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The Separation and Purification of Gases Using Solid Adsorbents

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REVIEW

The Separation and Purification of Gases Using Solid Adsorbents

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Abstract

This paper presents a bibliography of some of the published work concerning the adsorption of gases and vapors by solid materials. The papers considered all contain experimental data which are mainly adsorption equilibrium isotherm data, although some of the references include kinetic data. The references are grouped according to the gases adsorbed with a brief statement of the conditions under which the data were obtained. The aim is to provide a reference source for use in the design stage when considering applications of adsorption technology. The factors to be considered in the design of adsorption separation systems are considered and the areas identified where research and publication are required.

INTRODUCTION

The use of solid adsorbents in both gas and liquid systems is now well accepted as a separation and purification method. The successful use of adsorbents generally requires that when the material is saturated with gas it is then regenerated by a desorption stage. In certain applications the adsorbent may be discarded and a fresh charge of material used. In either case, this situation of adsorption–desorption lends itself to the use of several beds, each operating at a different part of the process cycle. This ensures that a continuous supply of product can be taken from the system.

The two main process alternatives are thermal swing adsorption (T.S.A.) and pressure swing adsorption (P.S.A.). T.S.A. operates so that gas is adsorbed at one temperature and desorption/regeneration is carried out at a higher temperature. This process operates at essentially constant pressure.

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The alternative P.S.A. process requires adsorption to occur at a higher pressure and the subsequent desorption at a lower pressure (or vacuum). This process is often considered to occur at a constant temperature, although in practice this depends upon the heat of adsorption which is generated, the nature of the adsorbed phase, and the equipment design.

The P.S.A. process is the one which has been most widely used and the majority of published data is presented as adsorption equilibrium isotherms.

ASSESSMENT OF DATA

A bibliography of references (*1–97*) concerning the adsorption of gases and vapors on fixed beds of solid adsorbents is presented in Tables 1 to 5. This is not intended to be a comprehensive review, which would probably have contained well over 1000 references [from Breck (*98*), Ruthven (*34*), and AIChE Symposium Series (*99–107*) alone]. Instead, the intention is to present in this paper a reference source to selected publications with some indication of their contents. References *1–97* contain experimental data or use previously published data. These references have been selected in order to provide the process design engineer, or researcher in the field of adsorption separation, with easy access to a wide range of available data.

To facilitate data acquisition from, and assessment of, these references, the information is tabulated according to the gas adsorbed. Gases are grouped according to their molecular properties: monatomic and diatomic gases in Table 1; saturated, unsaturated, and cyclic hydrocarbons in Table 2. The reason for this grouping is the differences in adsorption behavior exhibited by these classes of gases as shown by comparisons of the measured quantity of gas adsorbed with theoretical predictions, e.g., Ruthven's statistical thermodynamic model (*108, 109*) shows good agreement for light hydrocarbons on 5A sieves (*50, 109*) but not with inert gases and polar molecules. Additional details given in the tables are the solid adsorbents used and the conditions of temperature and pressure pertaining to the data. This format is used because most applications of adsorption technology are either for the removal of impurities from a gas stream or the separation of a gas mixture into product and waste gases. The selection of an adsorbent depends upon its ability to perform the required separation and also its availability. The process conditions most likely to vary are the temperature and pressure. This information is given in the tables so that the most appropriate reference, and hence data, can be selected.

Tables 1 and 2 contain references to publications relating to pure components, and Table 3 covers the adsorption of gas mixtures. One objective of this paper is to bring together and compare information related to similar gas adsorption systems and hence identify areas in which experi-

TABLE 1
Adsorption Equilibrium Isotherm Data for Inorganic Gases (pure components)

Gas	Adsorbent	Experimental conditions	Ref.
Argon (Ar)	Large port mordenite: 5.8 to 7.0 Å	−80, −46, −21°C; up to 760 torr	1
Ar	ZMS 4A (Na^+ and Ca^{2+} exchanged cations)	−196, −78°C; 10 to 760 torr	2
Ar	Na mordenite; ZMS 5A	20°C; up to 800 torr	3
Krypton (Kr)	CMS 4, 5, 6A; Low AC; medium AC; ZMS 5A	−78, 25°C; up to 400 torr. Adsorption and desorption at 25°C	4
Kr	Na 13X	Various temperatures from −150 to −25°C; up to 500 torr.	5
Kr	LiX, NaX	−100 to −25°C; up to 400 torr	6
Kr	Na mordenites (various treatments)	0°C; 400 torr	7
Xenon (Xe)	LiX, NaX	−60, −30°C; up to 150 torr	6
Xe	ZMS LiX, NaX	−80 to −30°C; up to 500 torr	8
Nitrogen (N_2)	Large port mordenite: 5.8 to 7.0 Å	−80 to 0°C; up to 760 torr	1
N_2	ZMS 4A (Na^+, Ca^{2+} exchanged)	−196, −78°C; 700 torr	2
N_2	Na mordenite, ZMS 5A	20°C; up to 800 torr	3
N_2	Mordenites (Ca^{2+}, Ba^{2+} exchanged)	−78 to 90°C; 450 torr	9
N_2	Various types of AC	−200°C; relative pressures 0.2 to 0.8	10
N_2	ZMS 5A, 10X	−130°C; up to 780 torr	11
N_2	ZMS 10X	−130°C; up to 2000 torr	12
Oxygen (O_2)	Large port mordenite: 5.8 to 7.0 Å	−77 to −21°C; up to 760 torr	1

(continued)

