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CRITICAL-FLUID EXTRACTION OF ORGANICS FROM WATER

Volume 1: Engineering Analysis

Final Report for the Period October 1, 1979—November 30, 1983

By

John M. Moses

Richard P. de Filippi

June 1984

Work Performed Under Contract No. AC01-79CS40258

Arthur D. Little, Inc.
Cambridge, Massachusetts

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ABSTRACT

Critical-fluid extraction of several organic solutes from water was investigated analytically and experimentally to determine the energy conservation potential of the technology relative to distillation. This Volume (I) gives the results of an engineering analysis; Volume II presents experimental results, both bench- and pilot-unit scale.

The process uses condensed or supercritical carbon dioxide as an extracting solvent to separate aqueous solutions of common organics such as ethanol, isopropanol and sec-butanol. Energy input to the systems is electric power to drive compressors.

A detailed process analysis included evaluation and correlation of thermophysical properties and phase equilibria for the two- and three-component systems involved. The analysis showed that a plant fed with 10 weight percent ethanol feed would consume 0.65 kilowatt-hours (kwh) of power for compression energy per gallon of alcohol. This energy consumption would be 5200 Btu of steam-equivalent, or 6500 Btu of fossil-fuel-equivalent energy. The extraction product, however, would require additional energy to produce high-purity alcohol. Doubling the ethanol feed concentration to 20 weight percent would reduce the energy required to about 0.30 kwh per gallon. Halving the ethanol feed concentration to 5 weight percent would increase the energy required to about 1.35 kwh per gallon.

For the same feed composition, isopropanol can be separated with 48% of the energy required for ethanol. The same separation of sec-butanol can be done with 25% of the ethanol energy requirement.

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I. SUMMARY

A research and development program was undertaken for the separation of dissolved organics from water using critical-fluid solvent extraction. The technology employs supercritical fluids or condensed gases as solvents under pressure for extraction; carbon dioxide is a specific solvent of choice.

Among common types of industrial distillations, water-oxygenated hydrocarbon systems rank highest in energy consumption, averaging about 2400 Btu per pounds of organic product. Many form azeotropes, which are responsible for energy-intensive distillations. Thus, there is a substantial incentive for the development of new separation processes as alternatives to existing distillations in the chemical process industries, particularly for water-organic mixtures. These incentives led to the research and development program described in this report; to test and evaluate solvent extraction with supercritical and liquid carbon dioxide as a technology with advantages leading to major energy economies in a wide range of separations.

The report is presented in two volumes. This volume is Volume I, Engineering Analysis, which contains background information on the nature of critical fluids (supercritical fluids and near-critical liquids) and their use in solvent extraction (Section II); a discussion of the important specific separations to which the process technology may be applicable (Section III); and a detailed analysis of the process (Section IV). Volume II describes the experimental program including laboratory studies; pilot-unit studies with carbon dioxide; and pilot-unit studies with carbon-dioxide-co-solvent mixtures.

As a low-energy alternative separation process, a solvent extraction system that employs carbon dioxide near its critical point appears to show significant promise. When liquefied or supercritical at pressures of 35-100 atm (500-1500 psia), CO_2 is an excellent solvent for organic compounds, and it has a low mutual solubility with water. Thus, its solution properties make it ideal as an extractant for organics from water. The key to energy conservation and overall economics is the fact that the solute-rich CO_2 extract stream can be separated inexpensively by a simple distillation step, yielding separated purified product and CO_2 solvent for recycle. Moreover, using vapor-compression to raise the temperature of the distillation overhead vapor, the vapor enthalpy can be used to provide much of the boiler energy requirement.

After reviewing a wide range of commercial distillations, it was concluded that the process should be tested experimentally with ethanol, isopropyl alcohol, and sec-butanol. The choices of ethanol and isopropyl alcohol were based on large volumes and high-energy intensity, and apparently favorable properties for extraction. Sec-butanol, while exhibiting lower total energy consumption, also satisfied these criteria.

Principal conclusions of the engineering analysis (this Volume) were the following:

1. A plant fed with 10 weight percent ethanol feed would consume 0.65 kilowatt-hours (kwh) of power for compression energy per gallon of alcohol fed to the system. Depending on the economics of heat exchange addition in portions of the system, this could be the entire energy consumption, or probably the great majority. Assuming that 8000 Btu of steam or 10,000 Btu of fossil fuel are required to generate one kwh of power, the energy consumption would be 5200 Btu of steam-equivalent, or 6500 Btu of fossil fuel equivalent energy. The extraction product, however, would have a composition of 85.1 mol percent, or 93.6 weight percent, less than the azeotropic composition. Thus, additional energy would be required to process this stream to high-purity alcohol.
2. Doubling the ethanol feed concentration to 20 weight percent would reduce the energy required to about 0.30 kwh per gallon. Halving the ethanol feed concentration to 5 weight percent would increase the energy required to about 1.35 kwh per gallon.
3. For the same feed composition, isopropanol can be separated with 48% of the energy required for ethanol. The same separation of 2-butanol can be done with 25% of the ethanol energy requirement.

To carry out the process simulation leading to these analytical conclusions, a wide range of published data were evaluated and correlated for use in computer-aided process design. Quantitative relationships were generated for CO₂-water mutual solubilities, which account for effects of temperature, pressure, and third (organic) component concentration. A phase diagram was developed for the CO₂-water system, particularly to clarify regions of solid-phase formation. The latter includes the CO₂ hydrate as well as solid-phase pure components. Literature data for solubilities of organics in CO₂ (liquid-liquid) were compiled, and vapor-liquid equilibria data for several CO₂-organic systems, such as CO₂ and lower alcohols, were correlated using the Peng-Robinson equation-of-state. Three component-phase equilibria (carbon dioxide-water-organic) were compiled for a wide range of organic compounds, and empirical relationships were developed based on literature models.

II. BACKGROUND

A. Description of the Problem: Energy Consumption in Chemical Separations

A significant portion of the energy consumption in the chemical and petroleum industries is utilized in separation processes. The most important process is distillation, which involves the separation of mixtures based on component volatility differences. Energy input is required for boiling and it is not usually recovered from vapor condensation. In 1976, fuel consumption for distillation in the two industries was about 2.0 quads (2.0×10^{15} Btu) per year, or 3% of the total U. S. consumption⁽¹⁾. This is equivalent to 900,000 barrels of oil per day. Thus, it is evident that any significant savings in this energy use would have an important impact in reducing total domestic energy needs.

Table II-1⁽¹⁾ presents a listing of distillation energy consumption in the manufacture of industrial chemicals and petroleum products. These are classified as follows: petroleum fuel fractions; light hydrocarbons; water-oxygenated hydrocarbons; aromatics; water-inorganics; and others. Because of their large volume, petroleum fuel fractions account for the largest percentage of the total distillation energy, about 56%. Light hydrocarbons are next with about 17%, and water-oxygenated hydrocarbons follow with about 7%. Perhaps as important, the water-oxygenated hydrocarbons rank highest in distillation energy intensity, about 2400 Btu/lb. Aromatics are second with 1500 Btu/lb, and light hydrocarbons third with 900 Btu/lb.

Among water/oxygenated-hydrocarbon binary systems, it is of interest to note that many form azeotropes, leading to the need for expensive extractive distillation capacity to produce the pure chemical product. A partial list of such azeotropes and their properties is given in Tables II-2 and II-3⁽²⁾. This second separation step is a significant factor in increasing distillation energy use.

An additional factor accounting for the high distillation energy intensity of this group is the high heat of vaporization of water relative to that of organics. Many of the water-oxygenated hydrocarbon distillations have bottoms-stream compositions close to that of pure water, thus requiring high heat input into the column reboiler.

All of these considerations underline the substantial incentives for the development of new separation processes as alternatives to existing distillations in the chemical process industries, particularly for water-organic mixtures. These incentives led to the research and development program described in this report: to test and evaluate solvent extraction with supercritical and liquid carbon dioxide as a technology with advantages leading to major energy economies in a wide range of separations.

TABLE II-1

Distillation energy consumption as a function of component classification

Component Classification	Total U.S. Distillation Energy Consumption, quads/yr.	Specific Distillation Energy Consumption, B.t.u./lb. product	Component Classification	Total U.S. Distillation Energy Consumption, quads/yr.	Specific Distillation Energy Consumption, B.t.u./lb. product
Petroleum Fuel Fractions			Methyl Ethyl Ketone		
Crude Distillation.....	0.36115.....	193		0.00481.....	9,431
Vacuum Distillation.....	0.08990.....	132	Terephthalic Acid.....	0.00426.....	1,756
Catalytic Hydro-treating, Hydro-refining.....	0.07726.....	101	Acetone.....	0.00417.....	2,172
Catalytic Cracking Fractionator.....	0.06803.....	112	Dimethyl Terephthalate.....	0.00412.....	1,567
Naphtha Fractionator.....	0.06105.....	132	Formaldehyde.....	0.00412.....	733
Catalytic Hydro-cracking.....	0.05964.....	632	Acetic Anhydride.....	0.00267.....	1,669
Catalytic Reforming.....	0.04988.....	132	Propylene Oxide.....	0.00219.....	1,217
Thermal Operations.....	0.00936.....	60	Glycerine.....	0.00202.....	14,870
Ethylene Primary Fractionator (naphtha gas oil cracking).....	0.00205.....	352	Acetaldehyde.....	0.00174.....	1,081
Total.....	0.77832.....	331	Total.....	0.10172.....	2,366
Light Hydrocarbons			Aromatics*		
Natural Gas Processing.....	0.07495.....	827	BTX.....	0.02437.....	933
Ethylene and Propylene.....	0.04821.....	1,517	Styrene.....	0.01554.....	2,467
Alkylation-HF.....	0.04701.....	1,046	Ethylbenzene.....	0.01388.....	2,264
Alkylation-H ₂ SO ₄	0.03065.....	570	o-Xylene.....	0.00538.....	6,019
Light Ends Processing.....	0.01729.....	699	Cumene.....	0.00390.....	1,450
Isomerization.....	0.01312.....	803	Total.....	0.06407.....	1,515
Butadiene.....	0.01024.....	3,151	Water-Inorganics*		
Cyclohexane.....	0.00021.....	98	Sour Water Strippers.....	0.02742.....	240
Total.....	0.24168.....	928	Sodium Carbonate.....	0.01398.....	1,875
Water-Oxygenated Hydrocarbons*			Urea.....	0.01030.....	133
Ethylene Glycols.....	0.01065.....	2,795	Total.....	0.05170.....	411
Ethanol.....	0.01003.....	9,008	Others*		
Phenol.....	0.00947.....	4,344	Vinyl Chloride (monomer).....	0.01256.....	2,188
Adipic Acid.....	0.00739.....	4,862	Oxygen and Nitrogen.....	0.00846.....	158
Methanol.....	0.00733.....	1,175	Acrylonitrile.....	0.00826.....	5,434
Vinyl Acetate (monomer).....	0.00710.....	4,797	Hexamethyl-enediamine.....	0.00612.....	8,164
Acetic Acid.....	0.00701.....	2,885	Total.....	0.03540.....	567
Isopropanol.....	0.00651.....	3,785	Remaining 30% of Chemicals Production*		
Ethylene Oxide.....	0.00554.....	1,325		0.10869.....	1,973
			Total for All Component Classifications		
				1.38158.....	623

*The chemicals listed represent only 70% of the total chemical production. The 30% not represented are expected to fall predominantly into the "water-oxygenated hydrocarbon" and "other" categories.

SOURCE: Reference 1

TABLE II-2

WATER-ALCOHOL AZEOTROPES

<u>ALCOHOL</u>	<u>MOL % ALCOHOL</u>	<u>MINIMUM BP, °C</u>	<u>ALCOHOL NORMAL BP, °C</u>	<u>AMBIENT-TEMP SOLUBILITY IN WATER, MOL %</u>
Ethanol	89.4	78.2	78.4	∞
Allyl	45.5	88.2	96.6	∞
n-Propyl	43.2	87.7	97.8	∞
i-Propyl	68.5	80.4	82.5	∞
i-Butyl	32.9	89.9	108	2.6
n-Butyl	25.0	92.3	117	2.3
s-Butyl	34.0	88.5	99.5	3.4
t-Butyl	64.6	79.9	82.9	∞
i-Amyl	17.2	95.2	114	0.6
t-Amyl	35.0	87.0	102	Low

Source: Reference 2

TABLE II-3

OTHER ORGANIC-WATER AZEOTROPES

<u>ORGANIC COMPONENT</u>	<u>MOL % ORGANIC</u>	<u>MIN. BP, °C</u>	<u>ORGANIC NORMAL BP, °C</u>	<u>AMBIENT-TEMP SOLUBILITY IN WATER, MOL %</u>
Formic acid	56.7	107.1 (max)	100.8	∞
Propionic acid	5.3	99.98	141.1	∞
Isobutyric acid	5.5	99.3	154.5	4.9
Methyl ethyl ketone	67.0	73.5	79.6	11.8
Ethyl acetate	76.0	70.4	77.1	1.9
Ethyl ether	95.0	34.1	34.6	1.9

Source: Reference 2

This report is presented in two volumes. Volume I, Engineering Analysis, contains background information on the nature of critical fluids (supercritical fluids and near-critical liquids) and their use in solvent extraction (Section II); a discussion of the important specific separations to which the process technology may be applicable (Section III); and a detailed analysis of the process (Section IV).

The above information served as the rationale for the experimental program presented in Volume II. The experimental program included laboratory studies; pilot-unit studies with carbon dioxide; and pilot-unit studies with carbon-dioxide-cosolvent mixtures.

B. Critical-Fluid Extraction

It was originally reported⁽³⁾ in 1879 that supercritical fluids could dissolve complex organic materials to high-concentration levels and that at pressures above the critical pressure of the fluid, the solubility depended strongly on pressure: small increases in pressure increased the solvent power of the fluid dramatically. Between 1879 and about 1950, a number of investigators studied supercritical fluid solubility phenomena, with most of the experimental work directed to spectroscopic studies of solution chemistry and molecular interactions in a large variety of supercritical fluid-organic compound systems.

