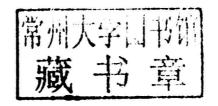Muthanna Ahmed

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ADSORPTION OF LIGHT HYDROCARBONS BY MOLECULAR SIEVES

A THESIS SUBMITTED TO THE COLLEGE OF ENGINEERING OF THE UNIVERSITY OF BAGHDAD IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING

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(B.SC. & M.SC. IN CHEMICAL ENGINEERING)
2005

Summary

Equilibrium adsorption isotherms were obtained for pure methane and ethane on 4A molecular sieve zeolite at 301°K. The pure component experimental data of these gases agreed well with the Langmuir and Freundlich equations.

Multi component adsorption isotherms for methane, ethane, and propane mixture on 4A molecular sieve zeolite at 301°K, and propane, n-butane, and i-butane mixture on 5A molecular sieve zeolite at 301°K were obtained experimentally. Both the extended Freundlich and modified extended Langmuir equations correlated the multi component experimental data fairly well. Other equations were also considered for both mixtures.

Breakthrough curves for methane, ethane, and propane mixture on 4A molecular sieve zeolite, and propane, n-butane, and i-butane mixture on 5A molecular sieve zeolite were obtained experimentally at various flow rates, concentrations, and compositions. The equilibrium and kinetic models were used to predict the breakthrough curves for both multi component mixtures. The equilibrium model gives a satisfactory fit for both mixtures. The model equations were solved by a numerical method based on backward finite difference with a fixed griding technique.

The simple pressure swing adsorption cycle was used successfully to separate propane from methane, ethane, and propane mixture using 4A molecular sieve as adsorbent, and to separate i-butane from propane, n-butane, and i-butane mixture using 5A molecular sieve zeolite as adsorbent. The principle of separation was based on the difference in size of molecules. Where 4A molecular sieve zeolite adsorbs methane and ethane but not propane, and 5A molecular sieve zeolite adsorbs propane and n-butane but not i-butane. The performance of pressure swing

adsorption cycle was represented by the purity and productivity of products. The measured value of purity and productivity of products are compared with those predicted by the equilibrium model. The results support the ability of equilibrium model to simulate the process performance variables for different operating conditions studied at the ambient temperature.

The effect of feed flow rate, concentration, and composition on products purity and productivity were examined experimentally and theoretically. The experimental results show that decreasing feed flow rate and adsorbate composition or increasing feed concentration increases purity, while increasing feed flow rate and concentration or decreasing adsorbate composition increases productivity.

Nomenclature

Notation

A	Cross sectional area of adsorption column (cm^2)
a_p	Specific surface area (1/cm)
B	Langmuir equation coefficient (L/mmole)
B_{ii}, B_{ij}	Modified extended Langmuir equation coefficients (L/mmole)
C	Gas phase concentration (mmole/L)
C_b	Bulk gas phase concentration (mmole/L)
C_s	Surface gas phase concentration (mmole/L)
D_e	Effective diffusivity (cm^2/min)
D_p	Pore diffusion coefficient (cm^2/min)
D_s	Surface diffusion coefficient (cm^2/min)
d	Diameter of adsorption column (cm)
d_c	Diameter of cylindrical particle (cm)
d_p	Diameter of spherical particle (cm)
F	Molar flow rate (mmole/min)
G	Gas mass velocity (g/cm^2.min)
g	Gravitational acceleration (cm/min^2)
j_D	Chilton and Colburn j-factor
K	Freundlich equation coefficient (L^n/$mmole^{n-1}$.g)
K_B	BET equation coefficient
K_f	Film mass transfer coefficient (cm/min)
K_G	Mass transfer parameter in linear driving force model (1/min)
$K_i^{'}$	Fritz and Schluender equation coefficient
K_{ij}	Extended Freundlich and Sheindorf equations coefficient
k_a	Rate constant for adsorption (L/g.min)
k_d	Rate constant for desorption (mmole/g.min)
L	Length of adsorption column (cm)
l	Length of cylindrical particle (cm)
M	Molecular weight (g/mole)
n	Freundlich equation parameter
n_{ii}, n_{ij}	Fritz and Extended Freundlich equations parameters
Q	Volumetric flow rate (L/min)
q	Adsorbate loading or adsorbed phase concentration (mmole/g)
Re	Reynolds number
r	Radial coordinate of spherical particle (cm)
Sc	Schmidt's number
T	Temperature (°K)
t	Time (min)
u	Interstitial gas velocity (cm/min)
u_c	Wave velocity through the bed (cm/min)

u_s	Superficial gas velocity (cm/min)
V_c	Cylinder volume (L)
V_1	Methanol volume (L)
V_y	Mercury volume (L)
W	Mass of adsorbent (g)
Y	Adsorbate composition or mole fraction (%)
y	component composition or mole fraction (%)
Z	Compressibility factor
z	Axial coordinate (distance from the bed inlet) (cm)

Greek

ϵ	void fraction
θ	Fraction of surface coverage
μ	Viscosity of gas (g/cm.min)
ρ	Density (g/L)
α_{ij}	Selectivity to adsorb component i over j
α_{ji}	Selectivity to adsorb component j over i

Subscripts

a	Adsorption step
b	Bed
d	Desorption step
E	Effluent
f	Film
g	gas
H	Highest level of cycle
I	Influent
i, j, n	Component i, j, and n, respectively
L	Lowest level of cycle
m	Mono layer
o	Over all
op	Operation condition
p	Particle
s	Solid
WE	Weakly adsorbed component in effluent stream
*	Saturation condition