TABLE 1 *(continued)*

Gas	Adsorbent	Experimental conditions	Ref.
O_2	ZMS 4A (Na^+, Ca^{2+} exchanged)	−196 to −78°C; up to 750 torr	2
O_2	Na mordenite; ZMS 5A	20°C; up to 800 torr	3
O_2	Mordenites (Ca^{2+}, Ba^{2+} exchanged)	−78 to 23°C; 450 torr	9
O_2	ZMS 5A, 10X	−130°C; up to 1400 torr	11
O_2	ZMS 10X	−130°C; up to 2000 torr	12
Carbon dioxide (CO_2)	ZMS 4A (Na^+, Ca^{2+} exchanged)	25°C; 700 torr	2
CO_2	Na mordenites (various treatments)	0°C; 400 torr	7
CO_2	ZMS X, Y, A (enriched with trivalent cations)	20°C; 300 torr	13
CO_2	LiA	20 to 140°C; up to 300 torr	14
CO_2	ZMS 5A	35°C; up to 600 torr	15
CO_2	AC	30 to 65°C; 1 atm	16
CO_2	ZMS 5A	35°C; up to 600 torr	17
CO_2 (<21,000 ppm vol) in air	ZMS 13X	5 to 25°C; 4 to 7 bar	18
CO_2	H-mordenite	0°C; up to 70 torr	19
CO_2	ZMS 4A, 5A	0 to 300°C; up to 1000 torr	20
Water vapor (H_2O)	ZMS 4A (Na^+, Ca^{2+} exchanged); SG and Al	25, 100°C; 0 to 24 torr	2
H_2O	H-mordenite; 0.5 *N* clinoptilolite	60°C; 100 torr	7
H_2O	ZMS; Al; SG	Various	20
H_2O	Various NaX cation exchanged, ZMS	23°C; 0 to 20 torr	21
H_2O	ZMS 3A; SG; Al	25 to 95°C	22
H_2O	Porous Al	25°C; 760 torr	23
H_2O	ZMS 4A	30 to 90°C; 760 torr	24

(continued)

TABLE 1 *(continued)*

Gas	Adsorbent	Experimental conditions	Ref.
Carbon monoxide (CO)	ZMS 4A (Na^+, Ca^{2+} exchanged)	−196 to 25°C; 700 torr	2
CO	ZMS 5A, 10X	−130°C; up to 830 torr	11
CO	ZMS 10X	−130°C; up to 2000 torr	12
Ammonia (NH_3)	ZMS 4A (Na^+, Ca^{2+} exchanged)	25°C; 700 torr	2
NH_3	Mordenites (Ca^{2+}, Ba^{2+} exchanged)	20 to 260°C; 450 torr	9
NH_3	ZMS X, Y, A (enriched with trivalent cations)	150 to 200°C; 300 torr	13
NH_3	ZMS 4A, 5A; SG	25°C; up to 1000 torr	20
NH_3	Na ZMS (CS exchanged)	100 to 290°C; up to 600 torr	25
Sulfur dioxide (SO_2)	ZMS 4A (Na^+, Ca^{2+} exchanged)	25°C; 700 torr	2
SO_2, some results for SO_2-CO_2 mixtures	Na and H-mordenites	0 to 75°C; up to 70 torr	19
SO_2	ZMS 4A, 5A	25°C; up to 700 torr	20
SO_2 effect of presorbed water vapor (1-5 wt%).	Natural mordenites	25°C; up to 180 torr	26
SO_2	Synthetic mordenite and natural erionite	25 to 29.5°C; 25 to 100 torr	27
Hydrogen sulfide (H_2S)	ZMS 4A (Na^+, Ca^{2+} exchanged)	25°C; 400 torr	2
H_2S	ZMS 4A, 5A, 13X	25, 75, 150°C; up to 1000 torr	20
H_2S (from natural gas)	ZMS 4A, 5A	5 to 25°C; 50 bar	28
H_2S (from natural gas)	ZMS	25°C; 40 bar	29
H_2S (in CH_4)	ZMS 4A, 5A	25 to 50°C; 33 to 66 bar	30

(continued)

TABLE 2
Adsorption Equilibrium Isotherm Data for Hydrocarbon Gases (pure components)

Gas	Adsorbent	Experimental conditions	Ref.
Methane (CH_4)	Gmelinite	−78, 20°C; 300 torr	9
CH_4 (with impurities)	ZMS 4A, 5A	5 to 25°C; 50 bar	28
CH_4 (with impurities)	ZMS	25°C; 40 bar	29
CH_4 (with impurities)	ZMS 4A, 5A	25 to 50°C; 33 to 66 bar	30
CH_4	Chabazite	0°C; 200 torr	31
	Analcite	20°C; 200 torr	31
CH_4 (with He)	ZMS 5A	20°C; up to 55 bar	32
CH_4	AC	20 to 50°C; up to 750 torr	33
CH_4	ZMS 5A	−88 to 0°C; up to 300 torr	34
Ethane (C_2H_6)	ZMS 4A (Na^+, Ca^{2+} exchanged)	25°C; 700 torr	2
C_2H_6	Gmelinite; mordenite	20, 130, 143°C; up to 300 torr	9
C_2H_6	ZMS 5A	35°C; up to 600 torr	17
C_2H_6	Chabazite	94°C; up to 200 torr	31
C_2H_6 (in He)	ZMS 5A	20°C; up to 55 bar	32
C_2H_6	AC	20 to 50°C; up to 750 torr	33
C_2H_6	ZMS 5A	−43 to 72°C; up to 300 torr	34
C_2H_6	ZMS NaX (cation exchange)	50°C; up to 700 torr	35
C_2H_6	ZMS 4A, 5A	−43 to 74°C; up to 750 torr	36
C_2H_6 (in He)	ZMS 4A (crystals)	25, 74°C; 760 torr	37
C_2H_6 (in He)	ZMS 4A	25 to 115°C; 1 atm	38
C_2H_6 (1–6 mol%) in He	ZMS 4A, 5A	0 to 150°C; 1 atm	39
C_2H_6 (2–8 vol%) in He	ZMS 4A	24 to 75°C; 1 atm	40

(continued)

