there may be a number of ways to overcome the problems and hence improve the separating efficiency of water elutriators operating in this region of velocity.

Firstly, attempts could be made to eliminate wall flow by forcing descending particles away from the wall and into the bulk fluid. This may be possible by incorporating discontinuities in the wall. Alternatively, a local region of increased fluid velocity may be introduced below the feed point by using an auxiliary pump to inject extra fluid in addition to the main fluid flow, the extra fluid being taken off as a sidestream immediately below the solids feed point. These possibilities will be incorporated in the next phase of the study, followed by a study of the separation of real solids waste mixtures containing a range of particle sizes and shapes.

NOTATION

A = number of fraction of the feed of a particle species leaving the top product
B = rate of loss of a species from bottom (particles/m^2·s)
C = separation factor
C_{min} = optimum value of separation factor
d_t = tube diameter (m)
De = eddy diffusivity (m^2/s)
F = feed rate of a species (particles/m^2·s)
G = feed rate of particles (particles/s)
H = height of a test zone (m)
K_1,K_2 = constants
N = number of particles in a test zone
T = rate of loss of a species from the top (particles/m^2·s)
U_t = terminal falling velocity in stationary fluid (m/s)
U_x = net velocity of a species X (m/s)
V_W = mean water velocity (m/s)
X = concentration of species X (particles/m^3)
Z = distance from top of elutriator (m)
Z_F = distance of feed from top of elutriator (m)
Re = fluid tube Reynolds Number

Subscripts

H = heavy species
L = light species
F = feed zone
B = bottom

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Separation of Benzene and Toluene from Close Boiling Nonaromatics by Extractive Distillation

Benzene and toluene are virtually impossible to separate from close boiling nonaromatic hydrocarbons by rectification. Benzene and toluene can be readily separated from similar boiling nonaromatics by using extractive distillation in which the extractive distillation agent is a proper mixture of organic compounds boiling higher than benzene or toluene. A typical extractive distillation agent for benzene is a mixture of phthalic anhydride, maleic anhydride, and adiponitrile; for toluene, phthalic anhydride, maleic anhydride, and glycerol triacetate.

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SCOPE

Extractive distillation is the name applied to the method of altering the relative volatility of two or more compounds by distilling them in the presence of a quantity of a higher boiling liquid. Typically the extractive distillation agent boils at least 20°C higher than the compounds being separated, forms no azeotrope with them, and is miscible with them at distilling temperature. It was the objective of this research to find extractive distillation agents which will increase the apparent relative volatility of benzene or toluene to similar boiling nonaromatic hydrocarbons to a value high enough to permit separation in a rectification column having a moderate number of theoretical plates thus making rectification an economically

more attractive way of separating these compounds.

The use of single compounds as the agent in extractive distillation has been reported by Mikitenko (1973) using dimethylformamide and dimethylacetamide to separate both benzene and toluene from close boiling nonaromatic hydrocarbons. It was the purpose of this research to find benign, nonreactive and noncorrosive organic compounds and mixtures thereof which are effective in the separation of benzene and toluene from similar boiling, nonaromatic hydrocarbons.

CONCLUSIONS AND SIGNIFICANCE

An experimental investigation of a considerable number of organic compounds showed more than 200 different combinations which enhanced the separation of benzene or toluene. One of the more effective combinations for benzene is the mixture phthalic anhydride, maleic anhydride, and adiponitrile; for toluene, the mixture phthalic anhydride, maleic anhydride, and glycerol triacetate.

BACKGROUND

Benzene Separation

Extractive distillation is the method of separating close boiling compounds by carrying out the distillation in a multiplate rectification column in the presence of an added liquid or liquid mixture, said liquid(s) having a boiling point higher than the compounds being separated. The extractive agent is introduced near the top of the column and flows downward until it reaches the stillpot or reboiler. Its presence on each plate of the rectification column alters the relative volatility of the close boiling compounds in a direction to make the separation on each plate greater and thus require either fewer plates to effect the same separation or make possible a greater degree of separation with the same number of plates. The extractive agent should boil higher than any of the close boiling liquids being separated and not form minimum boiling azeotropes with them. Usually the extractive agent is introduced a few plates from the top of the column to insure that none of the extractive agent is carried over with the lowest boiling component. This usually requires that the extractive agent boil 20°C or more higher than the lowest boiling component.

