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CRITICAL-FLUID EXTRACTION OF ORGANICS FROM WATER

Volume II: Experimental

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

By
Omar K. Abboud
Richard P. de Filippi
Kent E. Goklen
John M. Moses

June 1984

Work Performed Under Contract No. AC01-79CS40258

Arthur D. Little, Inc.
Cambridge, Massachusetts

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FINAL REPORT

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TABLE OF CONTENTS

	<u>Page</u>
TITLE PAGE	i
DISCLAIMER	ii
TABLE OF CONTENTS	iii
ABSTRACT	iv
TABLES	v-viii
FIGURES	ix
I. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS	1
II. INTRODUCTION	6
III. DESIGN BASIS	7
A. Feed Specifications	
B. Solvent CO ₂ Specifications	
C. Product Specifications	
D. Operation	
E. Utilities	
F. Control	
G. Data Collection	
H. Equipment	
IV. PROCESS FLOW DIAGRAM	11
A. Flowsheet	
B. Comparison with Commercial Scale Flowsheet	
C. Equipment List	
D. Operating Procedures	
V. EXPERIMENTAL	17
A. Program	
B. Data and Analysis	
VI. COSOLVENT STUDIES	106
REFERENCES	139
APPENDIX I NOMENCLATURE	140
APPENDIX II PILOT PLANT, COSOLVENT FEED SYSTEM RUN SHEET	142

ABSTRACT

Critical fluid extraction has been tested at the pilot plant scale as a method of separating organics from water. The process employed resembles a liquid-liquid extraction in which the solvent is near-critical carbon dioxide and the feed is an organic in aqueous solution. Carbon dioxide's solvent and other thermodynamic properties, and the effective utilization of a vapor recompression cycle in the process design have significantly reduced the energy required for these separations. This process is an energy-conserving alternative to the distillation processes which are currently employed.

The objectives of this portion of the project were to demonstrate the feasibility of this technology and to gather the engineering data required to evaluate the process. Three alcohols were tested in these experiments - ethanol, isopropanol and sec-butanol - and were all successfully extracted.

TABLES

		<u>Page</u>
TABLE V-1	ETHANOL RUN SCHEDULE	19
TABLE V-2	ETHANOL RUN SCHEDULE, "W" SERIES	20
TABLE V-3	ISOPROPANOL RUN SCHEDULE	21
TABLE V-4	SEC-BUTANOL RUN SCHEDULE	22
TABLE V-5	ETHANOL RUN E1 DATA SUMMARY	24
TABLE V-6	ETHANOL RUN E2 DATA SUMMARY	25
TABLE V-7	ETHANOL RUN E3 DATA SUMMARY	26
TABLE V-8	ETHANOL RUN E4 DATA SUMMARY	27
TABLE V-9	ETHANOL RUN E6 DATA SUMMARY	28
TABLE V-10	ETHANOL RUN E7 DATA SUMMARY	29
TABLE V-11	ETHANOL RUN W1 DATA SUMMARY	30
TABLE V-12	ETHANOL RUN W2 DATA SUMMARY	31
TABLE V-13	ETHANOL RUN W3 DATA SUMMARY	32
TABLE V-14	ETHANOL RUN W4 DATA SUMMARY	33
TABLE V-15	ETHANOL RUN W5 DATA SUMMARY	34
TABLE V-16	ETHANOL RUN W6 DATA SUMMARY	35
TABLE V-17	ETHANOL RUN W7 DATA SUMMARY	36
TABLE V-18	ETHANOL RUN W8 DATA SUMMARY	37
TABLE V-19	ETHANOL RUN W9 DATA SUMMARY	38
TABLE V-20	ETHANOL RUN W10 DATA SUMMARY	39
TABLE V-21	ISOPROPANOL RUN I1 DATA SUMMARY	48
TABLE V-22	ISOPROPANOL RUN I2 DATA SUMMARY	49
TABLE V-23	ISOPROPANOL RUN I13 DATA SUMMARY	50

TABLES
(continued)