TABLE 2 *(continued)*

Gas	Adsorbent	Experimental conditions	Ref.
C_2H_6	AC	Up to 450°C; up to 40 bar	41
C_2H_6 (in He)	ZMS 4A	25°C; 760 torr	42
Propane (C_3H_8)	ZMS 4A (Na^+, Ca^{2+} exchanged)	25°C; 600 torr	2
C_3H_8	ZMS 5A	25 to 99°C; up to 100 torr	8
C_3H_8	Gmelinite	67, 225°C; 240 torr	9
C_3H_8	Chabazite	165°C; 200 torr	31
C_3H_8	ZMS 5A	0 to 125°C; up to 350 torr	34
C_3H_8 (<5 mol%) in He	Al	30°C; 1 atm	43
C_3H_8	AC	25°C; up to 760 torr	44
C_3H_8	ZMS	25°C; up to 7240 torr	45
C_3H_8	AC	30, 50, 75°C; up to 730 torr	46
n-Butane (C_4H_{10})	ZMS 4A (Na^+, Ca^{2+} exchanged)	25°C; 700 torr	2
i-Butane	ZMS 4A (Na^+, Ca^{2+} exchanged)	25°C; 400 torr	2
n-Butane	ZMS 5A	25 to 139°C; up to 760 torr	8
n-Butane	ZMS 5A	35°C; up to 600 torr	17
n-Butane	Chabazite	179°C; up to 200 torr	31
	Analcite	115°C; up to 200 torr	31
n-Butane	ZMS 5A	0 to 225°C; up to 300 torr	34
n-Butane	ZMS 5A (crystals and pellets)	50 to 125°C; up to 300 torr	47
n-Butane	ZMS 5A	0, 50°C; 30, 60, 200 torr	48
Higher saturated hydrocarbons			
n-Pentane	ZMS 4A (Na^+, Ca^{2+} exchanged)	25°C; 205 torr	2
n-Pentane	ZMS 5A	60 to 300°C; up to 760 torr	8

(continued)

TABLE 2 *(continued)*

Gas	Adsorbent	Experimental conditions	Ref.
n-Hexane	ZMS 5A	38 to 316°C; up to 760 torr	8
n-Pentane	ZMS	300°C; up to 4370 torr	45
n-Heptane	ZMS	300°C; up to 5540 torr. 30°C; up to 46 torr	45
n-Decane	ZMS	30°C; up to 1.4 torr	45
n-Heptane	ZMS 13X	100 to 215°C; up to 50 torr	49
Iso-octane	ZMS 13X		49
Cyclohexane	ZMS 10X		49
Ethylene ($CH_2=CH_2$)	ZMS 4A (Na^+, Ca^{2+} exchanged)	25°C; 700 torr	2
$CH_2=CH_2$	AC	20 to 50°C; up to 750 torr	33
$CH_2=CH_2$	ZMS NaX (cation exchanged)	50°C; up to 700 torr	35
$CH_2=CH_2$	ZMS 5A	−43 to 85°C; 0 to 300 torr	50
$CH_2=CH_2$ (2–6 vol%) in He	ZMS 4A	25, 50, 75°C; 1 atm	51
Propylene (C_3H_6) and cyclopropane	ZMS 4A (Na^+, Ca^{2+} exchanged)	25°C; 700 torr	2
Propylene	AC	20 to 50°C; up to 750 torr	33
Propylene	AC	25 to 50°C; up to 760 torr	44
Propylene	ZMS	25°C; up to 8790 torr	45
Propylene	AC	30, 50, 75°C; up to 730 torr	46
Propylene and cyclopropane		0 to 185°C; 200 torr	50
Also comparison of adsorption of propylene, cyclopropane and propane	ZMS 5A	50°C; 10 to 100 torr	50

(continued)

TABLE 2 *(continued)*

Gas	Adsorbent	Experimental conditions	Ref.
Acetylene ($CH{\equiv}CH$)	ZMS 4A (Na^+, Ca^{2+} exchanged)	25°C; 700 torr	2
Butene-1	ZMS 4A (Na^+, Ca^{2+} exchanged)	25°C; 400 torr	2
Benzene	ZMS 4A (Na^+, Ca^{2+} exchanged)	25°C; 90 torr	2
Benzene	ZMS 10 X	164, 204, 224°C; up to 50 torr	49
Toluene	AC (various)	80 to 200°C; 760 torr	10
Benzene and toluene components and mixtures (in nitrogen)	AC	150°C; 760 torr	52

mental investigation has been limited. Much more work has been published concerned with the adsorption of pure gases than for gas mixtures, and also relating to adsorption equilibria rather than the kinetics of the adsorption process. Some references detailing the kinetics of the adsorption process are listed in Table 4. There have been few attempts to relate these results to applications of plant and process design.

Nearly all the references in Tables 1, 2, and 3 report exclusively adsorption equilibria isotherm data. A few also include breakthrough concentration times (*10, 39, 46, 51, 52, 57, 63*). Many papers developed theoretical models of gas adsorption and attempted to show the general applicability of the theory by comparison with experimental data. So far, none of these approaches is capable of predicting accurately the quantity adsorbed for a range of systems with different characteristics, e.g., polar inorganic gases and saturated hydrocarbons. However, several methods appear to hold promise of extension and have been used to make satisfactory predictions in several gas–solid systems.

Several papers have described industrial applications of adsorption techniques, e.g., hydrogen purification (*95, 96*), hydrocarbon separation (*86, 110*), and reducing pollution emissions (*89, 111*). However, technical design data are often omitted, for obvious reasons, and the emphasis is generally on process design and comparative costs. Some references to the applications of adsorption technology and plant design are given in Table 5.

TABLE 3
Adsorption Equilibrium Isotherm Data for Gas Mixtures

Gas mixtures	Adsorbent	Experimental conditions	Refs.
Oxygen–nitrogen Oxygen–carbon monoxide Nitrogen–carbon monoxide	ZMS 5A, 10X	−130°C; 760 torr	11
Oxygen–nitrogen Oxygen–carbon monoxide Nitrogen–carbon monoxide	ZMS 5A	−128 to 25°C; up to 1000 torr	53
Oxygen–carbon monoxide	SG	0, 100°C; 760 torr	54, 55
Oxygen–nitrogen–carbon monoxide	ZMS 10X	−130°C; 760 torr	12
Oxygen–nitrogen	ZMS 5A	−130°C; 760 torr	3
Methane–ethane	AC	20°C; 760 torr	54, 56
CH_4–C_2H_6	ZMS 5A	20°C; up to 55 bar	32
CH_4–nitrogen	ZMS 5A	−128 to 25°C; up to 1000 torr	53
CH_4 with H_2O vapor, CO_2, and H_2S (low concentrations)	ZMS 4A, 5A	25 to 50°C; 33 to 66 bar	30
C_2H_6 (7 vol%), CO_2 (2 vol%), N_2 (90 vol%)	ZMS 5A	25°C; 1 atm	57
C_2H_6 + *n*-butane; C_2H_6 + CO_2	ZMS 5A	35°C; 48 torr 35°C; 96 torr	17
Methane–ethane Methane–ethylene Ethane–ethylene Ethane–propylene Ethylene–propylene Methane–ethane–ethylene Ethane–ethylene–propylene	AC	20 to 50°C; up to 750 torr	33
Propane–propylene (C_3H_8–C_3H_6)	SG	25°C; 760 torr	54, 58
Ethylene–carbon dioxide (C_2H_4–CO_2)	AC	25°C; 200 to 250 torr	54, 59
Ethane–ethylene (C_2H_6–C_2H_4) (exchange adsorption)	AC	25°C; 760 torr	60, 61
Ethylene–cyclopropane	ZMS 5A	50°C; 8 torr	62
i-Octane–*n*-tetradecane (dynamic exchange adsorption)	ZMS 5A (various)	320 to 450°C; 1000 torr	63
Propane–propylene (in He) (exchange adsorption)	AC	25°C; 760 torr	44
Propane–propylene	ZMS	25°C; 760 torr	45
n-Heptane–*n*-pentane	ZMS	300°C; 550 torr	45
n-Heptane–*n*-decane	ZMS	30°C; 760 torr	45