In the early 1950's, Francis⁽⁴⁾ presented phase diagrams for 464 ternary systems with liquid carbon dioxide just below its critical temperature and pressure. Included were a number of water/oxygenated hydrocarbon/liquid CO₂ systems. At about the same time, Elgin and co-workers⁽⁵⁾ examined the phase equilibrium of a number of systems containing one component near its critical point. They investigated both binary and ternary systems containing carbon dioxide, ethylene, propane, and propylene as near-critical fluids in systems with various hydrocarbons and water. More recently, Baker and Anderson⁽⁶⁾ reported on the carbon dioxide-ethanol-water system, and Shultz and Randall on a mixture of alcohols and esters with carbon dioxide and water. All of these studies focused only on single-stage equilibria, rather than a multi-stage, countercurrent-flow, extractor performance.

A variety of studies with solvents such as carbon dioxide, ethylene, and ethane have been reported^(8,9a). These three gases are of interest because they fall in the near-supercritical regime at ambient temperatures, with critical pressures in the range of 50 to 75 atmospheres. In this regime, fluids have solvent properties similar to those of liquids, as demonstrated in Figure II-1 for naphthalene in CO₂⁽¹¹⁾.

FIGURE II-1

SOLUBILITY OF NAPHTHALENE IN CO₂

Several characteristics of this plot are of interest, and they serve to describe solubility behavior in solvents near the critical point in general. At pressures above 150 atmospheres, the solubility behavior is essentially an extension of that typically observed in the liquid phase: naphthalene solubility increases with increasing temperature, and there is a relatively small effect of increasing pressure. At temperatures above the critical but at pressures below about 80 atmospheres, the "solution" is gas-phase, and the "solubility" of solute is controlled mainly by its vapor pressure. In the intermediate pressure region at supercritical temperatures within 50° of the critical, there is a mixture of gas-like and liquid-like behavior. Among other phenomena, inversions of solubility trends with temperature at constant pressure are common. The general form of this solubility map is common to all partly-miscible solutes near the critical point of the solvent. Such behavior, of course, would not be seen where there is complete miscibility of solvent and solute in this near-critical regime; nevertheless, the naphthalene- CO_2 data give a good indication of the very large enhancement in solubility that has been observed in solvents that would normally be considered gases, when those solvents are in the near-critical or supercritical state.

Kinetic properties of fluids in the critical range show further why they represent excellent solvents for extraction processes in many respects. The diffusivity in the high-pressure liquid or supercritical fluid, while less than that expected for the gas phase, is nevertheless perhaps an order of magnitude greater than that seen in a normal liquid⁽¹²⁾. Thus, in an extraction process, the critical fluid is a solvent with the carrying capacity of a normal liquid, but with greatly enhanced diffusion properties.

C. Critical-Fluid Extraction of Organics from Water

As a low-energy alternative separation process, a solvent extraction system that employs carbon dioxide near its critical point appears to show significant promise. When liquefied or supercritical at pressures of 35-100 atm (500-1500 psia), CO_2 is an excellent solvent for organic compounds, and it has a low mutual solubility with water. Thus, its solution properties make it ideal as an extractant for organics from water.

The key to energy conservation and overall economics is the fact that the solute-rich CO_2 extract stream can be separated inexpensively by a simple distillation step, yielding separated purified product and CO_2 solvent for recycle. Moreover, using vapor-compression to raise the temperature of the distillation overhead vapor, the vapor enthalpy can be used to provide much of the boiler energy requirement. The process flow is shown in Figure II-2.

A qualitative analysis of the process indicates some important advantages:

1. In addition to its good solvent properties, CO_2 around its critical point has favorable diffusion coefficients compared to normal liquids. The resulting high mass-transfer coefficients may eliminate any significant transport resistance in the CO_2 phase, and the overall extraction rate would be increased accordingly.

FIGURE II-2

CRITICAL-FLUID EXTRACTION FLOW SCHEMATIC

2. Low mutual solubility of CO_2 and water helps to maintain low CO_2 losses in the raffinate stream. The impact of such losses is further diminished by the low cost of CO_2 . Also, solvent residuals in the aqueous effluent are non-polluting.
3. In the solvent-product distillation, the volatility of CO_2 relative to any organic liquid product of interest is very high, greatly facilitating the solvent-solute separation.
4. Because the distillation is carried out near the critical point, the heat of vaporization of CO_2 is very low. Under typical conditions, the value is about 75 Btu/lb. In contrast, the heat of vaporization of many solvents is of the order of 400 Btu/lb. In contrast, the heat of vaporization of many solvents is of the order of 400 Btu/lb; for water, it is 1000 Btu/lb. As a result, the boiler heat duty per unit of solvent distilled is lower than that for normal liquids.
5. This distillation is well-suited for the energy-saving advantage that results from the use of vapor recompression. The boiling-point-elevation of organics- CO_2 solutions is small over much of the concentration range. Therefore, the boiling point of the vapor (essentially pure CO_2) and that of the still bottoms are close. As a result, the required temperature increase in the compressed vapor is low, as is the compression ratio and thus the energy addition per pound of CO_2 compressed. Also, there are no unusual design requirements for the compressor in this case. This is often the limiting factor in using vapor recompression in other distillations, because the vapors are chemically corrosive and/or at high temperatures. Typical operation for the CO_2 system is near ambient temperature, and compression of CO_2 is common practice in industry today.

III. SELECTION OF TEST APPLICATIONS

Literally thousands of distillation separations are reported in the literature. Therefore, our first task was to focus on a workable number of applications for study. The screening procedure was two-fold: first, to identify the most energy-intensive distillations; second, to select those most likely to be technically amenable to critical-fluid extraction.

In a 1982 report,⁽¹³⁾ the Batelle Memorial Institute summarized major new technologies that may have a substantial future impact on energy use in industry. Prominent among these was the use of critical-fluid extraction for separation of industrial chemicals. In addition, a greater conservation potential would be realized from the use of critical-fluid extraction in ethanol production, if ethanol were to become a major blending stock in motor fuels. Also, it is apparent that the use of other alcohols as gasoline blending stocks, such as propanols and butanols derived from lower olefins, is under consideration by petroleum processors. These alcohols could also be manufactured using critical-fluid extraction in their separation and purification, thus providing an energy conservation potential beyond that outlined in the Batelle report.

To provide a parallel independent assessment, we reviewed the current consumption of energy for distillation processes in U. S. industry.⁽¹⁾ As summarized in Table III-1, the total energy consumption in the U. S. in 1983 was about 68 quads/yr (1 quad = 10^{15} Btu). Of that amount, approximately 20 quads are consumed in industrial energy, and about 10% (2 quads) of that amount is consumed in distillation processes.

The middle column of Table III-1 gives a breakout of the distillation energy consumption in various industry categories. Because CO_2 is a hydrophobic solvent, essentially immiscible with water and miscible with many hydrocarbon streams, it would not be usable for solvent extraction of most purely organic systems. Instead, as in much of industrial liquid solvent extraction, the focus would be separation from aqueous-based streams. Thus, we concluded that the impact of the critical-fluid extraction technology would be largely in water-oxygenated-hydrocarbon separations, which represent about 7.5% of the total distillation energy consumption. It is anticipated, however, that other distillations could also be favorably impacted by this technology.

The third column in Table III-1 shows the distribution of the organics/water distillation-energy consumption among major chemicals currently in production. Table III-2 presents a listing of the chemicals within that group which are potentially technically feasible for separation with critical-fluid extraction. These have been divided into two groups: those which would be separated using carbon dioxide alone as the solvent, and those which would involve the use of co-solvent separations.

Transportation Fuel		Distillation Processes	Total	Isopropyl Alcohol	
Industrial Energy	20	2	2.000	Methyl Ethyl Ketone	.001
Domestic Heating	24			Secondary Butyl Alcohol	.005
				Vinyl Acetate	.010
				Methyl Isobutyl Ketone	None
Total	68			n-Butanol	.011
				Acetone	.006
				Acetic Acid	.010
				Ethanol	.015
				Terephthalic Acid	.006
				Phenol	.013
				Adipic Acid	.010
				Other	.054
				Total	.150

(1) Data Based on Reference (1), Scaled from 1977 to 1983 Using a 3% Per Year Increase

TABLE III-2

WATER-OXYGENATED HYDROCARBON SEPARATIONS

CARBON DIOXIDE SEPARATIONS

Isopropyl Alcohol
Methyl Ethyl Ketone
Secondary Butyl Alcohol
Vinyl Acetate
Methyl Isobutyl Ketone
n-Butanol
Acetone

CO-SOLVENT SEPARATIONS

Acetic Acid
Ethanol
Terephthalic Acid
Phenol
Adipic Acid

The distinction between where a cosolvent is used along with CO₂ and where CO₂ is used alone is based on the equilibrium distribution coefficient (dc) of the organic chemical between the CO₂ and water. A preliminary analysis showed that chemicals with dc greater than about 0.25 (weight fraction in CO₂ divided by weight fraction in water) could be recovered most favorably using CO₂ alone, while chemicals with a dc less than about 0.1 would require a cosolvent in order to be economically recovered. Those chemicals with a dc between about 0.1 and 0.25 could be extracted either with or without a cosolvent, with the best method determined on a case-by-case basis. For the three alcohols tested in the experimental portion of this project, the dc's (at conditions of interest) were approximately 0.1, 0.25, and 0.8 for ethanol, isopropanol, and sec-butanol, respectively. At the time this evaluation was performed, ethanol was placed on the cosolvent-CO₂ list because it appeared to be borderline in dc properties. Because of the potential large volumes of separations involved with ethanol, it was decided that it should be included in initial studies with CO₂ alone, and that later studies with cosolvents and ethanol should be included also if they were needed. Those were, in fact, carried out as reported in Volume II.

In many cases, these chemicals are distilled not only in their manufacture, but in recycle usage also, particularly as solvents. For example, isopropanol is a component of many solvent mixtures used in the pharmaceutical industry, and the distillation of isopropanol carried out in that industry is probably far in excess of that carried out in the original manufacture of isopropanol. The recycle usage figures, however, are difficult to obtain; thus, relatively conservative estimates of the recycle usage energy consumption have been made. These are summarized in Table III-3, where they are combined with the manufacturing distillation consumption to give figures for distillation quads per year for those chemicals which could be separated with critical-fluid extraction. The total amounts to about 0.3 quads/year.

A series of engineering estimates were then made for the critical-fluid extraction process energy requirement, and these are summarized in the middle column of Table III-4. These energy requirements have been subtracted from the figures for distillation to give the estimated savings from use of the extraction process, summarized in the third column of Table III-4. The estimates show that about 80% (0.24 quads) of the 0.30 quads required for distillation could be conserved.

As a matter of interest, Table III-5 presents these figures converted to savings, expressed as dollars and barrels of crude oil. In Table III-6 these savings are summarized over a twenty-year period, a reference time-frame used by the U. S. Department of Energy for assessing future contributions to energy conservation. As can be seen, the energy, dollar, and crude oil conservation figures are very substantial: for the year 1983, this potential represents \$1.2 billion dollars, or 48 million barrels of crude. For the integrated time period of twenty years, this represents \$26 billion dollars, or 1 billion barrels of crude.

TABLE III-3

POTENTIAL CRITICAL FLUID EXTRACTION (CFE) APPLICATIONS
CURRENT DISTILLATION ENERGY CONSUMPTION
QUADS PER YEAR
1983

	In Manufacturing	Recycle Usage	Total
CARBON DIOXIDE SEPARATIONS			
Isopropyl Alcohol	.009	.022	.031
Methyl Ethyl Ketone	.001	.003	.004
Secondary Butyl Alcohol	.005	Negligible	.005
Vinyl Acetate	.010	.024	.034
Methyl Isobutyl Ketone	None	.001	.001
n-Butanol	.011	.028	.039
Acetone	<u>.006</u>	<u>.014</u>	<u>.020</u>
Subtotal	.042	.092	.134
CO-SOLVENT SEPARATIONS			
Acetic Acid	.010	.038	.048
Ethanol	.015	.015	.030
Terephthalic Acid	.006	Negligible	.006
Phenol	.013	Negligible	.013
Adipic Acid	.010	Negligible	.010
Other	<u>.054</u>	<u>Negligible</u>	<u>.054</u>
Subtotal	.108	.053	.161
Total	.150	.145	.295

TABLE III-4

1983
TOTAL QUADS PER YEAR

	DISTILLATION PROCESS ENERGY	ESTIMATE OF CFE PROCESS ENERGY	ESTIMATED SAVINGS WITH CFE PROCESS
<u>CARBON DIOXIDE SEPARATIONS</u>			
Isopropyl Alcohol	.031	.003	.028
Methyl Ethyl Ketone	.004	.001	.003
Secondary Butyl Alcohol	.005	Negligible	.005
Vinyl Acetate	.034	.003	.031
Methyl Isobutyl Ketone	.001	.001	Negligible
n-Butanol	.039	.012	.027
Acetone	.020	.004	.016
Sub-total	.134	.024	.110
<u>COSOLVENT SEPARATIONS</u>			
Acetic Acid	.048	.013	.035
Ethanol	.030	.003	.027
Terephthalic Acid	.006	.001	.005
Phenol	.013	.003	.010
Adipic Acid	.010	.002	.008
Other	.054	.010	.044
Sub-total	.161	.032	.129
Total	.295	.056	.239

TABLE III-5

TOTAL NATIONAL ENERGY USAGE
WATER-OXYGENATED HYDROCARBON SEPARATIONS
1983

	<u>Distillation Energy</u>	<u>Estimated Savings With CFE Process</u>		
	<u>Quads</u>	<u>Quads</u>	<u>Dollars</u>	<u>Barrels of Crude</u>
Carbon Dioxide Separations	.14	.11	550 Million	22 Million
Co-Solvent Separations	.16	.13	650 Million	26 Million
Total	<u>.30</u>	<u>.24</u>	1.2 Billion	48 Million

TABLE III-6

**WATER-OXYGENATED HYDROCARBON SEPARATIONS
ACCUMULATED ESTIMATED SAVINGS USING CFE PROCESS
TWENTY-YEAR PERIOD (1983-2003)**

	<u>Quads</u>	<u>1983 Dollars</u>	<u>Barrels of Crude</u>
Carbon Dioxide Separations	3.06	12 Billion	556 Million
Co-Solvent Separations	3.52	14 Billion	640 Million
Total	6.58	26 Billion	1 Billion

In reviewing the list shown in Tables III-2, -3, and -4, it was concluded that CO₂-based solvent extractions should be tested with ethanol, isopropyl alcohol, and sec-butanol. The choices of ethanol and isopropyl alcohol were based on large volumes and high-energy intensity, and apparently favorable properties for extractions. Sec-butanol, while exhibiting lower total energy consumption, also satisfied these criteria. Subsequently, ethanol was also selected for co-solvent studies as well, to obtain comparative data on co-solvent addition with a solute tested with CO₂ alone.