At the bottom of a continuous column, the less volatile components of the close boiling mixtures and the extensive agent are continuously removed from the column. The usual methods of separation of these two components are the use of another rectification column, cooling and phase separation, or solvent extraction.

Snyder (1978) suggests the selection of extractive agents on the basis of their properties of proton acceptance and dipole moment. To this I would add hydrogen bond forming capability as a major factor.

The operation of an extractive distillation system has been well described by Butler (1963). He suggests a large number of pure compounds including alcohols, glycol ethers and sulfolanes to separate both benzene and toluene. No information is given here on the relative volatility and thus relative performance of these compounds as extractive distillation agents. Atlani (1975) describes the use of several cyanamide derivatives as extractive agents for separating aromatics including benzene from naphthenes and dienes. Cooper (1953) employs molten phthalic anhydride as the extractive distillation agent to separate aromatics including benzene from nonaromatic hydrocarbons. Mikitenko (1978) uses dimethylformamide and dimethylacetamide with water to bring the nonaromatic hydrocarbons off overhead as a two-phase azeotrope and thus lower the boiling point. Eisenlohr (1972) reported on an improved equipment arrangement to separate both benzene and toluene from nonaromatic hydrocarbons by extractive distillation. Preusser (1971) described the use of morpholine and some of its derivatives for this separation. Improved equipment for this separation was presented by Mueller (1970). It should be noted that all the work reported to date deals with the use of a single organic compound as the extractive distillation agent.

The advantage of using extractive distillation in this separation can be seen from Table 1. The relative volatility of benzene to cyclohexane is about 1.02. To separate these two by conventional rectification requires a minimum of 750 theoretical plates. This, however, is at total reflux. At a specific reflux, it will be more. The theoretical plates have to be converted to actual plates. Plate efficiencies of 75% are commonly employed, and this is the basis of the actual plate listing in Table 1. Thus, more than 1,000 actual plates are required, clearly an impossible separation. Several extractive distillation agents presented here push the relative volatility as high as 4.5, and Table 1 shows that they will reduce the actual plate requirement to something close to 12 plates. Converting from total reflux to an actual reflux will increase the plate requirement somewhat but still make for a very attractive separation.

Extractive distillation typically requires the addition of an equal amount to twice as much extractive agent as close boiling compounds on each plate of the rectification column. The extractive distillation agents should be heated to about the same temperature as the plate into which it is introduced. Thus, extractive distillation imposes an additional heat requirement on the column as well as somewhat larger plates for the same product output. To be economically attractive, the extractive distillation system must save more in the reduction of the number of theoretical plates and the size of the column than it adds in the cost of larger plates and the additional heat requirement. Another consideration in the selection of the extractive distillation agent is its recovery from the bottoms product. The usual method is by rectification in another column. To keep the cost of this operation to a minimum, an appreciable boiling point difference between the compound being separated and the extractive agent is desirable.

A mixture comprising an organic compound admixed with benzoic acid, maleic anhydride, phthalic anhydride and/or two

TABLE 1. THEORETICAL AND ACTUAL PLATES REQUIRED VS. RELATIVE VOLATILITY

Relative Volatility	Theoret. Plates Req. at Total Reflux, 99.9% Purity	Actual Plates Req., 75% Eff.
1.02	750	1,000
1.25	100	133
1.5	34	45
2.0	20	27
2.5	15	20
3.0	13	17
3.5	11	15
4.0	10	13
4.5	9	12

TABLE 2. RELATIVE VOLATILITIES OF BENZENE AND CYCLOHEXANE OR 2,4-DIMETHYLPENTANE WITH MIXTURES OF PHTHALIC ANHYDRIDE, MALEIC ANHYDRIDE AND/OR A SOLVENT