TABLE 4
Adsorption Kinetics and Diffusivity Data

Gases	Adsorbent	Conditions	Refs.
Ar	ZMS NaA	−158, −135, −111°C; 1 atm	64
Ar, Ne, Kr, Xe	ZMS KA	50 to 600°C	65
Ne, Ar, Kr, Xe	CMS	−84 to 246°C	66
Xe	ZMS NaX	−123 to 327°C	67
N_2	AC	110, 140°C	10
N_2	ZMS NaA	−183 to −111°C; 1 atm	64
N_2	ZMS KA	300°C	65
N_2	CMS	−18 to 50°C	66
CO_2	CMS 5A	130 to 165°C	16
CO_2 (<21,000 ppm vol) in air	ZMS 13X	5 to 25°C; 4 to 7 bar	18
CO_2	Na mordenite	5 to 45°C; 75 to 87 torr	19
CO_2	ZMS KA	200 to 600°C	65
CO_2	ZMS 4A, 5A	50, 100°C; 20 to 80 torr	68
H_2O	Porous Al	25°C; 760 torr	23
H_2O	Florite	32 to 92°C	69
SO_2	Na and H-mordenites	0 to 75°C; up to 70 torr	19
SO_2	Synthetic mordenite and natural erionite	25 to 29.5°C; 25 to 100 torr	27
CH_4	ZMS 5A	−88 to 0°C; up to 300 torr	34
CH_4, C_2H_6, C_3H_6, C_3H_8, n-C_4H_{10}, C_6H_6	CMS	−20 to 400°C	66
CH_4, C_2H_6, C_3H_8, cyclopropane	ZMS 5A	0 to 125°C	70
n-Paraffin hydrocarbons (to n-C_8)	Erionite and ZMS CaA	93 to 207°C	71
CH_4, C_2H_6, C_3H_8, n-C_4H_{10}	ZMS CaA	−88 to 225°C	72, 73
n-Paraffins	Chabazite and ZMS A	20 to 225°C; 100 to 690 torr	34, 74
CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, i-C_4H_{10}	Na zeolon	25°C; up to 176 torr	75, 76
C_2H_6, C_2H_4 (exchange adsorption)	AC	25°C; 760 torr	60, 61
C_2H_6	ZMS 3A, 4A, 5A	103 to 254°C. Desorption	77
C_2H_6 (in He)	ZMS NaA, CaA	25°C	78
C_3H_8, n-C_4H_{10}	Chabazite	150, 200°C	79
n-C_4H_{10}	ZMS CaA	85, 125°C	80
n-C_4H_{10}	ZMS CaA	60 to 68 torr	81
n-C_4H_{10}, n-C_5H_{12}	ZMS NaY	105 to 240°C	82
n-C_5H_{12}	ZMS 5A	50, 100°C; 20 to 80 torr	68
n-C_7H_{16}, C_6H_{12}, C_6H_6, $C_6H_5.CH_3$	ZMS 5A	136 to 340°C; 0.1 to 100 torr	83

TABLE 5
Adsorption Plant and Process Data

Gases	Adsorbents	Conditions and data	Ref.
Solvents	AC	General review	84
Various	AC	Petrochemical industry	85
Butylene isomers separation	ZMS	Process and economics	86
Natural gas	ZMS	Process	29
Natural gas	ZMS	Review	87
L.P.G. drying and desulfurization	ZMS	Process	88
Air pollution control	AC	General principles	89
Dry sulfur dioxide and moist NO_x removal	ZMS (zeolon)	Processes, data and economics	90
Carbon dioxide removal from ethane/propane mixtures	ZMS	Process	91
Drying	ZMS 3A; SG; Al	Design data and processes	22
Air drying	SG	Design data	92
Air drying	ZMS; SG; Al	Process, design and data	93
Nitrogen from air	ZMS	Comparison with reversing heat exchanger	94
Oxygen from air	ZMS	Process and patent review	3
Hydrogen purification	ZMS	Process and economics	95
Hydrogen purification	ZMS	Process, alternatives and economics	96
Separation of hydrogen isotopes	Metallic palladium deposited on alumina	2–5% deuterium; 1.5 and 7 bar	97

Breck (*98*) has presented an excellent review of published work on gas–solid adsorption. His approach has been to categorize the available information according to the solid adsorbent used. Ruthven (*34*) has presented a review paper of gas adsorption, but the data and discussion relate mainly to hydrocarbon gases.

The remainder of this paper will consider the applicability of the available data and theories to design problems and the areas where research should be undertaken in order to facilitate future applications.

ADSORPTION APPLICATIONS

The aim is to provide ideas and information for those engineers faced with problems of gas purification or separation. These problems can take many forms. Some may be overcome by the use of standard adsorption plants and others may be solved quite easily by engineers specializing in either separation techniques or adsorption systems. This leaves problems which arise from technical developments, e.g., separation of hydrogen isotopes (*97*), or which have not previously been sufficiently important to merit research and publication, e.g., changes in legislation regarding air pollution emissions (*85*, *88*). The following are examples of these situations.