IV. ENGINEERING ANALYSIS

A. Introduction

This engineering analysis of critical-fluid extraction of organics from water has concentrated on three areas: the estimation and correlation of thermophysical property data; the calculation of material and energy balances for process flowsheets; and the design of process equipment.

A substantial amount of this work has been accomplished by computer. In general, computer calculations are an automation of normal hand calculations. However, in several cases, we have developed programs that would not be done by hand calculations because they involve tedious, iterative computations. This is the case, for example, for computing vapor-liquid equilibria using an equation of state.

B. The Estimation and Correlation of Thermophysical Property Data

The two kinds of thermophysical property data of greatest importance for an engineering analysis of critical-fluid extraction are pure component thermophysical properties for the solvent (carbon dioxide) and phase equilibria data for systems containing the solvent (liquid-liquid and vapor-liquid).

1. Pure Component Thermophysical Data for Carbon Dioxide

Some early calculations showed a strong sensitivity of computed energy inputs based on the accuracy of the thermophysical data. In many cases, calculations for compressor work use enthalpy and entropy values in the superheated region close to the critical point. For carbon dioxide, we have relied upon tables compiled by the Thermodynamic Tables Project of the International Union of Pure and Applied Chemistry (IUPAC).⁽¹⁴⁾

From conversations with representatives of IUPAC, we learned that a mathematical representation of the data over the entire range of temperature and pressure is possible, but would be too complex for routine computer-based calculations. Therefore, tabulated enthalpies and entropies for the vapor or supercritical phase were entered into the computer for temperatures ranging between 280K and 410K (at 10K intervals) and pressures ranging between 5 bar and 80 bar (at 5 bar intervals). A computer program was written to interpolate within the table for the necessary data. Given x and y , the program performs a two-dimensional interpolation for z , where z is a tabulated function of x and y . For example, given temperature and pressure, the enthalpy can be found. The inverse is also possible. Given z and either x or y , it is possible to find the other variable. The interpolations are performed using the method-of-divided-differences. A program for performing compressor calculations calls the tabulated data file and computes compressor work, for both isentropic and irreversible compression cycles. When the results obtained using the computer-based interpolations were compared with results obtained using graphical methods, excellent agreement was obtained.

We have also performed calculations for pure component fugacities and compressibility factors using a cubic equation of state, the Peng-Robinson⁽¹⁵⁾, shown below.

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)}$$

$$a(T) = a(T_c) \cdot \alpha(T_r, \omega)$$

where

$$a(T_c) = 0.45724 R^2 T_c^2 / P_c$$

$$\alpha(T_r, \omega) = [1 + \kappa (1 - T_r^{1/2})]^2$$

$$\kappa = 0.37462 + 1.54226 \omega^2$$

$$\omega = \text{the acentric factor}$$

$$b = 0.07780 R T_c / P_c$$

A comparison of computed and tabulated results is given in Tables IV-1 and IV-2. It shows differences on the order of a few percent in the superheated region, increasing to about ten percent for the liquid phase along the saturation curve. These values were computed in the course of developing a program based on the Peng-Robinson equation to correlate vapor-liquid equilibria data. The interpolation method, being more accurate than the equation of state, was used for all process calculations.

For conditions along the saturation curve, the pressure and properties for both liquid and vapor (density, enthalpy and entropy) were tabulated as a function of temperature for the range between 250K and 304.2K (at 2K intervals) from the IUPAC tables. Given any one of the eight variables, any other variable could be computed by linear interpolation. For selected conditions along the saturation curve, a table of transport properties has been compiled, summarized in Tables IV-3 and IV-4. These properties are useful for fluid flow calculations in the reboiler heat exchanger and sieve-trays of the extractor.

2. Phase Equilibria Calculations

The extraction process is basically a separation process involving both liquid-liquid and vapor-liquid equilibria. Three classes of chemical systems have been investigated: carbon dioxide-water, carbon dioxide-organics, and carbon dioxide-water-organic. The review which follows focuses on each system, with some possible overlap in the presentation of techniques used to correlate and estimate phase equilibria.

TABLE IV-1

COMPARISON OF FUGACITIES AND COMPRESSIBILITY FACTORS
FOR CARBON DIOXIDE: IUPAC DATA VERSUS CALCULATIONS FROM
THE PENG-ROBINSON (PR) EQUATION-OF-STATE

Temperature: 300K

Pressure: 0.1 to 1000 Bar

Pressure bar	State L or G	Z IUPAC	(1) (z/p) IUPAC	Z (2) PR	(z/p) PR	% error ⁽³⁾ (Z)	% error (z/p)
0.10		0.99951	0.99951	0.99954	0.99946	-0.00300	0.00500
0.50	G	0.99754	0.99754	0.99739	0.99732	0.0150	0.0220
1.00	G	0.99506	0.99508	0.99470	0.99465	0.0362	0.0430
5.00	G	0.97501	0.97501	0.97290	0.97337	0.216	0.168
10.0	G	0.94919	0.95124	0.94494	0.94709	0.448	0.436
15.0	G	0.92240	0.92717	0.91610	0.92115	0.683	0.633
20.0	G	0.89452	0.90327	0.88623	0.89552	0.927	0.858
30.0	G	0.83460	0.85588	0.82274	0.84508	1.42	1.23
40.0	G	0.76701	0.80878	0.75235	0.79550	1.91	1.64
50.0	G	0.68676	0.76145	0.67080	0.74636	2.32	1.98
60.0	G	0.57955	0.71285	0.56615	0.69678	2.31	2.25
65.0	G	0.49682	0.68719	0.48971	0.67111	1.43	2.34
67.095	G	0.44115	-	0.43948	0.65996	0.379	-
67.095 ⁽⁴⁾	L	0.17401	-	0.20113	0.65996	-15.6	-
70.0	L	0.17491	0.65220	0.19737	0.63805	-12.8	2.17
75.0	L	0.18030	0.61621	0.19921	0.60370	-9.99	2.03
80.0	L	0.18737	0.58459	0.20418	0.57338	-14.7	1.92
90.0	L	0.20324	0.53171	0.21727	0.52247	-6.90	1.74
100.0	L	0.21999	0.48932	0.23198	0.48147	-5.45	1.60
150.0	L	0.30548	0.36246	0.30985	0.35785	-1.43	1.27
200.0	L	0.38943	0.30026	0.38689	0.29654	0.652	1.24
300.0	L	0.55126	0.24176	0.53491	0.23790	2.97	1.60
400.0	L	0.70662	0.21708	0.67652	0.21221	4.26	2.24
500.0	L	0.85707	0.20665	0.81350	0.20038	5.08	3.03
600.0	L	1.0036	0.20397	0.94696	0.19599	5.67	3.91
800.0	L	1.2876	0.21234	1.2061	0.20005	6.33	5.79
1000.0	L	1.5622	0.23322	1.4578	0.21524	6.68	7.71

Notes: (1) IUPAC Values from Reference 14

(2) PR values from Peng-Robinson Program

(3) % Error = $\frac{(\text{IUPAC Value} - \text{Peng Robinson Value})}{\text{IUPAC Value}} \times 100$

(4) $P_{\text{SAT}}^{\text{CO}_2@300^\circ\text{K}} = 67.095 \text{ bar}$

TABLE IV-2

Fugacities and Compressibilities of
Saturated Liquid and Vapor of CO₂
(P = 6-70 bar, T = 219.28-301.93 K)

Pressure bar	Temp. K	IUPAC Data:			Peng-Robinson Values:			% Error:		
		Z _{Liq.}	Z _{Vap.}	($\bar{f}/p$)	Z _{Liq.}	Z _{Vap.}	($\bar{f}/p$)	Z _{Liq.}	Z _{Vap.}	($\bar{f}/p$)
6	219.28	0.01237	0.91068	0.91843	0.01187	0.91577	0.88848	4.04	-0.559	3.26
10	233.08	0.02032	0.87344	0.88836	0.01959	0.87787	0.89026	3.59	-0.507	-0.214
15	244.73	0.03034	0.83255	0.85775	0.02949	0.83497	0.85701	2.80	-0.289	0.0863
20	253.77	0.04057	0.79512	0.83184	0.03980	0.79559	0.82870	1.90	-0.0591	0.377
40	278.59	0.08521	0.65813	0.75297	0.08779	0.65297	0.74310	-3.03	0.784	1.31
60	295.25	0.14374	0.51069	0.69438	0.15975	0.50675	0.68044	-11.1	0.772	2.01
70	301.93	0.19261	0.40490	0.66884	0.22832	0.40856	0.65295	-18.8	-0.904	2.38

TABLE IV-3

PROPERTIES OF SATURATED CARBON DIOXIDE VAPOR

	Temperature; °C (K)					Notes
	10 (283)	15 (288)	20 (293)	25 (298)	30 (303)	
saturation pressure, bar	44.849	50.665	57.075	64.090	71.830	(1)
atmospheres	44.263	50.002	56.329	63.253	70.891	
molar volume, cm ³ /mol	327.77	275.64	228.31	182.86	130.30	(1)
density, g/cm ³	0.1343	0.1597	0.1926	0.2407	0.3378	(2)
enthalpy, J/mol	31913	31647	31264	30681	29456	(1)
entropy, J/mol·K	171.72	170.18	168.32	165.86	161.39	(1)
heat capacity (C _p), J/mol·K	110	133	169	364	804	(3)
dynamic viscosity, cP	0.01800	0.01900	0.02020	0.02190	0.02600	(4)
kinematic viscosity, m ² /s	13.403	11.897	10.477	9.098	7.697	(5)
thermal conductivity, w/m·K	-	-	0.02847	0.03236	0.03818	(6)
thermal diffusivity, m ² /s	-	-	-	-	-	
Prandtl number	-	-	2.725	5.598	12.441	(8)

TABLE IV-4

PROPERTIES OF SATURATED CARBON DIOXIDE LIQUID

	Temperature, °C (K)					Notes
	10 (283)	15 (288)	20 (293)	25 (298)	30 (303)	
saturation pressure, bar	44.849	50.665	57.075	64.090	71.830	(1)
atmospheres	44.263	50.002	56.329	63.253	70.891	
molar volume, cm ³ /mol	51.013	53.460	56.756	61.561	73.123	(1)
density, g/cm ³	0.8627	0.8232	0.7754	0.7137	0.6018	(2)
enthalpy, J/mol	23213	23837	24534	25359	26637	(1)
entropy, J/mol·K	140.97	143.06	145.35	148.00	152.09	(1)
heat capacity (C _p), J/mol·K	132	149	173	305	609	(3)
dynamic viscosity, cP	0.08135	0.07210	0.06330	0.05410	0.04300	(4)
kinematic viscosity, m ² /s, x10 ⁻⁸	9.430	8.759	8.164	7.580	7.145	(5)
thermal conductivity, W/m·K	-	-	0.08583	0.08164	0.06406	(6)
thermal diffusivity, m ² /s, x10 ⁻⁷	0.3608	-	0.2219	-	0.0279	(7)
Prandtl number	-	-	2.899	4.593	9.289	(8)

NOTES FOR TABLES IV-3 AND IV-4

Carbon Dioxide

molecular weight	44.009 g/mole
critical temperature	304.21 K (31.06°C, 87.91°F)
critical pressure	73.825 bar (72.860 atm, 1070.7 psia)
critical density	0.01059 mol/cm ³ (0.46606 g/cm ³ , 29.095 lb/ft ³)
boiling point at 1 atmosphere	194.7 K (-78.45°C, -109.21°F)

- (1) Carbon Dioxide, International Thermodynamic Tables of the Fluid State - Volume 3 (I.U.P.A.C.).
Temperatures in Carbon Dioxide are Kelvins, and are tabulated for even numbers. The value tabulated here is obtained by a linear interpolation of the Carbon Dioxide value. For example, the saturation pressure at 20°C (293 K) is obtained by interpolating the values at 292 K and 294 K.
Pressure in bar x 0.986723 = Pressure in atmospheres.

- (2) Density is computed from the molar volume, using 44.009 g/mol as the molecular weight of carbon dioxide.

$$\frac{\text{molecular weight (g/mol)}}{\text{molar volume (cm}^3\text{/mole)}} = \text{density (g/mol)}$$

$$\frac{1 \text{ g}}{\text{cm}^3} = 10^3 \frac{\text{kg}}{\text{m}^3}$$

- (3) Heat capacities are taken at the following saturation pressures

P, bar	T, K	T, °C	
		Tables V-3 & V-4	Actual IUPAC Value of T
45	283.27	10	10.12
50	287.57	15	14.42
55	291.55	20	18.40
65	298.71	25	25.56
70	301.93	30	28.78

- (4) Vukalovich and Altunin, Thermophysical Properties of Carbon Dioxide, p. 422.

$$1 \text{ cP} = 10^{-2} \frac{\text{g}}{\text{cms}} = 10^{-3} \text{ Kg/ms}$$

NOTES FOR TABLES IV-3 AND IV-4
(continued)

- (5) Kinematic viscosity = dynamic viscosity/density.
(6) Reference in (4), page 437.