Extractive Distillation Agent	Cyclohexane–Benzene	2,4-TriMeC$_5$-Benzene
Ph.anh., Mal.anh., Phenol	2.51	4.12
Ph.anh., Phenol	2.28	
Mal.anh., Phenol	2.52	
Phenol	2.01	
Ph.anh., Mal.anh., Dimethylformamide	3.04	3.36
Ph.anh., Dimethylformamide	2.35	
Mal.anh., Dimethylformamide	2.67	
Dimethylformamide	2.03	
Ph.anh., Mal.anh., Dimethylsulfoxide	3.73	4.03
Ph.anh., Dimethylsulfoxide	3.67	
Mal.anh., Dimethylsulfoxide	3.86	
Dimethylsulfoxide	2.65	
Ph.anh., Mal.anh., 2,4-Pentanedione	2.67	4.25
Ph.anh., 2,4-Pentanedione	2.31	
Mal.anh., 2,4-Pentanedione	2.51	
2,4-Pentanedione	2.93	
Ph.anh., Mal.anh., Ethylene glycol phenyl ether	3.13	3.27
Ph.anh., Ethylene glycol phenyl ether	2.38	
Mal.anh., Ethylene glycol phenyl ether	2.66	
Ethylene glycol phenyl ether	2.22	
Ph.anh., Mal.anh., Nitrobenzene	2.83	3.05
Ph.anh., Nitrobenzene	Will not dissolve	
Mal.anh., Nitrobenzene	3.07	
Nitrobenzene	2.15	
Ph.anh., Mal.anh., Benzophenone	2.98	3.45
Ph.anh., Benzophenone	Will not dissolve	
Mal.anh., Benzophenone	2.98	
Benzophenone	2.68	
Ph.anh., Mal.anh., Furfural	3.00	4.58
Ph.anh., Furfural	2.80	
Mal.anh., Furfural	3.09	
Furfural	2.50	
Ph.anh., Mal.anh., 1-Me-2-pyrrolidinone	4.21	4.01
Ph.anh., 1-Me-2-pyrrolidinone	4.18	
Mal.anh., 1-Me-2-pyrrolidinone	3.46	
1-Me-2-pyrrolidinone	2.51	
Ph.anh., Mal.anh., Sulfolane	3.55	5.66
Ph.anh., Sulfolane	2.83	
Mal.anh., Sulfolane	2.84	
Sulfolane	3.43	
Ph.anh., Mal.anh., N,N-diMe acetamide	3.43	4.13
Ph.anh., N,N-diMe acetamide	2.66	
Mal.anh., N,N-diMe acetamide	3.31	
N,N-diMe acetamide	3.07	
Ph.anh., Mal.anh., Glycerol triacetate	3.15	4.41
Ph.anh., Glycerol triacetate	Will not dissolve	
Mal.anh., Glycerol triacetate	3.35	
Glycerol triacetate	2.20	
Ph.anh., Mal.anh., Acetophenone	2.52	3.57
Ph.anh., Acetophenone	2.48	
Mal.anh., Acetophenone	2.70	
Acetophenone	1.92	
Ph.anh., Mal.anh., Ethylacetoacetate	2.54	2.54
Ph.anh., Ethylacetoacetate	2.16	
Mal.anh., Ethylacetoacetate	2.69	
Ethylacetoacetate	1.94	
Ph.anh., Mal.anh., N-IsoPr-2-pyrrolidone	2.35	
Ph.anh., N-IsoPr-2-pyrrolidone	2.20	
Mal.anh., N-IsoPr-2-pyrrolidone	2.06	
N-IsoPr-2-pyrrolidone	1.81	
Ph.anh., Mal.anh., Sulfolene	3.15	6.16
Ph.anh., Sulfolene	3.18	
Mal.anh., Sulfolene	3.15	
Sulfolene	2.93	
Ph.anh., Mal.anh., DiMeSulfone	3.24	
Ph.anh., DiMeSulfone	Will not dissolve	
Mal.anh., DiMeSulfone	Decomposes	
DiMeSulfone	Will not dissolve	
Ph.anh., Mal.anh., 2-Nitrotoluene	2.81	3.16
Ph.anh., 2-Nitrotoluene	2.29	
Mal.anh., 2-Nitrotoluene	2.82	
2-Nitrotoluene	2.13	
Ph.anh., Mal.anh., Isobornyl acetate	2.97	
Ph.anh., Isobornyl acetate	Will not dissolve	
Mal.anh., Isobornyl acetate	1.78	
Isobornyl acetate	1.27	
Ph.anh., Mal.anh., Adiponitrile	4.07	4.44
Ph.anh., Adiponitrile	3.84	
Mal.anh., Adiponitrile	3.68	
Adiponitrile	3.27	
Ph.anh., Mal.anh., BuBenzyl phthalate	3.18	4.66
Ph.anh., BuBenzyl phthalate	Will not dissolve	
Mal.anh., BuBenzyl phthalate	2.22	
BuBenzyl phthalate	2.44	
Ph.anh., Mal.anh., Benzyl acetate	2.96	3.90
Ph.anh., Benzyl acetate	1.59	
Mal.anh., Benzyl acetate	2.40	
Benzyl acetate	2.10	
Ph.anh., Mal.anh., Diethyl oxalate	2.87	
Ph.anh., Mal.anh., Phenyl acetate	2.64	
Ph.anh., Mal.anh., Dipropylene glycol	2.85	
Ph.anh., Mal.anh., Butoxypropanol	2.73	
Ph.anh., Mal.anh., Phenylacetic acid	2.67	
Ph.anh., Mal.anh., Anisole	2.67	