A. Standard Problems and Plants

	Suitable solid adsorbent
Removal of water vapor	ZMS 3A; SG; Al
Removal of impurities such as carbon dioxide, ammonia, hydrogen sulfide, sulfur dioxide	ZMS 3A; AC
Purification of hydrogen	ZMS 3A, 4A
Air separation plants designed to produce either oxygen or nitrogen product gas	ZMS 4A, 5A; CMS
Separation of higher paraffins	ZMS 5A, 10X, 13X

B. New Adsorption Applications

Separation of components in natural gas
Purification of helium associated with oil production
Purification of used helium from deep diving operations
Multicomponent separations
Biogas purification
Separation of saturated and unsaturated paraffins
Control of gaseous pollutants, e.g., NO_x, sulfurous gases

DESIGN FACTORS

The first stage in the design process is to define the problem in one of the following categories:

Removal of impurities, i.e., low concentrations of the gases to be removed, 2% or less

Gas purification, second component (impurity) of 5 to 20%

Bulk separation, the gas to be obtained as a product stream has concentration between 20 and 80% in the feed mixture

The second stage is to establish the degree of separation required, i.e., the purity of the product gas.

In the third stage determine the relevant properties of the components to be separated, e.g., high quadrupole moment, hydrocarbon chain length and degree of saturation, and especially the molecular sizes of the gaseous components. The latter property is of particular importance in assessing the difficulty of obtaining separation. The availability of solid adsorbents can then be investigated and their suitability for the application determined. This will depend upon the effective pore size, i.e., "window"aperture (*34*) for zeolite molecular sieves or the pore size distribution for activated carbons and alumina.

The effects of cation exchange, involving mainly Ca^{2+} and Na^+ ions, upon the adsorptive capacity of zeolite molecular sieves have been reported in the literature (*2, 112, 113*). It has also been reported that in certain cases the adsorptive capacity of a sieve can be significantly reduced by the presence of preadsorbed molecules (*2, 26, 114*). This is particularly effective when the preadsorbed molecules possess a high quadrupole moment e.g., water vapor and ammonia, and for some organic vapors, e.g., methylamine (CH_3NH_2). It may be possible therefore to improve the suitability of a zeolite for separation applications by the use of cation exchange or preadsorbed molecules or both.

Other factors which have been shown to influence the separation efficiency of a molecular sieve are:

The use of low temperatures
The use of high temperatures and pressures
Pore closure

At a temperature of 300°C the adsorption of ammonia by zeolite X or Y is slow, taking approximately 5 h to attain equilibrium. The amount adsorbed is equivalent to 6 molecules per unit cell. At a lower temperature, e.g., 100°C and 700 torr, adsorption is rapid and reversible and the equilibrium amount adsorbed is equivalent to 98 molecules per unit cell (*115*).

As the temperature is reduced from 0 to −200°C, the equilibrium adsorption capacity of zeolite NaA for oxygen increases rapidly. The same effect is observed for nitrogen and argon but the amount adsorbed reach maxima at approximately −100 and −150°C, respectively. As the temperature is further reduced, the amount of these gases adsorbed decreases

By using high temperatures and pressures, e.g., up to 400°C and 4000 atm, some zeolites will adsorb gases which are normally excluded due to their molecular sieving property. Zeolite KA will adsorb methane, argon, and krypton at 350°C and 2000–4000 atm; desorption can be achieved by heating to a higher temperature (*116, 117*). Neon, argon, and krypton were adsorbed by natural zeolites at 300°C and 600 atm (*118*). In both cases the gases become trapped, i.e., encapsulated, within the zeolite if the temperature and pressure are reduced. This is a reversible situation. For the natural zeolite it was found that surface rehydration was an effective encapsulation method, except for neon gas.

The molecular sieving property of a zeolite can be modified by hydrolytic pore closure caused by steam treatment, e.g., steam heating zeolite NaA to 550°C. It can also be used to prevent oxygen adsorption by zeolites at low temperatures.

The fourth stage involves the choice of a suitable process and the design of the appropriate operating plant. The choice of process depends upon the specifications within the problem and the variations permissable in the operating conditions. The two most common process alternatives, for gas separations, are pressure swing adsorption (P.S.A.) and thermal swing adsorption (T.S.A.); other processes have been developed, e.g., parametric pumping (*119*) and porous membranes (*120–125*). Most applications of adsorption technology have used the P.S.A. process. The reasons for this are the following advantages of P.S.A. over T.S.A. systems:

Plant and equipment are simpler, easier to operate, and more reliable

Quicker detection, response, and correction to changes in operating conditions

Shorter operating cycles

Smaller adsorption beds

PROCESS DESIGN

P.S.A. processes have been used for a number of years, and various patents (*126–130*) and papers (*5, 22, 29, 87, 95*) have been published detailing particular processes, modifications, and developments. P.S.A. separation systems fall naturally into the categories of high and low pressure processes. Differences between these processes are usually in the desorption step, with pressure release (blow-down) and/or use of vacuum, and the possibility of incorporating a purge step into the operating cycle.

For industrial separation and purification problems, the "product" gas is often required as a continuous flow at a pressure considerably above atmospheric. For an adsorption system to be an economic alternative to other separation methods, it is usually necessary to regenerate the adsorbent material when it becomes saturated with adsorbed gases. For these reasons a P.S.A. system is often a cyclic process with the adsorbent bed alternating between selective adsorption and desorption, i.e., regeneration, steps. Other steps may be included in the process cycle, e.g., utilization of low purity "product" gas. The adsorption plant normally comprises at least two fixed adsorption vessels to provide a continuous supply of product gas.

Adsorption separation can be achieved in one of two ways. The unwanted components and impurities are adsorbed by the adsorbent, and subsequently desorbed. In this case gas designated as "product" passes through the bed, gradually increasing in purity. Alternatively the "product" gas is adsorbed and impurities, i.e., waste gases, flow out of the bed. This "product" gas is then collected during the regeneration stage. In the first case the adsorption cycle continues until a certain level of impurity is detected in the product; this is termed "breakthrough." In the second case adsorption may be terminated when (some) product gas is detected in the exit gas from the bed, or adsorption may continue until the bed is saturated with product gas and the exit gas from the bed corresponds to the feed gas composition.