<u>T</u>	<u>Thermal Conductivity, 10⁻⁴ cal/cm·s·K</u>	
	<u>liquid</u>	<u>vapor</u>
20	2.050	0.680
25	1.950	0.773
30	1.530	0.912

$$\text{Conversion is } 10^{-4} \frac{\text{cal}}{\text{cm} \cdot \text{s} \cdot \text{K}} \times \frac{4.1868 \text{ J}}{\text{cal}} \times \frac{\text{W}}{\text{J/s}} \times \frac{100 \text{ cm}}{\text{m}}$$

- (7) Eckert and Drake, Analysis of Heat and Mass Transfer, page 777.
Note that these values are taken from B. Koch, Grundlagen des Wärmeaustausches (1950). While this reference contains nearly all the properties tabulated here, more recent sources have been used instead of Eckert and Drake.
Only the thermal diffusivity data come from Eckert and Drake.

- (8) Prandtl number = $\frac{\text{dynamic viscosity} \times \text{heat capacity}}{\text{thermal conductivity}}$

at 20°C

$$\text{PR} = \frac{6.33 \times 10^{-5} \frac{\text{kg}}{\text{m} \cdot \text{s}} \times 173 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times \frac{1 \text{ mol}}{44.009 \text{ g}} \times 10^3 \frac{\text{g}}{\text{kg}}}{0.08583 \frac{\text{W}}{\text{m} \cdot \text{K}}}$$

a. Carbon Dioxide-Water

In the extraction of organics from water, the purity of the extract and the amount of carbon dioxide lost in the raffinate are functions of the binary solubility of the two components. The data compiled by H. J. Greenwood and H. L. Barnes⁽¹⁶⁾ in Table IV-5 give the equilibrium phase compositions for carbon dioxide and water over a wide range of temperatures and pressures. It is possible to correlate the solubility of carbon dioxide in water with pressure using the Krichevsky-Kasarnovsky equation (see Reference 17 for an example based to the solubility of nitrogen in water). A satisfactory correlation was not obtained for the solubility of water in carbon dioxide using the same equation.

For process calculations, we developed an empirical expression for the solubility of water in carbon dioxide that takes into account the temperature dependency and the enhancement due to organic dissolved in the carbon dioxide. This expression is based on limited literature data and experimental data taken in our laboratory. It is a four constant expression, as shown in Figure IV-1, using two constants to correlate the temperature effect and two more to correct for the presence of a third component.

In the course of performing extractions at temperatures below ambient, an ice-like material was observed, which was identified as a carbon dioxide-water gas hydrate. To support the laboratory experimental program, and as an aid in evaluating process flowsheets, we compiled literature data to construct a phase diagram. Using published data for water, carbon dioxide, and the carbon dioxide-water hydrate, we identified the conditions of temperature and pressure at which the various phases were expected to be present. The phase diagram is shown in Figure IV-2.

Data for the gas hydrate curve between points 'B' and 'D' are given in Bozzo, Chen, Kass and Barduhn.⁽²⁰⁾ The high pressure dissociation curve has been investigated by Takenouchi and Kennedy.⁽²¹⁾ The dissociation curve below 200K has been reported by Miller and Smythe.⁽²²⁾ An equation for the freezing point depression of the gas hydrate in salt solutions is given by Bozzo, et al.⁽²⁰⁾

Also of interest is the effect of pH resulting from the solubility of carbon dioxide in water on the dissociation of weak acids and the possible formation of insoluble carbonates. In general, liquid carbon dioxide will not extract ionic species from water. Therefore, in the case of extracting a weak acid, such as acetic acid, it is the concentration of the undissociated species that should be used when computing the distribution of the component between the aqueous and solvent phases. We have computed the extent of dissociation for acetic acid in both buffered and unbuffered solutions, where the solution was saturated with carbon dioxide at high pressure. In unbuffered solutions, the hydrogen ion from the dissociation of carbonic acid shifts the acetic acid equilibria such that only 1 or 2 percent of the initial acetic acid is present as acetate ions. When sodium acetate is added to buffer the solution, dissociation is on the order of 20 percent if the concentrations of acetic acid and sodium acetate are each greater than 0.01 molar.

TABLE IV-5
H₂O-CO₂ TWO-PHASE REGION

P(bars)	12°C	25°C	50°C	75°C	100°C	150°C	200°C	250°C	300°C	330°C
25	.. 25.5	1.64 15.2	6.20 7.40	10.61 5.25	(77) 4.29	(200) ..	675 1.52			
50	.. 27.8	1.29 21.4	3.83 13.3	9.57 9.80	(52) 8.11	(140) (7)	410 5.50	807 2.4		
75	.. 28.4	2.30 24.4	3.49 17.8	8.85 13.38	(37) 11.34	(112) (10)	282 9.10	615 6.1		
100	.. 28.8	3.31 24.9	4.48 19.79	8.29 16.21	(27) 13.90	(93) (13)	211 12.3	535 10.7	890 3.8	
125	.. 29.4	3.46 25.4	5.38 21.07	8.51 18.07	(25) 16.2	(78) (16)	173 15.8	480 14.9	783 9.8	
150	.. 29.9	3.59 25.8	6.05 21.74	9.46 19.30	(25) 17.80	(72) (18)	162 18.9	435 19.2	718 15.8	930 8.6
200	.. 30.9	3.76 26.7	6.75 22.85	11.20 20.91	(22) 20.02	(64) (22)	155 24.7	358 27.8	625 27.8	830 25.6
250	.. 31.4	3.90 27.6	7.03 23.75	12.00 22.15	(22) 21.8	(62) (24.6)	157 29.3	328 36.8	563 41.3	745 43.8
300	.. 31.7	3.96 28.4	7.25 24.55	12.50 23.11	(22) 23.11	(63) (27)	158 33.1	318 44.0	538 55.0	715 62.8
350	.. 32.1	4.01 29.2	7.43 25.30	12.87 23.75	(23) 24.22	(65) (28.2)	162 36.4	315 50.6	538 69.4	725 (85)
400	.. (32.3)	4.01 30.1	7.56 26.05	13.16 24.52	(23) 25.30	(70) (30)	164 39.0	316 55.7	550 82.0	(755) (115)
500	..	3.98 (31.6)	7.76 27.32	13.57 26.0	(26) 27.0	(80) (32.6)	172 44.4	323 66.7	598 (145)	
600			7.88 28.60	13.89 27.6	(30) 28.5	(90) ..	183 (46)	(340) (73)	(725)* (275)*	
700			8.01 29.87	14.00 29.19	(35) 29.88	(102) ..	(202) (48)	.. (81)		

* On critical curve $x_{CO_2}^V = x_{CO_2}^L$

Compositions of co-existing phases at each pressure and temperature are given as paired values: x_{H_2O} in CO₂-rich phase ($\times 10^3$) and x_{CO_2} in H₂O-rich phase ($\times 10^3$).

FIGURE IV-1

SOLUBILITY OF WATER IN LIQUID CARBON DIOXIDE

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FIGURE IV-2

KEY FOR PHASE DIAGRAM

G = carbon dioxide Gas
L = carbon dioxide Liquid
S = carbon dioxide Solid
V = water Vapor
W = Water (liquid)
I = water, Ice
H = gas Hydrate

POINTS ON THE PHASE DIAGRAM

<u>Designation</u>	<u>Type</u>	<u>T, K</u>	<u>P, bar</u>
A	critical point pure CO ₂	304.21	73.825
B	quadruple point G-L-W-H	283.2	44.99
C	triple point CO ₂	216.58	5.185
D	quadruple point G-I-W-H	271.67	10.62
E	triple point	273.22	0.00613

SOME PROPERTIES OF THE CO₂/H₂O GAS HYDRATE

Formula CO₂ . 5.75H₂O
Density 1.14g/cm³
Heat of dissociation 15kcal/gmole
CO₂ . 5.75H₂O(s) → CO₂(g) + 5.75H₂O(l)

The possible formation of insoluble carbonate salts has also been considered. Many industrial water supplies contain alkaline ions that contribute to hardness (calcium and magnesium ions), and these might form insoluble carbonates in aqueous solutions pressurized with carbon dioxide. On the basis of literature data for the solubility products of these salts, and reported solubilities in solutions saturated with carbon dioxide, precipitate formation is unlikely if the concentration of the alkaline metal ions is less than 1000 ppm. For example, Table IV-6 shows the solubility of a crystalline form of calcium carbonate, calcite, in carbonic acid as a function of temperature and pressure. As can be seen in the table, the solubility of calcium carbonate at high pressures is greater than 1000 ppm. By comparison, water is considered to be very hard if it contains more than 181 ppm of calcium carbonate.⁽¹⁸⁾ These theoretical calculations are in agreement with experience gained in laboratory experiments.

b. Carbon Dioxide-Organic

Solubilities of organics in liquid carbon dioxide have been published in the literature, in particular, by A. W. Francis^(4,23) These data and our own laboratory observations show that all of the oxygenated hydrocarbons of interest to us are completely miscible with liquid carbon dioxide over the range of conditions encountered in the process. Therefore, for binary mixtures of carbon dioxide and oxygenated hydrocarbons, we are only interested in vapor-liquid equilibria. This information is of particular value in designing the distillation unit and flash vessel, where carbon dioxide is recovered from the organic product. It has been assumed that the carbon dioxide/organic mixtures could be modeled as binaries.

Vapor-liquid equilibria data are used in several ways. First, using the data in a McCabe-Thiele-type of construction, the number of stages in the solvent-solute distillation column can be computed. At the present time, the equilibria data are reduced to a single relative volatility, from which the equilibrium curve is computed. The boiling point elevation can be determined from either an isobaric temperature-composition plot or several isothermal pressure-composition plots. The boiling point elevation is an important parameter for estimating the energy requirement of the vapor recompression distillation unit, as described in Section C below. Finally, the solubility of carbon dioxide in liquid organics must be determined in order to design the flash units used to recover the solvent. Calculations involving the carbon dioxide solubility are made using Henry's law, where the partial pressure of carbon dioxide is equal to Henry's law constant times the mole fraction of carbon dioxide in the liquid phase.

The available vapor-liquid equilibria data were correlated using the Peng-Robinson version of the Redlich-Kwong cubic equation of state. Once the parameters are known for the equation of state, equilibria at other conditions can be computed. The Peng-Robinson equation expresses the pressure as a function of temperature, molar volume, and three pure-component parameters (critical temperature, critical pressure, and Pitzer's acentric factor). The equation also uses five numerical constants. The three constants in the expression for the acentric factor were obtained using vapor pressure data for thirteen substances frequently found in natural gas. These include light hydrocarbons, carbon dioxide, hydrogen sulfide, and nitrogen; they do not include water. The two remaining constants appearing in the expressions for "a" and "b" (Section B) are found in the usual manner for cubic equations of state; that is, by evaluating derivatives at the critical point. By in-

TABLE IV-6

SOLUBILITY (in gm/l) OF OPTICAL CALCITE IN WATER
AS A FUNCTION OF TEMPERATURE AND PRESSURE OF CO₂

Temperature (°C)	Pressure (bars)				
	1	10	20	50	100
20	.92	1.88	2.33		
40	.54	1.39	1.73	2.23	2.51
60	.35	.97	1.22	1.56	1.80
80	.26	.67	.82	1.08	1.24
100	.20	.52	.61	.77	.88

Reference: S. P. Clark, "Solubility", Section 19 in
Handbook of Physical Constants, Page 422.

incorporating the acentric factor and reduced temperature into "a", with the particular form used, the equation predicts liquid phase densities as well as or better than other cubic equations (such as the Soave-Redlich-Kwong). This then is the primary reason for using the Peng-Robinson equation. It is semi-empirical, but has been shown to be particularly reliable for dense phases.

When multicomponent mixtures are involved, the "a" and "b" parameters representing the mixture must be obtained from the pure component parameters. These additional equations are frequently called "mixing rules". Peng and Robinson⁽¹⁵⁾ suggest using a simple mole fraction-weighted expression for the "b" parameter,

$$b = \sum_i x_i b_i$$

For the "a" parameter, the average is found as the geometric mean,

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} (1 - \delta_{ij})$$

where δ_{ij} is an empirically determined binary interaction parameter characterizing the binary formed by components i and j. Note that only one adjustable parameter per binary is used to describe a multicomponent mixture.

The equation-of-state is then expressed in terms of the compressibility factor. It is a cubic expression, having at least two real roots for vapor-liquid equilibria. One root corresponds to the compressibility of the vapor phase, another root to the liquid phase, and the third root (if it exists) to some other situation of no relevance here. This then is the reason for using a cubic equation-of-state rather than a more complex one. The cubic equation can be solved analytically to determine all the possible roots and to identify the largest and smallest roots. Given the compressibility factors for the two phases, it is then possible to compute the fugacities for all components in each phase.

The Peng-Robinson equation was developed, and has been successful, in correlating phase equilibria data for non-polar hydrocarbon mixtures. Although the equation has been used for mixtures containing polar components, the agreement between prediction and experiment is less satisfactory than for non-polar mixtures. Whether for polar or non-polar mixtures, the dense phase properties are predicted less accurately than for the lighter phase. It is possible to use the Peng-Robinson equation for the vapor phase, and to compute the fugacities of components in the liquid phase using activity coefficients. We have avoided activity coefficients because of the difficulty in defining a suitable reference state for a supercritical component.