of these is more effective as an extractive distillation agent in the separation of benzene from close boiling nonaromatic hydrocarbons than the compounds when used alone. Extractive agents with benzene (b.p. = 80.1°C.)—cyclohexane (b.p. = 80.8°C., a naphthene) and with benzene—2,4-dimethylpentane (b.p. = 80.6°C, a paraffin) were evaluated. The relative volatility of benzene to cyclohexane is 1.02, to 2,4-dimethylpentane it is 1.01.

Table 2 shows the relative volatility of benzene to cyclohexane and benzene to 2,4-dimethylpentane with a number of solvents mixed with phthalic anhydride, maleic anhydride or both. Table 3 shows the relative volatility of benzene to cyclohexane and benzene to 2,4-dimethylpentane with a number of solvents mixed with benzoic acid, maleic anhydride or both. All of the systems in Tables 2 and 3 possess a relative volatility of 2.5 or greater. Table 4 shows a number of systems involving phthalic anhydride, maleic anhydride, benzoic acid and/or a solvent possessing a relative volatility in the range of 1.5 to 2.5. The relative volatilities shown in Tables 2 to 4 are the average of two runs, one at one part of extractive agent per part of hydrocarbon mixture and the other at 6/5 parts of extractive agent per part of hydrocarbon mixture. The wt. % of phthalic anhydride, maleic anhydride, benzoic acid and solvent in the ternarys, Tables 2 to 4, were equal to each other as were the binarys.

The data in Tables 2 to 4 were obtained in a glass vapor-liquid equilibrium still of the Othmer design.

The utility of extractive distillation can be demonstrated by referring to the data in Tables 1 to 4. When benzene is being separated from cyclohexane, relative volatility = 1.02, by rectification in 99.9% purity, Table 1 shows that more than 1,000 actual plates are required. Table 2 shows that a mixture of phthalic anhydride, maleic anhydride and adiponitrile changes the relative volatility to 4.07, and referring to Table 1, this requires only a little more than ten actual plates. Table 2 also shows that this mixture will change the relative volatility of benzene—2,4-dimethylpentane to 4.44.