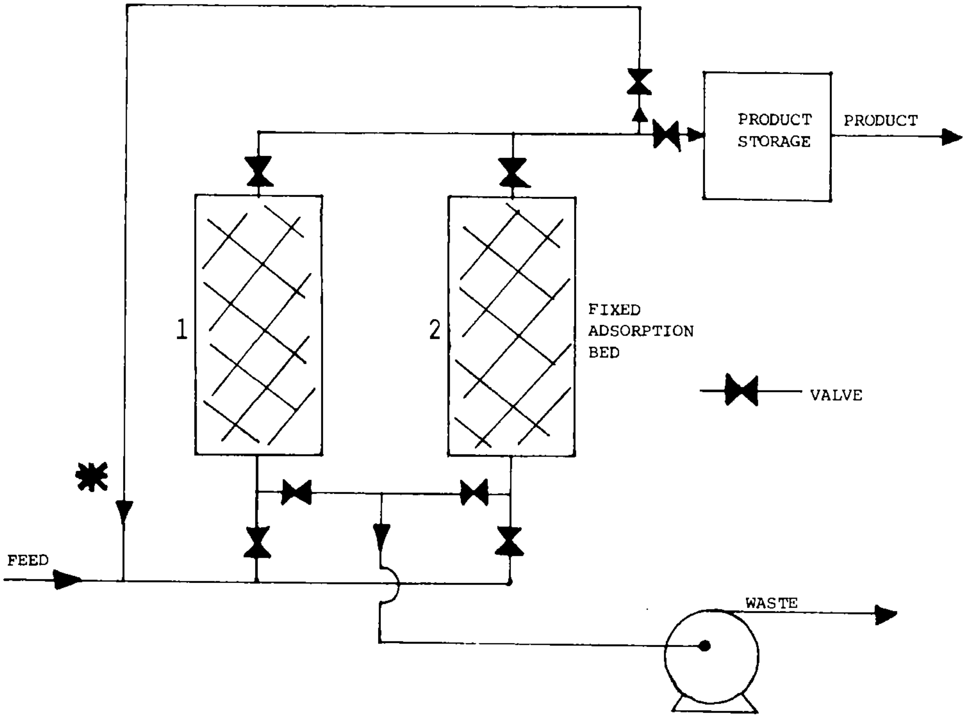
The simplest process would use two adsorption beds alternating between adsorption and desorption operations. The desorption time would then be set equal to the cycle time required for the adsorbing material to become saturated. This process, shown in Fig. 1, has two main disadvantages.

(1) The adsorbent is regenerated at a lower pressure, and when the regenerated bed begins to receive feed gas, it will take a certain time for the adsorption pressure to be established. Hence there will be a subsequent loss of product gas flow unless a product storage vessel is included.

(2) At the beginning of the adsorption stage the required product purity will not be obtained immediately. Similarly, at the end of the adsorption stage the product gas purity will fall until it reaches the feed composition if the product is the nonadsorbed species (the waste gas will become richer in the required product if the product gas is the adsorbed species). This low purity gas should be recycled, as shown in Fig. 1, at the appropriate part of the process cycle.

This gas fraction at the end of adsorption (referred to here as low product purity gas, or L.P.P. gas) can often be utilized within the process as shown by the process cycle in Fig. 2. In the case of a nonadsorbed product, the L.P.P. gas from the adsorbing bed (at the end of this stage) is fed to the top of the regenerated bed via valves V.1 and V.2. This has two effects. The bed pressure rises, although probably not to the operating pressure, as partially treated gas is used as feed and then becomes the first product gas upon changeover. This gas is partially treated in each bed and the economics of the process and product purity are improved. Second, the rise in pressure at the end of desorption means that product gas at the required pressure is obtained more quickly and the size of any product storage vessel can be reduced.

In order to obtain a continuous product flow, again considering the case of a nonadsorbed product gas, it is possible to use three adsorption beds as shown in Fig. 3. The processing cycle then falls naturally into three steps as

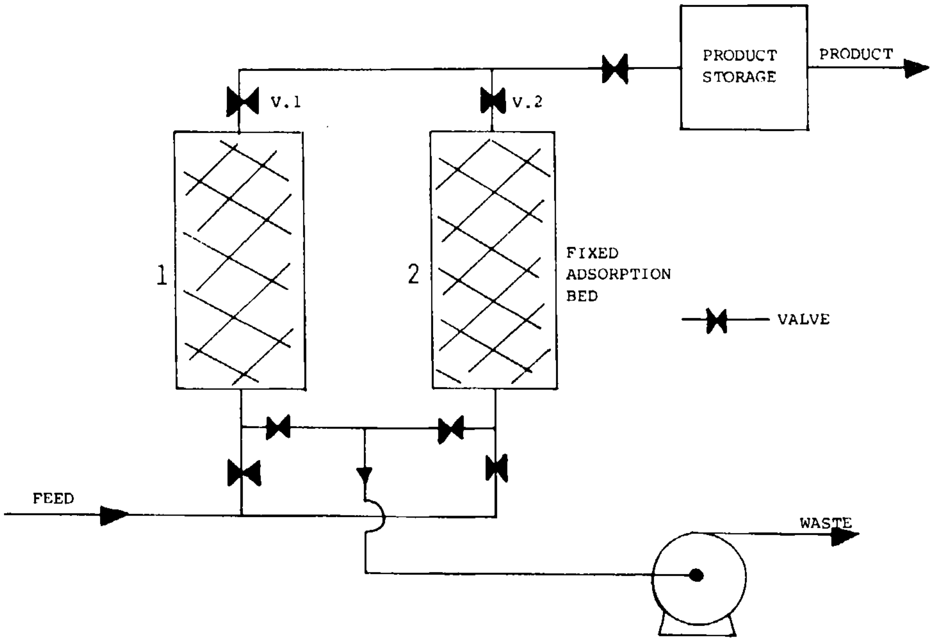


✱ L.P.P.GAS RECYCLED AT BEGINNING AND END OF ADSORPTION

PROCESS CYCLE:

<table>
<tr><th>BED</th><th colspan="6">OPERATION</th></tr>
<tr><td rowspan="2">1</td><td colspan="3">SELECTIVE ADSORPTION</td><td colspan="3" rowspan="2">DESORPTION
(WASTE)</td></tr>
<tr><td>L.P.P.GAS</td><td>PRODUCT</td><td>L.P.P.GAS</td></tr>
<tr><td rowspan="2">2</td><td colspan="3" rowspan="2">DESORPTION
(WASTE)</td><td colspan="3">SELECTIVE ADSORPTION</td></tr>
<tr><td>L.P.P.GAS</td><td>PRODUCT</td><td>L.P.P.GAS</td></tr>
<tr><td>CYCLE TIME</td><td colspan="3">t_1 =</td><td colspan="3">t_2</td></tr>
</table>

FIG. 1. Simple adsorption process (nonadsorbed product gas).