	<u>Page</u>
TABLE V-24	ISOPROPANOL RUN I4 DATA SUMMARY 51
TABLE V-25	ISOPROPANOL RUN I5 DATA SUMMARY 52
TABLE V-26	sec-BUTANOL DATA SUMMARY, RUN B-1 54
TABLE V-27	sec-BUTANOL DATA SUMMARY, RUN B-2 55
TABLE V-28	sec-BUTANOL DATA SUMMARY, RUN B-3 56
TABLE V-29	sec-BUTANOL DATA SUMMARY, RUN B-4 57
TABLE V-30	sec-BUTANOL DATA SUMMARY, RUN B-5 58
TABLE V-31	sec-BUTANOL DATA SUMMARY, RUN B-6 59
TABLE V-32	sec-BUTANOL DATA SUMMARY, RUN B-7 60
TABLE V-33	sec-BUTANOL DATA SUMMARY, RUN B-8 61
TABLE V-34	MATERIAL LOSSES AND RECOVERIES Ethanol Runs 64
TABLE V-35	MATERIAL LOSSES AND RECOVERIES Isopropanol Runs 65
TABLE V-36	MATERIAL LOSSES AND RECOVERIES sec-Butanol Runs 66
TABLE V-37	EXTRACTOR PERFORMANCE RAW DATA Ethanol Runs 68
TABLE V-38	EXTRACTOR PERFORMANCE RAW DATA Isopropanol Runs 69
TABLE V-39	EXTRACTOR PERFORMANCE RAW DATA sec-Butanol Runs 70
TABLE V-40	EXTRACTOR MASS TRANSFER EFFICIENCY 83
TABLE V-41	REBOILER COMPOSITIONS DURING ETHANOL RUNS 86
TABLE V-42	REBOILER COMPOSITIONS DURING ISOPROPANOL RUNS 87
TABLE V-43	REBOILER COMPOSITIONS DURING sec-BUTANOL RUNS 88

TABLES
(continued)

		<u>Page</u>
TABLE V-44	PRODUCT CONCENTRATION, ETHANOL	89
TABLE V-45	PRODUCT CONCENTRATION, ISOPROPANOL	90
TABLE V-46	PRODUCT CONCENTRATION, sec-BUTANOL	91
TABLE V-47	PRODUCT CONCENTRATION, SUMMARY	92
TABLE V-48	REBOILER AND STILL TEMPERATURES, Ethanol	94
TABLE V-49	REBOILER AND STILL TEMPERATURES Isopropanol	95
TABLE V-50	REBOILER AND STILL TEMPERATURES sec-Butanol	96
TABLE V-51	REBOILER BOTTOMS COMPOSITION AND BOILING POINT ELEVATIONS (BPE)	97
TABLE V-52	REBOILER HEAT TRANSFER COEFFICIENTS AND BOILING POINT ELEVATIONS Ethanol	100
TABLE V-53	REBOILER HEAT TRANSFER COEFFICIENTS AND BOILING POINT ELEVATIONS Isopropanol	101
TABLE V-54	REBOILER HEAT TRANSFER COEFFICIENTS AND BOILING POINT ELEVATIONS sec-Butanol	102
TABLE VI-1	CO-SOLVENT DATA ON ETHANOL-WATER-CO ₂ SYSTEM	107
TABLE VI-2	CO-SOLVENT EXTRACT EXPERIMENTS	109 & 110
TABLE VI-3	RUN CSE-1	116
TABLE VI-4	RUN CSE-2	117
TABLE VI-5	RUN CSE-3	118
TABLE VI-6	RUN CSE-4	119
TABLE VI-7	RUN CSE-5	120

TABLES
(continued)

		<u>Page</u>
TABLE VI-8	RUN CSE-6	121
TABLE VI-9	RUN CSE-7	122
TABLE VI-10	RUN CSE-8	123
TABLE VI-11	RUN CSE-9	124
TABLE VI-12	RUN CSE-10	125
TABLE VI-13	RUN CSR-1	127
TABLE VI-14	RUN CSR-2	128
TABLE VI-15	RUN CSR-3	129

FIGURES

		<u>Page</u>
FIGURE IV-1	PILOT-PLANT PROCESS FLOW SHEET	12
FIGURE V-1	UPCOMER VS DOWNCOMER SIEVE TRAY OPERATION	40
FIGURE V-2	SIEVE TRAY CONSTRUCTION	41
FIGURE V-3	EXTRACTOR CROSS SECTIONAL VIEW SHOWING SIEVE TRAY OPERATION WITH TEFLON AND WITH TEFLON/ STAINLESS SIEVE TRAYS	43
FIGURE V-4	CO-SOLVENT INJECTION SYSTEM	45
FIGURE V-5	McCABE-THIELE SAMPLE ANALYSIS FOR SEC-BUTANOL	69
FIGURE V-6	ETHANOL - CALCULATED YIELD LOSS VS SOLVENT-TO-FEED RATIO FOR VARIOUS NUMBERS OF THEORETICAL RATES	71
FIGURE V-7	ISOPROPANOL - CALCULATED YIELD LOSS VS SOLVENT-TO-FEED RATIO FOR VARIOUS NUMBERS OF THEORETICAL RATES	72
FIGURE V-8	SEC-BUTANOL - CALCULATED YIELD LOSS VS SOLVENT-TO-FEED RATIO FOR VARIOUS NUMBERS OF THEORETICAL RATES	73
FIGURE V-9	ETHANOL - YIELD LOSS VS SOLVENT-TO-FEED RATIO WITH DATA FROM THE "E" AND "W" SERIES OF RUN	77
FIGURE V-10	ISOPROPANOL - YIELD LOSS VS SOLVENT-TO- FEED RATIO WITH DATA FROM THE "I" SERIES OF RUNS	78

