, and many theoretical and empirical equations have been developed to describe these relationships (*8*). Up to the past few years, however, very little work has been done on the equilibrium relations of binary or multicomponent gas mixtures that would be of interest to designers of a unit for the separation of gases by selective adsorption as described in Part I.

In an analysis of the performance of the moving-bed adsorber in terms of the height of a transfer unit it is necessary that both equilibrium data on the systems involved and operating data on the actual apparatus be available. The experimental determination of all the equilibrium data required, though highly desirable, was considered outside the scope of the present investigation. Since a relatively large body of equilibrium data on similar adsorbate-adsorbent systems is reported in the literature (*31*), it was decided to develop methods for application of these data to the problem. Accordingly, two methods for establishing adsorption equilibria for multicomponent systems were developed for use with the experimental-adsorber data to determine the transfer-unit height. The correlations were checked at random against certain experimental equilibrium measurements as shown in Tables 2 and 3.

METHOD I: BINARY-SYSTEM ADSORPTION EQUILIBRIA, MODIFIED POLANYI THEORY

The Polanyi approach (*29* and *30*) was first chosen because of its relative simplicity. A complete description of the theory and its modifications for use in the present investigation is outside the scope of this paper, and the reader is referred to standard works such as Brunauer (*8*). A few brief comments, however, are introduced here in order to furnish a background for this method of estimation (*20*).

With the combined effects of vertical and lateral interactions taken into account as well as those of other surface forces (*2*) the net effect of which is to create a potential field similar to that

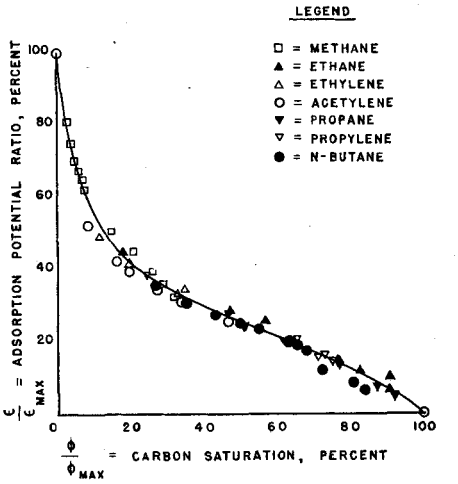


Fig. 11. Generalized adsorption potential curve for hydrocarbon gases. Adsorption on columbia grade L carbon.

of the atmosphere surrounding the earth, the adsorption potential, ϵ_i, is defined as

$$\epsilon_i = \int_{\rho_x}^{\rho_i} V\, dP \qquad (8)$$

where ρ_x and ρ_i are the densities of the adsorbate at point x in the external gas phase and at point i near the adsorbent surface, V is the molar volume, and dP the change in pressure between points x and i. Other investigators (*24* and *25*) have put Equation (8) into the form

$$\epsilon_i = RT_0 \ln \frac{f_0}{f_x} \qquad (9)$$