TABLE 3. RELATIVE VOLATILITIES OF BENZENE AND CYCLOHEXANE OR 2,4-DIMETHYLPENTANE WITH MIXTURES OF BENZOIC ACID, MALEIC ANHYDRIDE AND/OR A SOLVENT

Extractive Distillation Agent	Cyclohexane-Benzene	2,4-TriMe-Pentane Benzene
Benz.acid, Mal.anh., 3-Sulfolene	3.71	5.55
Benz.acid, 3-Sulfolene	3.35	
Mal.anh., 3-Sulfolene	3.15	
3-Sulfolene	3.22	
Benz.acid, Mal.anh., Dimethylsulfone	3.10	4.21
Benz.acid, Dimethylsulfone	Will not dissolve	
Mal.anh., Dimethylsulfone	Decomposes	
Dimethylsulfone	Will not dissolve	
Benz.acid, Mal.anh., Sulfolane	3.06	3.94
Benz.acid, Sulfolane	2.90	
Mal.anh., Sulfolane	2.84	
Sulfolane	3.42	
Benz.acid, Mal.anh., Adiponitrile	3.17	4.01
Benz.acid, Adiponitrile	1.81	
Mal.anh., Adiponitrile	3.68	
Adiponitrile	3.27	
Benz.acid, Mal.anh., 1-Me-2-pyrrolidinone	2.76	3.71
Benz.acid, 1-Me-2-pyrrolidinone	2.24	
Mal.anh., 1-Me-2-pyrrolidinone	3.46	
1-Me-2-pyrrolidinone	2.51	
Benz.acid, Mal.anh., N,N-diMe acetamide	4.21	3.30
Benz.acid, N,N-diMe acetamide	2.07	
Mal.anh., N,N-diMe acetamide	3.31	
N,N-diMe acetamide	3.08	
Benz.acid, Mal.anh., Nitrobenzene	2.97	3.62
Benz.acid, Nitrobenzene	2.12	
Mal.anh., Nitrobenzene	3.07	
Nitrobenzene	2.15	
Benz.acid, Mal.anh., Triethylene glycol diacetate	2.51	3.82
Benz.acid, Triethylene glycol diacetate	1.52	
Mal.anh., Triethylene glycol diacetate	2.17	
Triethylene glycol diacetate	2.07	
Benz.acid, Mal.anh., Dimethylformamide	2.67	
Benz.acid, Mal.anh., Formamide	3.83	2.22
Benz.acid, Formamide	3.35	
Mal.anh., Formamide	1.71	
Formamide	1.25	

These are the naphthene and paraffin boiling closest to benzene; therefore, all other hydrocarbons will be easier to separate than either of these two. Thus, extractive distillation by rectification in columns of ten to 12 actual plates will easily separate benzene from any other hydrocarbon.

The following experiment illustrates the utility of this separation. A column consisting of one ten-plate section of 1-in. (25-mm) diameter glass perforated plates equipped with a vacuum jacket was employed. The column was fitted with a Corad constant reflux ratio distilling head. Between the Corad head and the top of the column, a feed line from a constant flow bellows pump was introduced. The column had been calibrated with a test mixture of ethylbenzene and p-xylene, whose mixture possesses a relative volatility of 1.06. The column calibrated 4.5 theoretical plates at total reflux. A run was made with a charge comprising approximately 10% cyclohexane and 90% benzene in the stillpot. The column was operated at total reflux for about an hour and then the pump started at a rate to deliver about one part of extractive agent to one part of cyclohexane—benzene being boiled up. The extractive agent in this example was 33.3% phthalic anhydride, 33.3% maleic anhydride, and 33.3% adiponitrile. The following data were obtained:

Time, hours	Overhead Composition, % CH,	% Benz.	Stillpot Composition % CH,	% Benz.	Relative Volatility
1	90.7	9.3	7	93	2.93
2	96.1	3.9	4.9	95.1	3.92
3	96.2	3.8	4.2	95.8	4.09