FIGURES
(continued)

		<u>Page</u>
FIGURE V-11	SEC-BUTANOL - YIELD LOSS VS SOLVENT- TO-FEED RATIO WITH DATA FROM THE "B" SERIES OF RUNS	79
FIGURE V-12	BOILING POINT ELEVATION VERSUS WEIGHT FRACTION CO ₂ IN REBOILER	99
FIGURE V-13	ETHANOL - OVERALL HEAT TRANSFER CO- EFFICIENT IN THE REBOILER VS TUBE SIDE FLOWRATES OF CARBON DIOXIDE	103
FIGURE V-14	ISOPROPANOL - OVERALL HEAT TRANSFER COEFFICIENT IN THE REBOILER VS TUBE SIDE FLOWRATES OF CARBON DIOXIDE	104
FIGURE V-15	SEC-BUTANOL - OVERALL HEAT TRANSFER COEFFICIENT IN THE REBOILER VS TUBE SIDE FLOWRATES OF CARBON DIOXIDE	105
FIGURE VI-1	EXTRACTION UNIT FLOW SCHEMATIC	111
FIGURE VI-2	PILOT-PLANT CO-SOLVENT/PRODUCT RECOVERY SYSTEM	113
FIGURE VI-3	WEIGHT PERCENT ETHANOL IN RAFFINATE AS A FUNCTION OF TIME AND CO-SOLVENT FOR RUN CSE II	131
FIGURE VI-4	WEIGHT PERCENT ETHANOL IN THE RAFFINATE AS A FUNCTION OF TIME AND CO-SOLVENT FOR RUN CSE III	132
FIGURE VI-5	WEIGHT PERCENT ETHANOL IN THE RAFFINATE AS A FUNCTION OF TIME AND CO-SOLVENT FOR RUN CSE IV	133
FIGURE VI-6	ETHANOL CONCENTRATION REDUCTION VS CO- SOLVENT LEVEL	134
FIGURE VI-7	PRODUCT ETHANOL CONCENTRATION IN EXTRACT AND REBOILER	136
FIGURE VI-8	DISTRIBUTION COEFFICIENT OF ETHANOL VS CO- SOLVENT LEVEL	138

I. SUMMARY CONCLUSIONS AND RECOMMENDATIONS

Critical fluid extraction has been tested at the pilot plant scale as a method of separating organics from water. The process employed resembles a liquid-liquid extraction in which the solvent is supercritical or near-critical carbon dioxide and the feed is an organic in aqueous solution. Carbon dioxide's solvent and other thermodynamic properties, and the effective utilization of a vapor recompression cycle in the process design have significantly reduced the energy required for these separations. This process is an energy-conserving alternative to the distillation processes which are currently employed.

The objectives of this portion of the project were to demonstrate the feasibility of this technology and to gather the engineering data required to evaluate the process. Three alcohols were tested in these experiments - ethanol, isopropanol, and sec-butanol - and were all successfully extracted. The engineering data obtained were the mass-transfer efficiency in the extractor, the heat-transfer efficiency in the reboiler, the performance of each individual unit operation, the overall process performance, and some property measurements not previously obtained such as the boiling point elevation for alcohol-CO₂ solutions.

The alcohol product concentration was found to depend primarily on feed concentration and its equilibrium distribution between CO₂ and water. Other factors, such as the solvent-to-feed ratio, had little or no effect on product concentration. For feed concentrations of 10% (all concentrations in this report are given as weight percent) ethanol, isopropanol, and sec-butanol, the average product concentrations were 86%, 94%, and 94%, respectively. Similar product compositions were obtained when corn and molasses-based fermentation broths containing ethanol were tested. When lower feed concentrations were employed, the product concentration also decreased. For feeds containing less than 5% ethanol, isopropanol, and sec-butanol the average product concentrations were 77.6%, 87.2%, and 93.5%, respectively. Very high feed concentrations also resulted in reduced product concentration. Products containing 85.0% isopropanol and 91.0% sec-butanol were obtained when the feed contained more than 50% of these alcohols. Samples removed from the reboiler had a higher alcohol concentration than samples removed from the product flash tank, in the case of ethanol. Concentrations as high as 91-92% ethanol (CO₂-free basis) were observed in the reboiler. This decrease in product quality on flashing was not observed with the other two alcohols. The extracts obtained from isopropanol and sec-butanol feeds exceeded the azeotropic concentration for those alcohols of 88% and 68% respectively. However, this was not true with ethanol, for which the highest extract concentration measured was about 91%, falling short of the 95% azeotropic concentration.