In theory, the binary interaction parameter is a measure of the degree of interaction between unlike molecules and should be a function only of the chemical species and not the temperature, pressure or concentration. However, we know of no way to predict theoretically what the interaction parameter should be for a given binary pair. Therefore, it has to be found from experimental data. It is an adjustable parameter used to obtain agreement between measured and computed equilibria. When only one equilibrium data point is available, the parameter is mathematically unique. When more data are available, a statistical method must be used to select the parameter that gives the best agreement between computed and experimental results. One could compute an interaction parameter for each data point, then take the arithmetic average. We have modified programs published by Prausnitz⁽²⁴⁾ to perform a more sophisticated statistical calculation called the "maximum likelihood estimation".

There are two possible explanations for poor agreement between computed and experimental values. The first is that the computed results are in error because the equation-of-state is not able to model a system containing interacting species (for example, polar molecules like ethanol and quadrupolar molecules like carbon dioxide). These interactions are accounted for using the binary interaction parameter. Small changes in this parameter may have a profound effect on the computed results. The second explanation for disagreement between computed and experimental values is that the experimental data are in error. For the system ethanol-carbon dioxide, data reported by Buchner⁽²⁵⁾ are in apparent disagreement with data reported by Snedeker⁽²⁶⁾ for methanol-carbon dioxide and n-propanol-carbon dioxide. Table IV-7 lists binary interaction parameters we have computed.

c. Carbon Dioxide-Organic-Water

A. W. Francis⁽⁴⁾ experimentally determined several hundred ternary systems in which one component was liquid carbon dioxide. Of those systems, a number were for systems also containing water and an oxygenated hydrocarbon. Francis experimentally determined the binodal (or solubility) curve from the densities of the phases present. The densities were determined by comparison with glass spheres of known density in his high pressure sight gauge. The tie-lines joining phases in equilibrium were not actually measured, but were included to indicate the probable distribution between phases. In addition, the ternary diagrams were not prepared at constant pressure. The sight gauge was maintained at constant temperature and contained three components. Apparently, there was a vapor phase in equilibrium with the two liquid phases for many of the measured systems. According to the phase rule, there must be two degrees of freedom for a three-component system with three phases in equilibrium. With temperature fixed, the equilibrium compositions can vary only if the pressure is not fixed.

Published ternary diagrams⁽⁴⁾ were copied and enlarged, using graphical techniques and known binary solubilities for carbon dioxide and water to insure consistency. Several of those ternary diagrams are shown in Figures IV-3a through d. According to the most common classification scheme for ternary systems, they may be grouped according to the number of immiscible binary pairs in the system. Type I systems contain only a single immiscible

TABLE IV-7

BINARY INTERACTION PARAMETERS FOR THE
 PENG-ROBINSON EQUATION OF STATE --
 ALKANOLS + CARBON DIOXIDE

<u>Alkanol</u>	<u>δ_{ij}</u>	<u>T, K</u>	<u>P, bar</u>	<u>Data Reference</u>
methanol	0.058	298.15	7.9-59.6	(27)
	0.060	313.15	5.8-80.6	(27)
	0.062	292.0-475.0	50.68	(26)
	0.056	298.15	1.0	(29)
ethanol	0.11	290.0-450.0	50.62	(25)
	0.085	298.15	1.0	(28)
1-propanol	0.125	289.0-400.0	50.68	(26)
2-methyl-1-propanol (isobutanol)	0.150	298.15	1.0	(29)

FIGURE IV-3a

TERNARY DIAGRAM FOR METHANOL-WATER-CARBON DIOXIDE

FIGURE IV-3b

TERNARY DIAGRAM FOR ETHANOL-WATER-CARBON DIOXIDE

FIGURE IV-3c

TERNARY DIAGRAM FOR 2-PROPANOL-WATER-CARBON DIOXIDE

FIGURE IV-3d

TERNARY DIAGRAM FOR 2-BUTANOL-WATER-CARBON DIOXIDE

binary. The ternary systems for methanol-water-carbon dioxide, ethanol-water-carbon dioxide, and propanol-water-carbon dioxide are all of this form. The distributed component (alcohol) is completely miscible with each of the other two components (alcohol-water and alcohol-carbon dioxide). Type II systems contain two immiscible binary pairs. The ternary systems for butanol-water-carbon dioxide are of this type, because there is a miscibility gap for mixtures of butanol with water as well as for carbon dioxide and water. Butanol is completely miscible with carbon dioxide. The ternary diagrams for the series of lower alcohols form a family, beginning with the comparatively shallow binodal curve for methanol and extending to the Type II system for butanol.

Within a single Type I ternary diagram, the tie-lines joining phases with equilibrium compositions are coincident with the immiscible binary pair at one extreme, and collapse to a single point (plait point) on the binodal curve at the other extreme. Type II systems do not have a plait point; the tie-lines coincide with the immiscible binary pairs at either extreme. It then moves toward the water-rich corner, still on the binodal curve, progressing from methanol to propanol. An imaginary plait point occurs outside the ternary in the case of the Type II butanol system.

The slope of the tie-line is related to the distribution coefficient. When the distributed component is at infinite dilution, the slope of the tie-lines approaches a limiting value of the distribution coefficient. This value is the same as the ratio of the activity coefficients for the distributed component in the two phases. Schultz and Randall⁽⁷⁾ compared the limiting values of these distribution coefficients for the series of alcohols, and found them to be correlated well when the logarithm of the distribution coefficient was plotted versus the number of carbon atoms in the molecule. The good correlation obtained by Schultz and Randall is consistent with recent developments in solution thermodynamics where activity coefficients are estimated from group contributions. However, it is in general not possible to correlate the activity coefficients at high concentrations using the same method.

If one has a few distribution coefficients, or the compositions at the ends of the tie-lines, an empirical correlation procedure may be used. One such correlation is known as the "Hand" plot.⁽³⁰⁾ A correlation for the isopropanol-water-carbon dioxide ternary with data from Francis⁽⁴⁾ is shown in Figure IV-4.

Other recent studies (31, 32, 33) of the ethanol-water-carbon dioxide system by M. Paulaitis et al, M. A. McHugh, et al, and M. S. Kuk and J. C. Montagna give results which are consistent with the results published by Francis.⁽⁴⁾

FIGURE IV-4

"HAND" PLOT FOR THE SYSTEM 2-PROPANOL-WATER-CARBON DIOXIDE

The compositions of equilibrium phases, where organic is distributed between a water-rich phase and a carbon dioxide-rich phase, are found using a distribution coefficient and mutual solubilities. That is, the concentration of organic in each phase is found using,

$$\text{distribution coefficient} = \frac{(\text{moles organic/moles CO}_2)_{\text{CO}_2\text{-rich}}}{(\text{moles organic/moles H}_2\text{O})_{\text{H}_2\text{O-rich}}}$$

When the two phases are primarily carbon dioxide and water, the distribution coefficient is equal to the K-value (defined as the ratio of mole fractions). The amount of water in the carbon dioxide-rich phase is found using a solubility relationship. Similarly, the amount of carbon dioxide in water is found from solubility data. For dilute solutions, the mutual solubilities should be affected only moderately by the amount of organic present. Also, the distribution coefficient used is independent of composition. Therefore, the material balances for processes using dilute organic solutions can be computed if the distribution coefficients can be determined. The distribution coefficients used in the engineering analysis are based on the Francis ternary diagrams,⁽⁴⁾ the Schultz and Randall correlation⁽⁷⁾ and laboratory data.

C. Material and Energy Balances for Process Flowsheets

1. Process Description

A process flowsheet for the extraction of ethanol from water is shown in Figure IV-5, along with the associated material and energy balances (Tables IV-8 and IV-9).

Ethanol, at a concentration of 10 weight percent is fed into a liquid-liquid, counter-current extraction column (EX) where liquid carbon dioxide is the solvent. The extract from the column consists of the solvent, 95% of the ethanol in the feed, and water soluble in liquid carbon dioxide. This mixture enters the three-phase flash vessel (F1) operating at the same pressure as the distillation column (ST). As carbon dioxide is vaporized, the water that had been dissolved in the liquid carbon dioxide splits to form a water-rich phase. The three phases are water-rich liquid, carbon dioxide-rich liquid and carbon dioxide-rich vapor. In most cases, about 20% of the carbon dioxide in the extract is vaporized. The two carbon dioxide-rich phases enter the still as feed. This acts primarily as a stripper, removing carbon dioxide from the ethanol product. The distillate is nearly pure carbon dioxide, and is recompressed (C1) to a pressure near that of the extractor. The compression work raises the temperature of the compressor discharge to the point that it is warmer than the boiling point of the still bottoms. Heat is exchanged between the compressor discharge and the still bottoms (RB), cooling and condensing the solvent return and providing boilup in the still. The still bottoms contain the product ethanol. Both the still bottoms and raffinate are flashed, first to 30 atmospheres then to 1 atmosphere, to recover carbon dioxide. The carbon dioxide is recompressed, condensed, and returned to the extractor.

The process is similar to conventional liquid-liquid extraction processes, with the most significant difference being that it operates at pressures high enough to be above the saturation pressure of the working solvent. The organic is separated from water in the extractor by partitioning the organic between the aqueous and solvent phases. The distribution of the organic is the result of different solute-solvent interaction energies for the organic solute in each of the two liquid phases. In the ideal case, the two liquid phases are completely immiscible. In practice, there is a small mutual solubility, as has been previously discussed for carbon dioxide and water. As long as the distribution of the organic between the two phases results in a solvent-free extract with a composition different from the initial aqueous phase, it is possible to separate the organic from water. However, the process appears most favorable when the organic distributes preferentially in the solvent phase.

Following the extraction process, the organic must be separated from the solvent. This is performed by a simple distillation, in which the solvent is the more volatile component. Whereas the separation in the extractor

FIGURE IV-5

PROCESS FLOW SHEET

LEGEND FOR FIGURE IV-5

<u>Unit</u>	<u>Description</u>
EX	counter-current liquid-liquid extractor
ST	distillation column
F1	three-phase flash vessel
F2	still bottoms flash to 30 atm
F3	raffinate flash to 30 atm
F4	product flash to 1 atm
F5	product flash to 1 atm
C1	main vapor recompression compressor
C2	flash vapor recompression from 30 atm
C3	flash vapor recompression from 1 atm
M1 to M6	mixing points
RB	reboiler heat exchanger
HX1	cooler for C2 discharge
HX2	cooler for C3 discharge
HX3	trim heat exchanger for the process

TABLE IV-8

MATERIAL BALANCE FOR ETHANOL EXTRACTION FROM WATER

STREAM	TEMPERATURE K	PRESSURE Bar	Ethanol	FLOW RATES, lb-mole/hr.	
				Water	Carbon Dioxide
1	299.1	66.9	178.6	4112.	0.0
2	299.1	66.9	175.0	77.6	19260.
3	290.1	53.3	5.058	1.810	4842.
4	290.1	53.3	168.4	42.60	14420.
5	290.1	53.3	1.553	33.23	0.7217
6	290.1	53.3	173.5	44.41	19260.
7	290.1	53.3	0.0	0.0	0.0
8	290.1	53.3	19.95	7.138	19070.
9	307.5	66.9	19.95	7.138	19070.
10	299.9	66.9	19.95	7.138	19070.
11	293.1	53.3	0.0	0.0	15240.
12	293.1	53.3	0.0	0.0	15240.
13	293.1	53.3	153.5	37.27	190.8
14	298.1	30.4	0.4338	0.1646	155.1
15	298.1	30.4	153.1	37.10	35.69
16	298.1	30.4	0.1322	0.05018	47.29
17	298.1	30.4	8.800	4036.	53.46
18	299.1	66.9	8.932	4036.	100.7
19	298.1	30.4	0.5660	0.2148	202.4
20	337.5	66.9	0.5660	0.2148	202.4
21	309.1	66.9	0.5660	0.2148	202.4
22	298.1	1.0	3.038	1.209	34.71
23	298.1	1.0	4.459	1.775	50.95
24	298.1	1.0	150.1	35.89	0.9814
25	298.1	1.0	4.341	4034.	2.511
26	298.1	1.0	7.497	2.984	85.66
27	401.7	66.9	7.497	2.984	85.66
28	309.1	66.9	7.497	2.984	85.66
29	303.1	1.0	0.0	76.74	0.0
30	320.0	1.0	0.0	76.74	0.0
31	303.1	1.0	0.0	91.78	0.0
32	320.0	1.0	0.0	91.78	0.0
33	309.1	66.9	8.063	3.199	288.1
34	299.9	66.9	28.01	10.34	19360.
35	299.1	66.9	28.01	10.34	19360.
36	299.1	66.9	28.01	10.34	19360.
37	299.1	66.9	5.339	1.915	19360.

TABLE IV-9

ENERGY BALANCE FOR ETHANOL EXTRACTION
FROM WATER, in kilowatts

Compressor C1	1064
Compressor C2, 2 stage	54.88
Compressor C3, 4 stage	158.1
Heat exchanger HX1	-59.93
Heat exchanger HX2	-71.67
Heat exchanger HX3	-1497
Flash vessel F2	191.8
Flash vessel F3	49.77
Flash vessel F4	44.55
Flash vessel F5	65.39

NOTES

Power ratings for compressors are for shaft work including gas and compressor efficiencies, but do not include motor drives.

Enthalpies in flash vessels based on the enthalpy of evaporation of pure carbon dioxide. If the enthalpy is provided by a side-stream from a compressor, it will reduce the duty on the heat exchangers.

was based on chemical properties (solubilities and solute-solvent interactions), the separation in the distillation unit is based on physical properties (volatilities and densities).

The distillation unit must always operate at a pressure that is less than the critical pressure of the solvent, taken overhead as the distillate. Above the critical point only one phase exists, hence a separation based on differences in vapor and liquid properties is not possible. The distillate from the still is compressed using a mechanical compressor. The compression process raises the temperature of the distillate stream. If the compression ratio is large enough, the compressed distillate will be at a temperature greater than the temperature of the still bottoms. Heat may then be exchanged between the cooling distillate and the boiling still bottoms. If the distillate is at a pressure above its saturation pressure at the lowest temperature in the condenser, the vapor will condense. Liquefied solvent is then returned to the extractor.