TABLE 4. RELATIVE VOLATILITIES OF BENZENE AND CYCLOHEXANE WITH SEVERAL SOLVENT MIXTURES

Extractive Distillation Agent	Cyclohexane-Benzene
Ph.anh., Mal.anh., N(N,N-diMe aminopropyl)-2-pyrrolidone	1.48
Ph.anh., Mal.anh., Tetrahydrofurfuryl alcohol	2.38
N(N,N-diMe aminopropyl)-2-pyrrolidone	2.18
Ph.anh., Mal.anh., Diethyl maleate	2.45
Ph.anh., Mal.anh., Isophorone	2.42
Ph.anh., Mal.anh., Methylbenzoate	2.46
Ph.anh., Mal.anh., Diethylene glycol	1.60
Ph.anh., Mal.anh., n-Octanol	2.39
Benz.acid, Mal.anh., 2-Nitrotoluene	2.28
Benz.acid, Mal.anh., Furfural	1.78
Benz.acid, Mal.anh., Ethylene glycol diacetate	2.33
Benz.acid, Mal.anh., Phenol	2.22
Benz.acid, Mal.anh., 3-Nitrotoluene	1.80
Benz.acid, Mal.anh., Acetophenone	1.75
Benz.acid, Mal.anh., Ethylene glycol phenyl ether	2.06

It will be noted that after two hours, equilibrium has been achieved, and the relative volatility remains essentially constant in the range of 3.9 to 4.1. Without the extractive agent it would have been 1.02.

Toluene Separation

The separation of toluene by extractive distillation has been reported as far back as 1945 when Dunn (1945) determined the effectiveness of a number of pure compounds on the separation from a naphtha fraction. Thompson (1970, 1973, 1975) reported on the use of sulfolane as the extractive distillation agent in the separation of toluene from nonaromatic hydrocarbons. Thompson (1973) described the use of tetramethylene sulfone. Preusser (1971) reported on the use of morpholine and some of its derivatives for this separation. It should be noted that all of the work reported to date deals with the use of a single compound as the extractive distillation agent. The advantage of using extractive distillation in this separation can be seen from Table 1. The relative volatility of toluene to methylcyclohexane is 1.50. To separate these two in 99.9% purity by conventional rectification requires a minimum of 45 actual plates. The best extractive distillation agents listed in Table 5 push the relative volatility as high as 4.9, and Table 1 shows that they will reduce the actual plate requirement to about 12 plates.

A mixture comprising an organic compound admixed with phthalic anhydride and/or maleic anhydride is more effective as an extractive distillation agent in the separation of toluene from close boiling nonaromatic hydrocarbons than the compounds when used alone. To demonstrate this, extractive distillation agents were evaluated with toluene—2,2,4-trimethylpentane (b.p. = 99.2°C., a paraffin), with toluene (b.p. = 110.8°C.)—2,4,4-trimethylpentene-1 (b.p. = 101°C., an olefin) and with toluene—methylcyclohexane (b.p. = 100.8°C., a naphthene). These three compounds are available in high purity and boil fairly close to toluene. The relative volatility of toluene to methylcyclohexane is 1.50, to 2,4,4-trimethylpentene-1 is 1.61 and to 2,2,4-trimethylpentane is 1.79.

Table 5 shows the relative volatility of toluene to methylcyclohexane, 2,4,4-trimethylpentene-1 and 2,2,4-trimethylpentane with a number of solvents mixed with phthalic anhydride and maleic anhydride or both. The relative volatilities shown in Table 5 are the average of two runs, one at one part of extractive distillation agent per part of hydrocarbon mixture and the other at 6/5 parts of extractive agent per part of hydrocarbon mixture. This appears to be the preferred ratio of extractive distillation agent to hydrocarbon in this separation. The amount of phthalic anhydride, maleic anhydride and solvent in the ternarys shown in Table 5 was approximately equal to each other, as were the binarys. The exact ratio does not appear to be critical. Likewise, the relative volatilities