High recovery of alcohol from the feed is important for both economic and environmental reasons. Equilibrium data obtained in the laboratory and from the literature were used to construct x-y diagrams for the distribution of alcohol between the water-rich phase and the carbon dioxide-rich phase for ethanol, isopropanol, and sec-butanol. A McCabe-Thiele-type analysis predicted alcohol concentrations in the raffinate and extract streams when the feed and solvent concentrations, the solvent-to-feed ratio, and the number of theoretical stages were specified.

The extractor tray efficiencies were estimated by plotting values of x_r/x_f and S/F obtained in the pilot plant against the equilibrium predictions, for those cases with a 10% feed concentration. For a seven-inch extractor tray spacing, the tray efficiencies were estimated for ethanol, isopropanol, and sec-butanol to be 19%, 45% and 50%, respectively. For ethanol and sec-butanol, a doubling of tray spacing (which required halving the number of trays) doubled the tray efficiencies. Thus, the effectiveness of the extractor on a per unit of height-basis remained constant, with a height equivalent of a theoretical stage, HETP, for ethanol of approximately 3 feet and for sec-butanol of 14 inches.

The use of an inverted tray stack, or "upcomer" trays, in which CO_2 instead of water was the continuous phase, caused a reduction in the tray efficiencies for both ethanol and sec-butanol. This disadvantage was balanced by an increase in the capacity of the column when used in the upcomer mode. The extent of this increase was not determined. Another advantage of the upcomer configuration was its ability to process feeds which emulsified when processed in a downcomer configuration.

Extractor capacity, defined as the total column flowrate (solvent plus feed), remained constant over a wide range of solvent-to-feed ratios. For synthetic solutions of ethanol, isopropanol, and sec-butanol the maximum flowrates achieved, while maintaining both hydraulic performance and the set S/F, was about 12 lbs/min for the 4" diameter extractor. This is the equivalent of a velocity of approximately 2.5 lbs/(ft² x sec).

The increase in the boiling temperature of mixtures of CO_2 and alcohol over the boiling temperature of pure CO_2 , at any given pressure, is the boiling point elevation (BPE) of the mixture. BPE data was obtained from the still during pilot plant operation. BPE values of 3°F were observed for ethanol solutions containing 40 to 95% CO_2 . A 4°F BPE was observed for a sec-butanol solution with 45% CO_2 . Thus, it appears these two alcohols have "flat" BPE curves in the 45-90% CO_2 range. The BPE data for isopropanol on the other hand is not flat. A 70% CO_2 solution has a 7°F BPE, while a 45% CO_2 solution has a BPE of roughly 10°F. Thus, an optimization for isopropanol will be more involved than that required for ethanol or sec-butanol.

The S/F for the process is related to the equilibrium distribution of the alcohol between water and CO_2 . The desired range of S/F are ten to twelve for ethanol, four to six for isopropanol, and one to two for sec-butanol. Thus, the separation energy for the higher molecular-weight alcohols is much lower than for the lower molecular-weight alcohols, such as ethanol. It should be noted that as S/F is decreased, the compression load shifts from the vapor recompression cycle compressor to the auxiliary compressors on flash vessels.

The low energy consumption of this process is the key to its attractiveness. The primary energy consumer in the process is the main CO_2 recycle compressor. The capacity of the compressor is determined primarily by the design capacity of the plant and the S/F ratio; while the compression ratio selection takes into account the BPE, and the reboiler heat transfer coefficient. Since all of these factors have been measured in the pilot plant to compare favorably with predictions which were used

to estimate energy consumption for the process on a commercial scale, it appears that the low energy consumption prediction for the process will hold.

The pilot-plant energy consumption is not directly related to commercial-scale plants. In the pilot plant, all CO_2 streams were flashed to 250-300 psi before recompression. Also, the streams were compressed to 1500 psi, well above commercial requirements, to allow for flow control. In addition, the compressor was oversized to allow system flexibility. Thus, a pilot-plant energy balance would not be representative of a commercial plants.