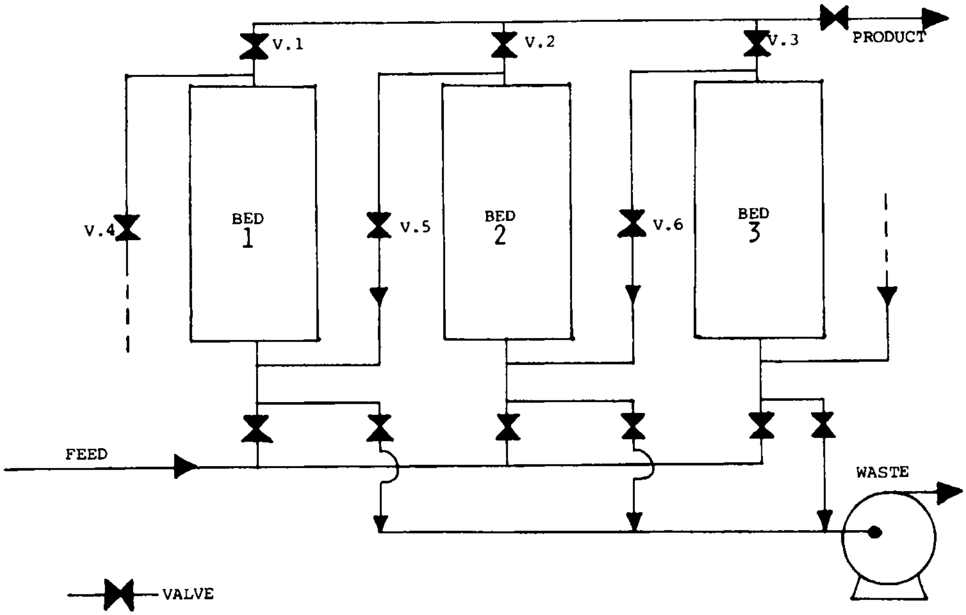


PROCESS CYCLE:

BED	OPERATION			
1	SELECTIVE ADSORPTION (PRODUCT)	L.P.P.GAS TO BED 2 VIA V.2 ↓	DESORPTION (WASTE)	L.P.P.GAS FROM BED 2 ↑
2	DESORPTION (WASTE)	L.P.P.GAS FROM BED 1	SELECTIVE ADSORPTION (PRODUCT)	L.P.P.GAS TO BED 1 VIA V.1
CYCLE TIME		$t_1 =$	t_2	

FIG. 2. Adsorption process utilizing L.P.P. gas (nonadsorbed product gas).

shown by the process cycle in Fig. 3. Improved process performance is obtained by allowing a fraction of the product gas from the adsorbing bed to enter and repressurize a regenerated bed (via valves V.1, V.2, V.3). This bed will then be in a condition to produce gas of the required purity and pressure, immediately it receives feed gas. The product purity will also be higher for a three-bed process. The product gas fed to the regenerated bed is analogous to the use of a reflux stream in distillation. The penalty in terms of process



PROCESS CYCLE:

<table>
<tr><td>BED</td><td colspan="6">OPERATION</td></tr>
<tr><td rowspan="2">1</td><td colspan="2">ADSORPTION</td><td colspan="2" rowspan="2">DESORPTION
(WASTE)</td><td rowspan="2">RE-PRESSURISE FROM BED 2</td><td rowspan="2">L.P.P.GAS → PRODUCT</td></tr>
<tr><td>PRODUCT + RE-PRESSURISE BED 3 VIA V.3</td><td>L.P.P.GAS TO BED 3 VIA V.4</td></tr>
<tr><td rowspan="2">2</td><td colspan="2" rowspan="2">DESORPTION
(WASTE)</td><td rowspan="2">RE-PRESSURISE FROM BED 3</td><td rowspan="2">L.P.P.GAS → PRODUCT</td><td colspan="2">ADSORPTION</td></tr>
<tr><td>PRODUCT + BED 1 VIA V.1</td><td>L.P.P.GAS VIA V.5</td></tr>
<tr><td rowspan="2">3</td><td rowspan="2">RE-PRESSURISE WITH SOME PRODUCT FROM BED 1</td><td rowspan="2">L.P.P.GAS FROM BED 1 → PRODUCT</td><td colspan="2">ADSORPTION</td><td colspan="2" rowspan="2">DESORPTION
(WASTE)</td></tr>
<tr><td>PRODUCT + BED 2 VIA V.2</td><td>L.P.P.GAS VIA V.6</td></tr>
<tr><td>CYCLE TIME</td><td colspan="2">t_1 =</td><td colspan="2">t_2 =</td><td colspan="2">t_3</td></tr>
</table>

FIG. 3. Adsorption process giving continuous product flow-rate and higher product purities (nonadsorbed product gas).

economics is that for a particular plant size, less gas is taken as product, although higher purities can be obtained. Use is also made of L.P.P. gas at the end of the adsorption stage as discussed for Fig. 2. However, in this case (Fig. 3) the L.P.P. gas is fed to the bottom of a bed via valves V.4, V.5, V.6. Product gas is then obtained from the receiving bed during this part of the cycle, thus ensuring continuous product flow rate, purity, and pressure. The process shown in Fig. 3 does not require a product storage vessel, effectively using the third bed for this purpose; however, extra adsorbent material and plant equipment, e.g., valves and pipework, will be required. The plant economics of two- and three-bed processes can be compared but the choice often depends largely upon specifications of continuous flow rate, purity requirements, and the elimination of pressure fluctuations. Various patents exist giving details of the type of process variations shown in Fig. 3 (*131–134*).