The distillation unit may be at a pressure greater than, equal to, or less than the extractor. In general, the process operates with the distillation unit at a pressure less than the extractor. As a result, the liquid extract from the extractor is reduced in pressure by flashing across a valve before entering the still. The compressor discharge pressure is then set equal to the extractor pressure. Because the solvent most commonly considered for this process is carbon dioxide, which has a critical temperature of 31°C , the extractor is operated near ambient conditions and the distillation unit is operated at lower temperatures.

The operating conditions for the still can be selected by working back from the extractor, keeping in mind the allowable temperature approaches in the reboiler/condenser. Starting at the extractor, it is known that the solvent returning to the extractor must be a liquid at a temperature corresponding to the extractor pressure. Next, there must be a temperature difference between the condensing side of the reboiler and the evaporation side for heat flow to occur. A minimum temperature approach, at the cold end, of 6°C was specified. This stems from the general observation that a hot surface must be several degrees warmer than the liquid boiling at its surface, if nucleate boiling is to take place. If the temperature difference is too small, heat transfer will be by free convective boiling, and if too large, by film boiling. The nucleate boiling regime corresponds to a higher heat transfer coefficient than either of the two other regimes. It has been noted in the literature that the temperature driving force for nucleate boiling decreases as pressure increases. 6°C is a conservative estimate, with the possibility that the actual value may be only 2 or 3 degrees.

With the temperature of the still bottoms established, the temperature of the distillate can be determined. The distillate temperature will be less than the bottoms temperature, because the distillate is nearly pure carbon

dioxide and the bottoms are a mixture of organic and carbon dioxide. If the distillate is pure carbon dioxide, the difference is the boiling point elevation. It was assumed that the still is isobaric, and that the pressure is the saturation pressure of the distillate at the temperature computed as above. Having specified the still pressure, the amount of still feed that is vaporized can be computed, and the compression ratio of the vapor recompressor is also determined.

The vapor recompressor is essentially a heat pump. The distillate is compressed from one temperature and pressure, to a higher temperature and pressure. Heat is then allowed to flow back to the lower temperature. The process is similar to a Carnot cycle, and can be graphically represented as shown in Figure IV-6. The high temperature reservoir is the condenser side of the reboiler. The low temperature side is the distillate; physically, heat flows from the condenser to the evaporation side of the reboiler, then this heat flows from the hot still bottoms to the cooler still distillate.

As shown in Figure IV-5, all of the energy input to the process is mechanical work. In the overall process, heat must be removed at a rate equal to the work input, minus the difference between the outlet and inlet enthalpies of the various streams. Within the process, the heat flows across the reboiler are much greater than the net power input. Figure IV-6 is a thermodynamic representation, very similar to a refrigeration cycle using carbon dioxide as the refrigerant. The coefficient-of-performance for this cycle is given by:

$$\text{COP} = \frac{Q}{W} = \frac{T_{\text{cold}}}{T_{\text{hot}} - T_{\text{cold}}}$$

The hot reservoir operates near 300K, and the cold reservoir at 290K for our process. Therefore, the theoretical coefficient-of-performance is on the order of 29. As noted before, the difference between the hot and cold reservoirs (condenser and reboiler) is the sum of the allowable temperature approach in the reboiler (6K) and the boiling point elevation. The strong dependence of the heat pump efficiency upon the boiling properties of the organic/carbon dioxide mixtures can be seen in the equation.

Some general conclusions can be drawn about the performance of the process from the description just given. First, the three major equipment components are the extractor, reboiler/condenser and vapor compressor. Secondly, the sizes for these components are proportional to the solvent flow rate. That is, the extractor capacity, the heat transfer area, and the vapor compressor capacity are all related to the amount of solvent that must be handled. The amount of solvent is determined primarily by the total feed to the extractor and the distribution coefficient for the organic. Thirdly, the amount of energy put into the process is a function of both the solvent flow rate and the pressure ratio of the vapor compressor. As described above, once the allowable approach for the heat exchanger is set, the various pressures are found from the boiling point elevation.

FIGURE IV-6

APPROXIMATE REPRESENTATION OF THE EXTRACTION PROCESS ON A T-S DIAGRAM

These conclusions can provide guidelines for a "first cut" evaluation of the feasibility of the process for different separations. Since the solvent flow is based on the total feed to the extractor, the amount of solvent handled per pound of organic will be much greater for a dilute aqueous stream than for a more concentrated one. For example, if one wishes to produce 10 million gallons of alcohol product per year, almost twice as much solvent will be required with a 5-mole percent aqueous feed than with a 10-mole percent aqueous feed. A process that may not be attractive at low concentrations of organic in water may become very attractive at higher concentrations. Similarly, for a fixed feed composition, doubling the distribution coefficient will roughly halve the solvent requirement.

Some additional considerations should also be noted. The raffinate from the extractor is primarily water, with several weight percent of dissolved carbon dioxide. Depending upon how the still is to be operated, the bottoms contain 50 to 90-mole percent of carbon dioxide.

The cost to recover carbon dioxide from the raffinate and still bottoms consists of the energy cost to recompress the carbon dioxide, the capital costs for the compressor, and costs associated with cooling and condensing the compressed gas. The cost to replace this lost carbon dioxide by purchasing liquid carbon dioxide consists of the same three costs, plus the cost of make-up solvent. The energy cost to recover carbon dioxide is less than 1¢ per pound. The purchase price of carbon dioxide is about 4¢ per pound. Therefore, it is more economical to recover the carbon dioxide in the two streams by flashing to the discharge conditions, than to simply vent carbon dioxide and buy replacement solvent. Therefore, both the raffinate and product leave the process at one atmosphere of pressure and with carbon dioxide dissolved in these streams at this pressure. The lost carbon dioxide is provided as makeup.

The amount of work required to recover the carbon dioxide from the raffinate and product can be reduced if these streams are flashed to an intermediate pressure and a portion of the vapors are recompressed from the intermediate pressure rather than recompressing all of the vapor from one atmosphere. In the example shown in Figure IV-5, the still operates near 50 atmospheres and the product and raffinate streams leave at 1 atmosphere. The intermediate flash is at 30 atmospheres. There is a substantial amount of cooling as a large fraction of the carbon dioxide flashes. Therefore, the flash vessels or feed to the vessels must be provided with a means for adding heat. The vessel is also equipped with a demister or similar device to separate liquid from the flashing vapor. The result is a flash vessel that is essentially the stripping section of a distillation column. When the 30 atmosphere and 1 atmosphere flash vessels are placed in series with the 50 atmosphere still, they perform as a staged cascade of distillation units. The enthalpy for warming the flash vessels may be provided in the same manner as for the main still. Vapors from each flash are returned to a compressor at a point where the suction pressure is similar to the flash vessel pressure. The staged cascade then consists of vapor-recompression

distillation units. A process flowsheet showing staged flash units, a multiple inlet compressor, heat exchanger for balancing the process, and a means of determining the makeup rate, is shown in Figure IV-7.

Depending upon the boiling point characteristics of the process, the amount of carbon dioxide evaporated in each stage may become progressively smaller, or may be more equal. In an ethanol extraction case, described in a later section, 99% of the carbon dioxide is recovered in the main distillation unit. As the concentration of organic in the extract increases, the fraction of carbon dioxide recovered by the distillation unit decreases. If the still bottoms are specified as 50-mole percent carbon dioxide, and the feed to the still contains 50-mole percent organic, then the only carbon dioxide generated in the main still is that required for reflux and all of the carbon dioxide is recovered in the flash units. This is a limiting case, but does indicate how the distribution of compressor power required can shift among the various flash vessels depending upon operating conditions in the rest of the process.

2. Ethanol-From-Water Extraction

Among oxygenated hydrocarbons that might be separated from aqueous solutions, ethanol is of great interest. Because of its chemical and physical properties, and the amount of information available about current technologies for ethanol separations from water, it is a good model compound for the development of experimental and computational techniques. Using the process models described above, we have simulated the performance of a plant nominally rated with a capacity of 10 million gallons per year. A study was conducted in which parameters in the process simulator were varied, and the resulting variations in process performance noted.

The purpose of the study was to determine qualitative trends which might serve as a guide in optimizing the process. The results of the study are summarized below and in the accompanying tables. This flowsheet is somewhat different than Figure IV-5, in that only one flash vessel is used for the product and one for the raffinate. C2 is the first stage compressor between the flash vessel pressure and a pressure intermediate between the flash vessel and the extractor. C3 is the second and final stage of compression. The results computed are only as accurate as the model and the physical properties used in the model. Calculations performed since the parameter studies were made support the general validity of the results.

a. Effect of varying feed concentration (Table IV-10)

The alcohol concentration in the broth produced by many fermentation processes is in the range of 8 to 12 weight percent. To simulate the variation in feed composition, values of 5, 10, 15 and 20 weight percent ethanol in water were used. Because the total amount of ethanol was held constant, the total amount of feed decreased as the ethanol concentration increased. The amount of solvent is a function of the total amount of feed, not the

FIGURE IV-7

COMPLETE PROCESS FLOW SHEET

FIGURE IV-7

LEGEND

<u>Unit</u>	<u>Description</u>
f1	1st flash unit, normally the main vapor recompression unit
f2	2nd flash unit, intermediate flash the still bottoms
f3	3rd flash unit, final flash for the product stream
f4	4th flash unit, raffinate flash vessel
f5	5th flash unit, recycle solvent is flashed to an intermediate pressure to cool the solvent to the extractor temperature. This vessel helps control the overall solvent inventory.
p1	solvent feed pump to extractor
p2	solvent makeup pump
P	pressure control loops
T	temperature control loops
L	liquid level control loops
F	flow control loops
S/F	solvent-to-feed monitor

TABLE IV-10

EFFECT OF VARYING FEED COMPOSITION

	<u>Weight percent ethanol in feed</u>			
	<u>5</u>	<u>10</u>	<u>15</u>	<u>20</u>
C1, kW	1611	760	476	334
C2, kW	45.1	34.5	30.9	29.0
C3, kW	21.7	16.6	14.9	13.4
Total power, kW	1678	811.1	521.8	376.4
Product, mole% EtOH	69.8	85.1	90.5	93.2

amount of ethanol in the feed. Therefore, the amount of solvent per unit of ethanol decreases as the ethanol concentration increases. Since the energy into the process is a function of the solvent recycle rate, the energy consumption of the process varies inversely with the feed concentration. Per unit of product ethanol, approximately twice as much energy is required when the feed is 5 weight percent than when the feed is 10 weight percent, and approximately half as much energy is required for a 20 weight percent feed than for a 10 weight percent feed.

Varying the feed composition also influences the final product composition. Solvent enters the extractor near the bottom of the column and is repeatedly dispersed and coalesced as it passes from tray to tray. Therefore, it seems reasonable to assume that the water-rich phase is saturated with carbon dioxide, and that the carbon dioxide-rich phase is saturated with water. As the amount of solvent per unit mass of organic increases, so does the amount of water in the product. Using a 5 weight percent feed, the fraction of the product that is water (on a molar basis) is very close to twice the fraction produced using a 10 weight percent ethanol feed. For example, a 5 weight percent feed might produce a product having 30-mole percent water whereas a 10 weight percent feed might produce a product having 15-mole percent water.

b. Effect of flash vessel conditions (Table V-11)

The total power input and the product composition are influenced by the conditions in the flash vessels that are downstream of the distillation unit. When the flowrate of carbon dioxide in the main recycle loop of the process is much greater than the flowrate of carbon dioxide out the still bottoms, the energy inputs associated with the flash units will be small in comparison with the main compressor. However, as concentrations of organic in the feed increase, and as the liquid-liquid distribution coefficients improve, the balance of energy inputs shifts. In cases where the extract contains more than 10-mole percent of organic, the flash gas compressors consume a significant fraction of the total process energy.

The final flash unit should generally operate at 1 atmosphere, with the vapors compressed, condensed, and returned to the process. When the flash units are operated in this manner, the carbon dioxide makeup rate is simply given by the solubility of carbon dioxide in water and organic at the product and raffinate flow rates. This is on the order of 0.02 pounds of carbon dioxide per pound of ethanol product.

c. Effect of operating conditions in the distillation unit.
(Tables IV-12, IV-13 and IV-14)

Since most of the process energy is used in the form of compression work to the distillation unit, changes in the operating conditions of the still will influence the overall energy consumption. However, the still plays no significant role in establishing the final product composition. The

TABLE IV-11

EFFECT OF VARYING THE FLASH VESSEL PRESSURES

	<u>Flash vessel pressure, atm</u>				
	<u>10</u>	<u>20</u>	<u>30</u>	<u>40</u>	<u>50</u>
C1, kW	759.6	759.6	759.6	759.6	759.6
C2, kW	99.9	50.3	26.3	12.3	4.2
C3, kW	96.0	48.4	25.2	12.2	4.7
Raffinate CO ₂ , lb-mole/hr	17.0	34.0	50.9	67.9	84.9
Product CO ₂ , lb-mole/hr	9.00	20.6	32.1	44.8	60.3
Total work, kW	955.5	858.3	811.1	784.1	768.5
Total CO ₂ loss, lb-mole/hr	26.0	54.6	83.0	112.7	145.2

Ethanol product rate is 145 lb-mole/hour.