Abbreviations

ASTM	American standard for testing methods
BET	Brunauer, Emmett, and Teller equation
GC	Gas-solid chromatography
IUPAC	International union of pure and applied chemistry

LDF   Linear driving force
LRC   Loading ratio correlation
LSAC   Less selectively adsorbed component
MSZ   Molecular sieve zeolite
MSAC   More selectively adsorbed component
MTBE   Methyl-tert-butyl ether
MTZ   Mass transfer zone
PSA   Pressure swing adsorption
PZ   Plateau zone
TCD   Thermal conductivity detector
TSA   Thermal swing adsorption
TSF   Texaco selective finishing
TZ   Transfer zone
WAC   Weakly adsorbed component

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As a result of the rapid development in the field of petrochemicals, the recovery of light hydrocarbons such as methane, ethane, propane, n-butane and i-butane to be used as a fuel or petrochemical feed stocks has been necessary. As petroleum gases such as natural gas, deethanizer or depropanizer overhead mixtures, and liquefied petroleum gas contain these light hydrocarbons, they can be used as a source for the recovery of these components. Ethane and propane constitute an important source for the manufacture of polyethylene and polypropylene [1]. N-butane has been replacing benzene as the raw material for producing maleic anhydride. It is less expensive, more available, and non-toxic. I-butane find expanded applications in the production of methyl-tert-butyl ether (MTBE), methacrylate, and butyl rubber. MTBE is currently used as a gasoline additive because of its octane enhancement properties and aid in reduction of pollutant emissions [2].

The last four decades have witnessed a tremendous growth of gas adsorption processes that have made adsorption systems a key tool both for purification and for bulk separation in chemical, biochemical and petroleum industries. The growth is a result of a series of significant scientific and engineering developments, initiated by the invention of synthetic molecular sieve zeolites and the adsorption cycles. These inventions were followed by a succession of technological and theoretical advances. Among them are the development of more efficient adsorption cycles, new and improved adsorbents, theories of adsorption from mixtures, and theories on multi component adsorber dynamics. The main advantages of adsorption as a separation technique, compared with the other processes are that in many cases a much higher selectivity can be obtained by adsorption than by any of the other techniques, and adsorbents have a relatively high capacity for volatile materials, even at low concentration [3].

Gas adsorption processes involve the attraction of a gas to the surface of solid. Depending upon the type of attraction forces between the gas molecules and the molecules of the solid, adsorption may be classified as physical adsorption (Vander Waals adsorption) or chemisorption (activated adsorption). Physical adsorption from a gas occurs when the intermolecular attractive forces between molecules of an adsorbent and the gas are greater than those between molecules of the gas itself. Physical adsorption, which may be a monomolecular layer, or may be two, three or more layers thick (multi-molecular), occurs rapidly. In contrast, chemisorption involves the formation of chemical bonds between the adsorbent and adsorbate. Chemisorption from a gas generally takes place only at temperatures greater than $473°K$ and may be slow. The attractive forces causing the physical adsorption are generally weaker than those of chemical bonds and are such that, by increasing the temperature of the adsorbent or reducing the adsorbate concentration, the adsorbate can be desorbed [4].

Gas solid contact can be accomplished in a number of ways, such as in fixed beds, fluidized beds, and moving beds. Generally, it is preferable to operate an adsorption process continuously, but the difficulties associated with the handling of solids often make fixed beds more attractive, as well as, it is simple, inexpensive to construct and give minimum attrition in the adsorbent [5].

Commercial adsorbents which are generally used for the adsorption separation processes include organic adsorbents such as activated carbon and polymers, and inorganic adsorbents such as silica gel, activated alumina, and molecular sieve zeolites. Zeolites are distinct from other adsorbents in that for each type, there is no distribution of pore size because the crystal lattice into which the adsorbate molecules can or cannot enter is precisely uniform. For this reason, zeolites are capable of

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separating effectively on the basis of molecular size. Zeolites separate not only by molecular size and shape, but also by polarity. Thus, they can also separate molecules of similar size [6].

Adsorbate desorption is quite important in the adsorption separation processes. First, because desorption allows recovery of adsorbates in those separations where they are valuable, and second, because it regenerate the adsorbent to be reused for further cycles. According to adsorbent regeneration method, adsorption separation processes are classified as, pressure swing adsorption processes (PSA), temperature swing adsorption processes (TSA), displacement- purge swing processes, and inert-purge swing processes [7].

In PSA process, which is initially invented by Skarstrom [8] as a two bed process for air drying, the adsorption step is carried out by contacting the feed gas with the adsorbent in a fixed bed at the highest concentration level of the cycle. The more selectively adsorbed components (MSAC) are retained in the bed, and gas stream enriched in the less selectively adsorbed components (LSAC) of the feed mixture is produced as bed effluent. The desorption is achieved by lowering the total concentration of the bed or by flowing a gas stream enriched in the (LSAC) of the feed gas through the bed or by combination of these methods. The column effluents during the desorption steps are gas stream enriched in the (MSAC) of the feed mixture.

The adsorptive separation is achieved by one of the three mechanisms, steric, kinetic or equilibrium effect. The steric effect derives from the molecular sieving property of zeolites. In this case only small and properly shaped molecules can diffuse into the adsorbent, whereas other molecules are totally excluded. Kinetic separation is achieved by virtue of the differences in diffusion rates of different molecules into the adsorbent. By far, however, most processes operate through the