PLANT DESIGN

The design of an adsorption system requires three main decisions to be made.

(1) The selection of an adsorbent material and process operating conditions, e.g., temperature and pressure, which make separation feasible.

(2) Choice of a suitable operating process in order to satisfy the product specifications, including efficient utilization of available conditions. The availability of feed gases at high pressures suggests the use of a P.S.A. process, whereas high temperature feeds and suitable heat transfer media indicate adoption of a T.S.A. process. The process should also make efficient use of all gas fractions created during the process cycle, as discussed in connection with L.P.P. gas in the processes shown in Figs. 2 and 3.

(3) Specification of the size of the adsorption bed. This requires calculation of the quantity of a particular adsorbent necessary in each bed. It is usually obtained from adsorption equilibria isotherm data as the quantity of gas adsorbed per mass of adsorbent. The main problem, as shown previously by the discussion of the data presented in Tables 1, 2, and 3, is the availability of such data and specifically the lack of published data relating to gas mixtures. Various methods have been suggested which use the adsorption data of pure components to predict the adsorption capacity of a sieve for multicomponent separations (*15, 45, 135*). However, no method has yet been proposed which can make accurate predictions for a variety of gas mixtures.

> Appropriate data may be available from the adsorbent manufacturers, but as shown in this paper, the lack of published data may limit the accuracy of design calculations.

Isotherm data are obtained under equilibrium conditions but practical separations seldom, if ever, allow sufficient time for equilibrium to be achieved. A knowledge of the kinetics of the adsorption process is also required. Data have been published, although not as extensively as isotherm data, and results are usually presented in terms of the diffusivity of the gas in a particular system. Wide variations in these values have been reported, even for similar systems, although Ruthven (*34*) proposed that this is partly attributable to an incorrect interpretation of results. Some studies have reported breakthrough times for the adsorbent and gases studied (*10, 39, 46, 51, 52, 57, 63*), although these results are obtained for specific process conditions, e.g., often 25°C, atmospheric pressure, small bed diameters (typically less than 5 cm diameter), and low flow rates.

Several other factors need to be considered when attempting to use published data for the design of adsorption vessels. In experimental studies the adsorbent is generally prepared by heating under very low vacuum for several hours, e.g., 400°C at 1 torr for 12 h, so that all results can be related to the material in a standard condition.

In practice, and especially with large adsorber beds, it will be impossible to carry out this type of pretreatment. Often the best sieve conditions that can be achieved are by packing the vessels with adsorbent while passing a stream of dry inert gas through the bed. This may by followed by passing hot inert gas through the packed bed and subsequently a period under vacuum (typically 150 to 200 torr), depending upon the plant equipment.

When gases are adsorbed, heat is evolved and the bed temperature rises. The temperature swing between adsorption and desorption (heat adsorbed) must be known before isotherm data can be used correctly to calculate the amount of adsorbent required for a desired separation. The development of a theoretical analysis of the adsorption process, and interpretation of results, becomes complex if the process is adiabatic (*38, 49, 57*). For this reason many papers have been published considering only isothermal adsorption conditions (*17, 32, 39, 40, 43*). This will only be true if small amounts of gas are adsorbed, or cycle times are short, or there is good heat conduction within a bed, i.e., small diameter beds. The quantity of gas adsorbed generally decreases as the temperature is increased, and the temperature within the bed must be known in order to use appropriate isotherm and kinetic data. For bulk separations and/or large diameter beds, then temperature changes become more significant. If cycle times are long, then it will become necessary to calculate the quantity of gas adsorbed as a function of time by using the appropriate isotherms as the temperature changes. If ambient temperature changes are significant, either during each day or between seasons, then this effect will also have to be considered.

For bulk gas separations, velocity changes will occur within the bed. This effect will have to be considered in relation to the pressure drop and appropriate corrections made to the type of calculations presented in Kohl and Riesenfeld (*20*), based on data presented by Union Carbide. The pressure drop within a bed will influence the selection of plant equipment, especially for a P.S.A. process, and the choice is often for large diameter beds (say 1 m) with a bed height of 1 to 2 m. For large diameter beds, axial (or radial) mixing may occur, but published information of the effect on adsorption has been limited (*136, 137*).

CONCLUSIONS

There is an abundance of publications detailing experimental data for the adsorption of gases by solids. However, the use of these data for design purposes is limited due to the range of experimental conditions usually employed, e.g., 10 to 760 torr and 25°C. The data are mainly equilibrium isotherm data whereas, in most adsorption equipment, cycle times are short and equilibrium is rarely established. The cycling between different process conditions of temperature or pressure, for both P.S.A. and T.S.A. processes, means that more data are required for nonequilibrium and nonisothermal conditions. The effects of temperature changes within an adsorption bed, due to the heat of adsorption (or desorption), have not been well documented.

More publications are required in areas where adsorption applications have not been widely employed, such as bulk separations. The effects of velocity changes, a large pressure drop, and large temperature changes need further investigation. The uniform sieve size of zeolite materials makes them particularly useful as a separation media; however, more research is needed into ways of tailoring these materials, and other common adsorbents, for use with unusual and difficult separations.

TERMINOLOGY AND ABBREVIATIONS

Adsorbate	the gas or vapor adsorbed
Adsorbent	the solid material adsorbing the gas
Adsorption	sometimes sorption, the adsorption of gas by a porous solid
Adsorption, chemical	adsorption of gas by a solid involving electron transfer

Adsorption, physical	adsorption of gas by a solid without electron transfer, normally a reversible process
Breakthrough	when the adsorbent ceases to effectively adsorb a gas; may not necessarily correspond to saturation
Desorption or regeneration	removal of adsorbed gas from the solid by suitable operating conditions
Fixed bed	a bed of static adsorbent, cf. a fluidized bed
Saturation	when the adsorbent can adsorb no more gas under a particular set of operating conditions
AC	activated carbon
Al	alumina
CMS	carbon molecular sieve (possessing a uniform pore size)
SG	silica gel
ZMS	zeolite molecular sieve
P.S.A.	pressure swing adsorption
T.S.A.	thermal swing adsorption
L.P.P. gas	low product purity gas

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