TABLE 5. RELATIVE VOLATILITIES OF TOLUENE TO METHYLCYCLOHEXANE, 2,4,4-TRIMETHYLPENTENE-1 AND 2,2,4-TRIMETHYLPENTANE WITH SEVERAL EXTRACTIVE DISTILLATION AGENTS

Extractive Distillation Agent	MecycloHex-Toluene	244TMP-1 Toluene	224TMP Toluene
Ph.anh, Mal.anh, Glycerol triacetate	4.25	3.45	5.18
Ph.anh, Glyceroltriacetate	3.20	3.43	4.03
Mal.anh, Glyceroltriacetate	3.10	3.70	4.14
Glycerol triacetate	2.85	2.79	3.01
Ph.anh, Mal.anh, Dimethylformamide	4.04	3.81	5.20
Ph.anh, Dimethylformamide	3.76	3.60	4.50
Mal.anh, Dimethylformamide	4.65	3.41	4.82
Dimethylformamide	3.60	3.73	3.90
Ph.anh, Mal.anh, Ethylene glycol phenyl ether	4.00	3.45	4.39
Ph.anh, Ethylene glycol phenyl ether	3.35	3.07	3.72
Mal.anh, Ethylene glycol phenyl ether	3.00	3.68	4.00
Ethylene glycol phenyl ether	2.80	2.90	3.69
Ph.anh, Mal.anh, Dichlorodiethyl ether	4.10	3.48	3.96
Ph.anh, Dichlorodiethyl ether	3.30	2.95	3.85
Mal.anh, Dichlorodiethylether	3.15	3.00	3.56
Dichlorodiethyl ether	2.70	2.05	3.50
Ph.anh, Mal.anh, Ethylene glycol diacetate	3.91	3.30	3.94
Ph.anh, Ethylene glycol diacetate	3.10	3.60	4.15
Mal.anh, Ethylene glycol diacetate	3.63	3.35	4.26
Ethylene glycol diacetate	3.10	2.92	3.27
Ph.anh, Mal.anh, Phenol	3.75	3.60	5.65
Ph.anh, Phenol	3.10	3.05	4.66
Mal.anh, Phenol	3.85	3.35	4.86
Phenol	2.95	2.70	4.00
Ph.anh, Mal.anh, Dimethylsulfoxide	4.51	4.96	5.23
Ph.anh, Dimethylsulfoxide	3.91	4.28	5.73
Mal.anh, Dimethylsulfoxide	3.59	3.30	4.25
Dimethylsulfoxide	3.84	4.22	3.55
Ph.anh, Mal.anh, Furfural	4.10	3.55	5.22
Ph.anh, Furfural	3.10	3.35	5.02
Mal.anh, Furfural	4.00	3.55	3.91
Furfural	3.35	3.25	4.41
Ph.anh, Mal.anh, Nitrobenzene	3.58	3.50	4.46
Ph.anh, Nitrobenzene	3.10	3.10	4.16
Mal.anh, Nitrobenzene	3.50	3.65	4.45
Nitrobenzene	2.60	2.95	3.29
Ph.anh, Mal.anh, Acetophenone	3.47	3.22	4.13
Ph.anh. Aceptophenone	2.95	2.85	4.73
Mal.anh, Acetophenone	3.45	3.25	3.33
Acetophenone	2.68	2.53	2.80
Ph.anh, Mal.anh, Ethylacetoacetate	2.65	3.51	3.44
Ph.anh, Ethylacetoacetate	3.08	2.95	3.58
Mal.anh, Ethylacetoacetate	3.54	3.25	3.02
Ethylacetoacetate	2.80	2.46	2.30
Ph.anh, Mal.anh, Benzophenone	3.45	3.75	4.30
Ph.anh, Benzophenone	2.50	3.20	4.46
Mal.anh, Benzophenone	2-ϕ	2.95	4.24
Benzophenone	2.05	2.42	3.26
Ph.anh, Mal.anh, 2,4-Pentanedione	3.50	3.83	4.90
Ph.anh, 2,4-Pentanedione	3.35	2.80	4.47
Mal.anh, 2,4-Pentanedione	3.25	3.20	3.90
2-4-Pentanedione	2.80	2.52	3.14
Ph.anh, Mal.anh, 2-Nitrotoluene	3.45	3.38	4.05
Ph.anh, 2-Nitrotoluene	3.45	3.15	3.58
Mal.anh, 2-Nitrotoluene	3.60	3.15	4.13
2-Nitrotoluene	2.55	2.70	3.50
Ph.anh, Mal.anh, Sulfolane	4.95	3.95	5.55
Ph.anh, Sulfolane	3.50	2-phase	5.54
Mal.anh, Sulfolane	3.75	2.80	4.75
Sulfolane	2.25	1.95	6.31
Ph.anh, Mal.anh, Triethylene glycol diacetate	3.68	3.30	4.95
Ph.anh, Triethylene glycol diacetate	3.10	3.60	4.15
Mal.anh, Triethylene glycol diacetate	3.63	3.35	4.26
Triethylene glycol diacetate	3.10	2.92	3.27