TABLE IV-12

EFFECT OF CHANGING BOTH THE STILL BOTTOMS
COMPOSITION AND BOILING POINT ELEVATION

	<u>Mole percent CO₂ in still bottoms</u>					
	<u>40</u>	<u>50</u>	<u>60</u>	<u>70</u>	<u>80</u>	<u>90</u>
Boiling point elevation, °C	5.99	1.91	1.61	1.21	0.80	0.40
C1, kW	1169	668.6	641.3	605.0	569.4	519.1
C2, kW	23.6	34.6	50.8	77.9	132.5	298.1
C3, kW	11.4	16.7	24.5	37.5	63.8	143.5
Total, kW	1204	720	717	720	766	961

TABLE IV-13

EFFECT OF VARYING STILL PRESSURE

	<u>Still pressure, atm</u>			
	<u>30</u>	<u>40</u>	<u>50</u>	<u>60</u>
C1, kW	4103	2391	1045	-
C2, kW	33.0	33.6	34.3	35.2
C3, kW	15.9	16.2	16.5	17.0
Total, kW	4152	2441	1096	-
Mole% ethanol	95.5	91.6	86.6	80.4
Weight% ethanol	98.2	96.5	94.3	91.3

TABLE IV-14

EFFECT OF BOILING-POINT ELEVATION AT CONSTANT
STILL BOTTOMS COMPOSITION

	<u>Boiling point elevation, C</u>				
	<u>0.0</u>	<u>3.0</u>	<u>6.0</u>	<u>9.0</u>	<u>12.0</u>
C1, kW	223.7	759.6	1168	1725	2054
C2, kW	34.84	34.47	34.17	33.93	33.71
C3, kW	16.77	16.59	16.45	16.33	16.23
Total, kW	275	811	1219	1775	2104

Approximately --

$$\text{Power for C1} = 154 \text{ (bpe)} + 260$$

composition, on a solvent-free basis, is determined primarily by the extract composition. The still does determine the pressure in the three-phase flash unit, and by determining this it influences the amount of water-rich phase that may be removed from the extract. However, this changes only slightly the solvent-free extract composition. Within the still the two most significant parameters are the temperature difference between the bottoms and distillate (boiling point elevation) and the fraction of carbon dioxide in the bottoms.

It is important to note that the vapor recompression unit operates like a heat pump cycle, with the boiling point elevation contributing to the temperature difference between the heat source and sink. A minimum temperature difference of 6°C is specified to allow for a minimum temperature approach in the reboiler. The total temperature difference is the sum of the reboiler temperature approach and the boiling point elevation. If the boiling point elevation is roughly equal to the heat exchanger temperature difference, the energy input will be roughly twice what it would have been had the boiling point elevation been zero.

The boiling point elevation is the boiling point of a mixture minus the boiling point of the pure solvent at the same pressure. Therefore, the boiling point elevation will vary with the composition of the still bottoms. The amount of solvent in the distillate and the amount recovered by the flash units will vary as the still-bottoms composition varies. Therefore, one cannot minimize the energy to the process by operating the still with the bottoms rich in carbon dioxide (low still boiling point elevation) because this carbon dioxide must eventually be recovered in a flash vessel operating at a pressure lower than the still pressure. To correctly minimize the energy inputs to the process, one must consider the total for the main compressor and compressors associated with the flash vessels. This minimum will be a function of the temperature-composition characteristics of the mixture at the specified still pressure (see Table IV-12).

d. Effect of product recycle (Table IV-15)

Finally, the process was simulated with product recycle to the extractor for product quality improvement. Various fractions of the ethanol product were recycled back to the feed stream to increase the ethanol concentration in the feed. Since the solvent flow rate is a function of the total amount of feed, for feed compositions with only a small amount of organic, increasing the organic by a factor of 50% or 100% will not significantly increase the total feed rate, nor the solvent rate. The result is that recycling ethanol does not significantly affect the energy inputs. However, because the extract contains the same amount of water and 50% or 100% more ethanol, the final product is richer in ethanol. With feeds containing higher concentrations of ethanol, the number of equilibrium stages in the extractor must be increased to effect the same ethanol recovery. Otherwise, the improved product composition is obtained at the expense of increased losses of ethanol in the raffinate.

TABLE IV-15

EFFECT OF RECYCLING PRODUCT TO FEED

	<u>Recycle</u>			
	<u>0.0</u>	<u>0.5</u>	<u>1.0</u>	<u>1.5</u>
C1, kW	759.6	756.3	752.9	749.6
C2, kW	34.47	46.85	59.16	71.39
C3, kW	16.59	22.56	28.48	34.37
Total ethanol, lb-mole/hr	145.5	227.1	308.1	388.7
Total water, lb-mole/hr	25.52	25.43	25.35	25.27
Mole % ethanol	85.08	89.93	92.40	93.90
Weight % ethanol	93.6	95.80	96.88	97.52
Total work, kW	810.66	825.71	840.54	855.36
Net ethanol, lb-mole/hr	145.5	141.98	137.86	133.34
Btu/lb	413	431	452	475

$$\text{Recycle} = \frac{\text{moles of ethanol recycled}}{\text{moles of ethanol in feed}}$$

3. Comparison of Alcohol Extractions

As part of a project to simulate various extraction processes, calculations were performed for the extraction of ethanol, isopropanol and 2-butanol from water. For the purpose of comparison, a plant rated at 10 million gallons of alcohol per year was selected as the basis. In each case, the feed was assumed to contain 10 weight percent of organic in water of which 95% was to be recovered. The optimum operating point for the still must be determined using the boiling point characteristics for each of the alcohols. The boiling point elevation was assumed to be 3°C at 50-mole percent carbon dioxide in all three cases.

In the absence of firm experimental data for the compositions of the equilibrium phases, it was assumed that the water equilibria were the same as previously used for the ethanol extraction studies. The distribution coefficients were estimated from the diagrams published by A.W. Francis(4).

Given the basic assumptions concerning physical properties, equilibria, and the operation of the process, the only significant variable is the distribution coefficient. The distribution coefficients used (on a molar basis) were 0.25 for ethanol, 0.65 for isopropanol and 2.00 for 2-butanol.

The solvent flow rates were computed to be in the ratio of 1 for ethanol, 0.38 for isopropanol and 0.13 for 2-butanol. Because there is an energy input associated with recovering carbon dioxide from the flash vessels (an energy input unrelated to the main carbon dioxide recycle), the total energy is not directly proportional to the recycle solvent rate. Instead, the total energy is in the ratio of 1 for ethanol, 0.48 for isopropanol and 0.25 for 2-butanol. The product composition also reflects the differences in solvent flow rates, with 2-butanol having approximately one-eighth as much water as in the ethanol product.

The results of these calculations are shown summarized in Tables IV-16, IV-17, and IV-18.

D. Design of Process Equipment

1. Extractor

To develop a separation process that takes advantage of the distribution of an organic compound between an aqueous phase and a liquid carbon dioxide phase requires a device in which the two phases are brought into intimate contact (enhancing mass transfer) then separated into two phases. To achieve the most concentrated extract, the extract should have been in contact with the most concentrated aqueous stream (feed) before leaving the device. Similarly, to produce an aqueous (raffinate) stream in which the organic concentration is lowest, it should contact the purest solvent before leaving

TABLE IV-16

PHYSICAL PROPERTY CONSTANTS

	<u>ethanol</u>	<u>isopropanol</u>	<u>2-butanol</u>
distribution coefficient, molar basis	0.25	0.65	2.00
relative volatility	100	200	300
Henry's constants,			
1 atm	192	150	144
30 atm	162	116	132

TABLE IV-17

PROCESS DESCRIPTION

	<u>ethanol</u>	<u>isopropanol</u>	<u>2-butanol</u>
<u>Extractor</u>			
feed organic, lb-mole/hr	178.6	136.4	113.6
feed water, lb-mole/hr	4112	4096	4205
solvent, lb-mole/hr	19,260	7393	2483
theoretical stages	11.8	11.8	11.6
approximate dimensions, diameter x length	12' x 66'	7-1/2' x 44'	4-1/2' x 30'
vessel weight, tons	243	63	15
<u>Distillation Unit</u>			
stages at 80% efficiency	4	4	5
reflux, minimum	0	0	0
reboiler duty, MMBtu/hr	43.9	16.6	5.38
reboiler area, square feet	12,500	4,730	1,530
extra cooling, MMBtu/hr	6.94	2.67	0.91
<u>Compressor, Main</u>			
suction, psia	774	774	774
discharge, psia	970	970	970
flow, lb/hr	840,000	319,000	104,000
power, hp	1427	542	177
coefficient-of-performance	14	14	14

TABLE IV-17

PROCESS DESCRIPTION
(continued)

	<u>ethanol</u>	<u>isopropanol</u>	<u>2-butanol</u>
<u>Flash Units, heat in MBtu/hr</u>			
raffinate at 441 psia	170	171	176
raffinate at 14.7 psia	223	224	231
product at 441 psia	655	458	394
product at 14.7 psia	152	162	118
<u>Compressors, flash vessels</u>			
441 psia to 970 psia			
stages	2	2	2
power, hp	74	56	52
14.7 psia to 970 psia			
stages	4	4	4
power, hp	212	219	197
<u>Heat Exchangers, Recompressed Vapors</u>			
for 2-stage compressor			
area, square feet	46	35	32
cooling water, lb/min	112	86	78
for 4-stage compressor			
area, square feet	20	21	18
cooling water, lb/min	134	135	118

TABLE IV-18

PROCESS DESCRIPTION, SUMMARY

	<u>ethanol</u>	<u>isopropanol</u>	<u>2-butanol</u>
<u>Utilities</u>			
shaft work, total hp	1713	817	426
shaft work, Btu/lb prod. alc.	545	260	134
heating, MBtu/hr	1200	1020	920
cooling water, lb/min	246	220	196
cooling, refrigeration, tons	578	223	76
<u>Product Specifications</u>			
rate, lb/hr	8030	8000	8100
composition, wt% alc.	91.5	96.0	98.0
Makeup solvent, lb/hr	154	153	151
<u>Effluent</u>			
organic, lb/hr	200	202	318
water, lb/hr	72,700	73,100	75,400
composition, wt% alc.	0.27	0.27	0.42

NOTE: 1 ton of refrigeration = 12,000 Btu

the device. Finally, given the high flow rates most frequently encountered with organic aqueous streams, a continuous process is probably more feasible than a batch process.

As a result of these three considerations, the extractor should be a staged cascade of mixer-settler devices operating in continuous, counter-current flow. Because the process operates at elevated pressures, simple box-type mixer-settlers are not attractive. The capital investment per unit of capacity would be greater than for other possible devices, in particular, for a column. Therefore, the continuous, counter-current flow liquid-liquid extraction column was selected as the separation device.

There are two guiding considerations in the design of a separations device: capacity and efficiency. For an extraction column, the capacity is given by the cross-sectional area per unit of throughput. The efficiency refers to the mass transfer efficiency of a mixing/separating stage. Columns filled with packing enhance mass transfer by creating area as droplets of one phase contact packing elements. These droplets later coalesce, either on the same packing element or some other element. This differential contactor is not particularly efficient because the formation and coalescence of droplets is haphazard. It should be noted that the packing elements generally have a primary dimension that is larger than the dispersed phase droplets. Although wire elements are efficient in distillation processes, where they provide extended area for mass transfer, they are generally not effective in liquid-liquid extraction. Only two types of devices have characteristics that make them suitable for continuous extraction processes using liquid carbon dioxide: sieve-tray type columns, and columns with moving internals.

A column with an internal mixing device provides a means for increasing the mass transfer efficiency of the stage. The mixing device breaks droplets up into a smaller size, providing more area for mass transfer and providing better contact between the two phases. The capacity is not necessarily much better than for a simple sieve-tray extractor, because one of the limiting factors for both types of equipment is the velocity of buoyant dispersed phase droplets in the continuous phase. The energy input to the mixer is generally small, and is often little more than for a simple mixer in the continuous phase. If carbon dioxide is selected as the continuous phase, the mixing energy could be very small, due to the low viscosity of liquid carbon dioxide. The principal difficulty in using a mechanical agitator is the problem of sealing the shaft entering the pressure vessel. In a pilot-scale unit, it is possible to enclose the electric drive inside the pressure vessel. It is also conceivable that a magnetically driven mixer could be used with a pilot plant. These systems may be difficult to implement in a large-scale commercial plant. For that reason, we have directed our efforts toward the most efficient column not having moving internals, the sieve-tray column.

The sieve-tray extraction column has been designed using a combination of procedures as outlined by Treybal(30) and Skelland(34). Both published

procedures are very similar except that Skelland performs much more detailed calculations for the mass transfer efficiency. In both cases the droplet size and velocity is first computed. From this tray, hydraulics and various column cross-sectional areas can be computed. In our computer implementation of these calculations, the designer has several options regarding the parameters to be specified. Depending upon the specific selection, the program uses equations from both sources (30,34).

One must first decide which phase is to be the continuous phase and which one is the dispersed phase. In a sieve-tray column, one liquid is dispersed into the second phase as small droplets. There are several considerations in choosing which phase to disperse and which to run continuously. Among the considerations are mass transfer efficiency; ease of dispersion; column capacity, length, and diameter requirements; and the presence of suspended solids. Generally, the phase with the poorer mass transfer coefficient is selected as the continuous phase. This phase benefits to some extent by the mixing provided by rising droplets. Within the droplets, mass transfer to the droplet surface is by diffusion or internal circulation. Since the diffusion coefficients for organics in liquid carbon dioxide are greater than in water, and the viscosity of the carbon dioxide phase is less, the aqueous phase would have the poorer mass transfer coefficient and is selected as the continuous phase. This arrangement gives the best mass transfer efficiency. It is also generally observed that it is easier to disperse the low density, low viscosity phase into the phase with higher density and viscosity than vice versa.

The arrangement of phases described above gives the best mass transfer efficiency. This in turn results in a column with the smallest number of actual stages and consequently, the shortest length. However, the capacity or cross-sectional area, is a function of the hydraulics. The dispersed phase passes through sieve-tray holes as it passes from stage-to-stage. The continuous phase flows across a tray before passing through a downcomer to the next stage. Ordinarily, the phase with the smaller volumetric flow is dispersed in the other phase. This results from the fact that active hole area occupies only about 15% of the tray area. For the downcomers, flow passes through the entire cross-sectional area. Therefore, to minimize the total column cross-sectional area, the phase with the larger volumetric flow rate should pass through the downcomer. In some of our processes, the solvent-to-feed ratio is large, resulting in volumetric flow rates for the carbon dioxide-to-aqueous phase on the order of 10 to 1. Simply on the basis of flow rates, the carbon dioxide phase should normally be the continuous phase.

Another consideration is the viscosity of the aqueous phase, and the possibility of suspended solid particulates in the aqueous phase. Difficulties might arise when attempting to disperse this phase by passing through a sieve-tray hole.

There is a great deal of evidence to show that carbon dioxide can be dispersed in water. The density difference between the carbon dioxide phase and water phase is large enough that the extractor operating with the aqueous phase as the continuous one resembles a sieve-tray distillation column.

Since all indicators, except for column capacity in some cases, favor dispersing the carbon dioxide into the aqueous phase, that is the way the process was designed.

The flow rate of the dispersed phase is found from the velocity of the fluid passing through the sieve-tray holes. The optimum linear velocity is the one resulting in a jet of fluid issuing from the sieve-tray hole. Subsequently, the jet breaks up into droplets of roughly the same size. At higher and lower velocities, the droplet dispersion has a broader distribution of sizes. Given the linear velocity, and the fraction of tray area available as holes, the cross-sectional area for the dispersed phase flow rate can be determined.

The continuous phase flows through the downcomers. The linear velocity should be less than the terminal droplet velocity, so droplets will rise if caught in the downcomer. The tray spacing must be large enough that the linear velocity of the continuous phase is less than the dispersed phase velocity. Otherwise, dispersed phase droplets will be swept toward the downcomer and the accumulation of the dispersed phase will cause flooding. The dispersed phase is forced through the sieve-tray holes by a layer of coalesced dispersed phase beneath the tray. The density difference between the continuous phase and the dispersed phase produces the buoyant force. The thickness of the dispersed phase results from a pressure balance across the tray. In the area with holes, there is a pressure drop across the orifice holes. Equal to this is the pressure drop across the downcomer plus the hydraulic head beneath the tray. Therefore, to ensure that there is sufficient pressure drop in the downcomer to produce a corresponding liquid layer beneath the sieve-tray (which results in fluid jetting through the orifice holes), a constriction is sometimes placed in the downcomer. Various kinds of flooding conditions may result from hydraulic imbalances.

An estimate has been made of the mass transfer efficiency of a sieve-tray extractor, using a procedure outlined by Skelland (34). In this method, mass transfer correlations are used to estimate the amount of material transferred between the disperse and continuous phases. Correlations are used for droplet formation, droplet rise (as a rigid sphere, sphere with internal circulation, or oscillating droplet), and for droplet coalescence. The interfacial area for mass transfer is found from an estimate of the average droplet size, and the total number of droplets produced. One can then compute a "pseudo-equilibrium curve" by adjusting the bulk concentration for a differential section of an extractor so the amount of material transferred between the dispersed and continuous phases is consistent with an overall material balance for the differential section. One then uses the pseudo-equilibrium curve and the operating line to compute the number of actual stages for a stage-wise extractor. These calculations have been performed using a computer program that is in principle the same as the one Skelland has published. Mass transfer efficiencies of 80 to 90% have been estimated. However, these must be regarded as speculative because no systematic study has yet been undertaken with this model, even comparing computed results with published results for conventional systems.

2. Vapor Recompression Distillation

The extract stream leaving the extractor consists of liquid carbon dioxide with extracted organic and smaller amounts of water, depending upon the phase equilibria in the extractor. The solvent carbon dioxide is separated from the organic by a simple distillation. As the more volatile component, the carbon dioxide leaves the still as the distillate stream, and organic with dissolved carbon dioxide leaves as bottoms.

The distillate composition is fixed by specifying the composition of the solvent entering the extractor, since the distillate when compressed and condensed is the solvent return to the extractor. The specification in the extractor is based on the phase equilibria relationships and the amount of organic allowed in the raffinate. In general, the relative volatility of carbon dioxide with respect to organics is very large. Therefore, high purity distillate is obtained simply by flashing the extract entering the still. In other words, the rectifying section of the still is frequently not needed, and there is no need for reflux. It is still necessary to strip solvent carbon dioxide from the organic component, but only a few trays are required to do that. The number of trays is determined by the amount of carbon dioxide to be recovered from the feed, or, what is equivalent, the amount of carbon dioxide in the bottoms.

In terms of phase equilibria, the still must operate at conditions below the critical point of the solvent, so vapor and liquid phases will co-exist. Operating too close to the critical point also introduces other difficulties. At the solvent-rich end of the y-x plot, the equilibrium curve develops an inflection as the critical point is approached.⁽³⁵⁾ This can lead to a pinch in the McCabe-Thiele construction for the distillation unit, making it impossible to obtain the desired distillate purity. Also, as the critical point is approached, the densities of the liquid and vapor phases become more nearly equal. This results in more liquid entrainment in the vapor phase, and a lower distillation tray efficiency. In the current design, the still is operated approximately 20 atmospheres below the critical point, believed to be an adequate margin of safety.⁽³⁶⁾

The arrangement of compressor and distillation column described above is a classic vapor recompression distillation. The compressor acts as a heat pump, moving heat from the lower temperature of the distillate to the higher temperature of the condenser-reboiler. The cycle can be analyzed in a manner that is similar to a Carnot cycle. The co-efficient-of-performance thus obtained relates the ratio of heat transferred/work to the temperatures of the heat source and sink. It is clear from such an analysis that a great deal more heat can be transferred per unit of work when the heat source and sink are more nearly equal than when they are very different. When the temperature difference is on the order of 10C, the co-efficient-of-performance is roughly 30. Allowing for inefficiencies, a process would have an actual value about half of this.

The net energy balance for the vapor- recompression unit may be positive or negative, depending upon the flow rates and efficiency of the cycle. For example, in many cases the feed to the still is a mixture of 20% vapor and 80% liquid. Thus, the compressor feed contains not only the vapor from boil-up, but also the 20% vapor in the still feed. Therefore, when balancing the heat flows across the reboiler, there is 20% more material flowing through the compressor and condensing than boiling up. The result is often excess heat that must be removed. Generally, the enthalpy differences that must be trimmed are small compared with the work input, and much smaller than the amount of heat transferred across the reboiler surface.

The distillation unit is a small stripping column mounted on a large kettle-type shell-and-tube reboiler. This is not necessarily the optimum configuration. It is possible that a thermosiphon design, resembling a long-tube evaporator, would be a less costly device. However, design calculations have not been performed for these alternative configurations.

The principal difficulty in computing the heat transfer for cooling super-heated carbon dioxide is the fact that the physical properties change drastically as the fluid conditions approach the critical point. We therefore did calculations for a single horizontal tube, inside of which carbon dioxide was flowing. Tubes with standard dimensions used in heat exchangers were modeled by dividing the tube length into increments. The calculations were then performed iteratively for each increment in sequence from the hot end of the tube to the cold end. For each increment, an energy balance was performed, using heat transfer correlations and physical properties at the increment conditions. From the calculations, heat transfer coefficients and pressure drops were computed. The results for the case studied are shown in Table IV-19.

3. Flash Vessels

While the major unit operations are performed in the extractor, distillation column and compressor, there are several important flash vessels. One is a three-phase flash vessel, also serving as a decanter which has as its feed the extractor extract stream and sends most of its flow to feed the distillation unit. At least two vapor-liquid flash units are also used, one for the high pressure raffinate stream and a second for the high pressure still bottoms stream.

The extract stream consists primarily of liquid carbon dioxide, saturated with water, and an amount of organic determined by liquid-liquid equilibria in the extractor. If this stream is flashed to a lower pressure, a carbon dioxide-rich vapor stream is formed in addition to the liquid carbon dioxide stream. Since the solubility of water in the vapor stream is less than in the liquid, the liquid carbon dioxide stream becomes super-saturated with water. This leads to the formation of a third phase, which is water-rich.

TABLE IV-19

HEAT TRANSFER COEFFICIENTS

tube diameter	3/4 inch
tube length	20 feet
pressure drop	1 atm
inlet pressure	66 atm
cooling gaseous carbon dioxide	750 Btu/hr.ft.°F
condensing carbon dioxide	1500 Btu/hr.ft.°F
cooling liquid carbon dioxide	680 Btu/hr.ft.°F

The organic is distributed between the three phases according to vapor-liquid and liquid-liquid equilibria. The flashed mixture also cools. The solubility of water in carbon dioxide decreases with decreasing temperature, further enhancing the formation of the third, water-rich phase. Generally, the water-rich phase has a lower organic concentration than the solvent-free extract entering the flash. Therefore, removing the water-rich phase will increase the organic product purity by a slight amount.

A detailed design for the three-phase flash unit has not yet been carried out. Because the water-rich phase is formed by flashing the carbon dioxide-rich phase, water phase droplets will nucleate throughout the mixture as small droplets. The flash vessel would probably contain some type of fibrous coalescence device to enhance the separation of water and liquid carbon dioxide. Entrainment of liquid carbon dioxide in the vapor phase is generally not important, since both of these phases will go to the distillation unit. In some cases, the vapor phase is rich enough in carbon dioxide that it need not go to the still, but may be combined with the distillate to feed the compressor. If this is the case, a demister pad is needed to prevent liquid droplets from entering the compressor.

The two-phase, vapor-liquid flash units are essential to the recovery of carbon dioxide. The aqueous raffinate stream is degassed in a flash vessel operating at 1 atmosphere before leaving the process. Generally, a second flash vessel is staged before the final one-atmosphere flash, with the intermediate flash operating near 30 atmospheres. Thus, the raffinate leaving the extractor is flashed to successively lower pressures, with the carbon dioxide recovered at each stage recompressed, condensed, and returned to the extractor. The raffinate flash vessels are horizontal drums, with fairly small demister pads to remove entrained water from the vapors.

A similar cascade of flash vessels is used to remove carbon dioxide from the still bottoms. The flash vessels may be horizontal, but it is more likely that at least the higher-pressure vessel will be vertical, because the ratio of vapor-to-liquid is fairly large. Demister pads will be required, as with the raffinate flash vessels. However, the concentration of organic in the vapor is significant. Therefore, the vapor, when condensed, will probably be returned to the extractor above the solvent feed. If the total stream flow rate from the product flash vessels is small relative to the solvent flow rate, it may be combined with the solvent without significantly increasing the organic content.

The vapors from the two raffinate flash vessels and two product flash vessels must be recompressed. In general, we expect that this would be done with a multistage compressor. The one-atmosphere vapors for both raffinate and product flashes are combined and compressed. Similarly, the 30-atmosphere vapors from both raffinate and product flashes are combined and compressed. Depending upon the volumes, the compression might be accomplished using a single, multiple-inlet compressor, or two compressors might be used with a common driver.

The amount of carbon dioxide in the still bottoms is usually a large fraction of the total stream flow. In this case, heat must be provided to warm the still bottoms, and flash the carbon dioxide. Flashing the still bottoms may produce dry ice or carbon-dioxide hydrate, depending upon the final pressure, the amount of heat added, and the amount of organic present. We expect cold liquid mixtures of carbon dioxide and organic in most cases. The requirement for heating, a demister pad, and possibly some stripping of the carbon dioxide from the liquid phase, may result in a flash vessel that is essentially the stripping section of a distillation column. It appears as though there is enough excess heat from the main compressor discharge to provide the required enthalpy of evaporation.

E. Conclusions

1. Tabulated thermophysical-property data for carbon dioxide were found to be most accurately accessed as continua by means of conventional interpolation methodology. The Peng-Robinson equation-of-state was tested, but found to be less satisfactory. Given the large volume of tabulated data available, the interpolation method was selected and incorporated as a design subroutine in a computer-based design technique.

2. Carbon Dioxide-Water-Phase Equilibria

(a) Quantitative relationships were developed for CO₂-water mutual solubilities. They account for effects of temperature, pressure, and third (organic) component concentration.

(b) A phase diagram was developed for the CO₂-water system, particularly to clarify regions of solid-phase formation. The latter includes the CO₂ hydrate as well as solid-phase pure components.

(c) CO₂-water chemical equilibrium calculations were carried out to help define concentration ranges of alkaline-earth metal ions that would cause solid carbonate formation.

3. Carbon Dioxide-Organic Phase Equilibria

(a) Literature data for solubilities of organics in CO₂ (liquid-liquid) were compiled.

(b) Vapor-liquid equilibria data for several CO₂-organic systems, such as CO₂ and lower alcohols, were correlated using the Peng-Robinson equation. The level of accuracy was found to be adequate.

4. Three component-phase equilibria (carbon dioxide-water-organic) for a wide range of organic compounds were compiled. Empirical relationships were developed based on literature models, but tabulated data were used in design simulations.

5. A process flow sheet was developed for CO₂ solvent extraction of an organic from water. Material- and energy-balance computer programs were also developed for the flow sheet. These were used to carry out a series of optimization and simulation studies. The results were intended largely to help guide pilot-unit testing. Recognizing the possible inaccuracies in a purely analytical set of simulations of this kind, the following initial conclusions about the process may be drawn.

(a) A plant fed with 10 weight percent alcohol feed would consume 0.65 kilowatt-hours (kwh) of power for compression energy per gallon of alcohol fed to the system. Depending on the economics of heat exchange addition in portions of the system, this could be the entire energy consumption, or probably the great majority. Assuming that 8000 Btu of steam or 10,000 Btu of fossil fuel are required to generate one kwh of power, the energy consumption would be 5200 Btu of steam-equivalent, or 6500 Btu of fossil fuel equivalent energy. The extraction product, however, would have a composition of 85.1 mol percent, or 93.6 weight percent, less than the azeotropic composition. Thus, additional energy would be required to process this stream to high-purity alcohol.

(b) Doubling the ethanol feed concentration to 20 weight percent would reduce the energy required to about 0.30 kwh per gallon. Halving the ethanol feed concentration to 5 weight percent would increase the energy required to about 1.35 kwh per gallon.

(c) For the same feed compositions, isopropanol can be separated with 48% of the energy required for ethanol. The same separation of 2-butanol can be done with 25% of the ethanol energy requirement.

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