shown in Table 5 do not change appreciably when the ratio of toluene to nonaromatic hydrocarbon is varied. The data in Table 5 were obtained in a glass vapor-liquid equilibrium still of the Othmer design.

The following experiment will illustrate the utility of this separation. A column consisting of one ten-plate section of 1-in. (25-mm) diameter glass perforated plates equipped with a vacuum jacket was employed. The column was fitted with a Corad constant

reflux ratio distilling head. Between the Corad head and the top of the column, a feed line from a constant flow bellows pump was introduced. The column had been calibrated with a test mixture of ethylbenzene and p-xylene, whose mixture possesses a relative volatility of 1.06. The column calibrated 4.5 theoretical plates at total reflux. A run was made with a charge comprising approximately 10% methylcyclohexane and 90% toluene in the stillpot. The column was operated at total reflux for about an hour and then the pump started at a rate to deliver about one part of extractive agent to one part of methylcyclohexane—toluene being boiled up. The extractive agent in this example was 33.3% phthalic anhydride, 33.3% maleic anhydride, and 33.3% glycerol triacetate. The following data were obtained:

Time, hours	Overhead Composition, % MCH,	% Tol.	Stillpot Composition, % MCH,	% Tol.	Relative Volatility
1	88.7	11.3	6.4	93.6	2.87
2	97.0	3.0	5.3	94.7	4.11
3	97.8	2.2	4.9	95.1	4.48

It will be noted that after about two hours, equilibrium has been achieved and the relative volatility remains essentially constant in the range 4.1 to 4.5. Without the extractive agent it would have been 1.50.

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Pore-Diffusion Model for Cyclic Separation: Temperature Swing Separation of Hydrogen and Methane at Elevated Pressures

A pore-diffusion model is developed for temperature swing separation in a packed bed of sorbent. The model is applied to interpret experimental data for separation of H_2 of CH_4 in a packed bed of activated carbon operated in the temperature swing mode, at pressures up to 5.52 MPa. Experimental results on the effects of total pressure, particle size, adsorption temperature, and flow rate on separation efficiency compared favorably to the model predictions. The importance of pore diffusion in separation has been clearly demonstrated.

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SCOPE

There is an increasing number of important industrial applications being found for temperature and pressure swing separation processes. Designs and performance models have been made and illustrated with various examples (Pigford et al., 1969, 1971; Kadlec et al., 1972, 1973; Wankat et al., 1975, 1978; Hill et al., 1980, 1982). In these models it has been assumed that the adsorbed phase is in instantaneous equilibrium with the bulk flow phase of the fluid. More specifically, in the model for temperature swing separation by Baker and Pigford (1971), pore diffusion is assumed instantaneous and a linear or Freundlich equilibrium adsorption isotherm is assumed. The first objective of this work is to formulate a more general model which incorporates pore diffusion limitation and Langmuir isotherm, the latter being more applicable for gases. Experimental results are also presented for separation of H_2 and CH_4 at elevated pressures using temperature swing in a packed bed of activated carbon.

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