The CO_2 compression ratio is determined by the temperature increase required for efficient heat transfer to the reboiler liquid from the condensing solvent. The BPE, which is a function of composition, is important as it effects the amount of compression work required. The optimum reboiler composition is a balance of the increased compression ratio required to boil-up mixtures of higher alcohol concentration against the work required to recompress CO_2 flashing from the still bottoms product. Thus, the BPE as a function of reboiler composition was determined.

In conclusion, it was observed that the process is well-suited to the separation of alcohols from water. Low energy consumption, high product concentration, and high alcohol recovery can all be obtained. The higher alcohols operated at conditions leading to lower energy consumption than for the extraction of ethanol.

Further experimentation, refinements of equipment and procedures, and process modifications are recommended. This additional work will increase our knowledge of the system and the accuracy of the results of the analysis, as well as testing potential improvements to the process.

There are several opportunities to improve the system performance. Increased product concentration and decreased S/F might be achieved if the proper co-solvent is employed. Extraction at sub-ambient temperatures may also improve product quality. Increased recovery can be achieved by adding a rectifying section to the solvent recovery still. These changes are recommended primarily for ethanol and isopropanol and would require both a technical and economic analysis. The ethanol separation could benefit by modifying the flash process of the reboiler bottoms. As noted before, a decrease in alcohol concentration (CO_2 -free basis) from 91.5 to 87% is frequently observed as the bottoms are flashed to the product tank.

While the necessary measurements were made in the pilot plant, some modifications would allow complete closure of the heat and material balances. Gas meters could be added to all carbon dioxide inlet and vent lines, allowing the material balance to include CO_2 in addition to alcohol and water. Additional thermocouples, water flowmeters, and a mass flowmeter on the compressor by-pass stream would allow completion of the heat balance on the compressor. A data logging computer would also allow more frequent recording of data and faster turnaround of experimental analysis.

Alcohol concentrations as high as 92% EtOH (CO₂-free basis) have been observed in the reboiler, but the highest EtOH² product concentration obtained was 89.5% EtOH. In addition, it is often observed that the fraction of alcohol lost from the system is greater than the fraction of alcohol and water lost. This suggests that the product flash vessel and CO₂ vent line be redesigned.

Adding a rectifying section to the still, to study the effect of solvent purity on minimum raffinate concentration would also provide some needed information. Although it would be difficult to increase the size of the pilot plant extraction system significantly a larger scale demonstration plant would be appropriate at this time particularly for SBA and IPA extractions.

Finally, it must be remembered that industrial feeds will frequently be more complex than the synthetic feeds often used in the pilot plant. To maximize the effectiveness of the extractor, the industrial feeds of interest must be identified and tested. Pre-treatment methods for removal of solids and trace contaminants from these feeds should be studied. Avoiding the reductions in capacity and recovery, which these elements can cause, is likely to make such a pre-treatment economically desirable.

Industrial feedstreams would be generated by a number of different processes. Ethanol feedstreams could result from fermentation. Isopropanol is used in several pharmaceutical processes, and must be concentrated before being recycled. Sec-butanol is an intermediate in MEK production. In all these cases, it is possible that the feedstream would contain more than just the alcohol and water. Most pilot plant feeds were mixtures of pure alcohol and tap water. However, corn- and molasses-based fermentation broths were tested as part of the ethanol experiments and we can draw some conclusions on the effect of other components on the extraction. In all cases, the presence of solids and other components in the feed did not harm the quality of the product, although it did impact on the efficiency and operability of the process. Product obtained had ethanol concentrations as high or higher than average products obtained using synthetic feeds. These products also contained some of the color and aroma elements present in their feed. However the presence of trace components in the fermentation broths tested led to reductions in the amount of alcohol recovered in the product. These results indicate that pretreatment of some feeds may be desirable.

In the course of these experiments only one type of column internals was tested, sieve trays. While their performance was satisfactory it would be desirable to test a variety of other internal designs; for example, mechanical trays such as rotating discs or pulsed sieve trays, and packings both loose as well as fixed mesh types should be tried. Finally, additional runs should be performed with ethanol to obtain yield loss data over a broader range of solvent-to-feed ratios and to obtain additional reboiler composition data.

The use of sub-ambient temperatures in the extractor should also be investigated, as there is a possibility that this will increase product concentration. Other variations in the process which could potentially improve product quality should also be tested; these tests would involve the operation of the decanter, reboiler, and flash operations as well as modifications to simulate reflux in the extractor.

The use of a co-solvent is recommended for the ethanol-water separation. The intent of addition of a co-solvent would be to increase the distribution coefficient for the ethanol between the solvent and water. An optimal co-solvent would increase alcohol recovery and product concentration, and reduce energy consumption. It would only moderately increase the complexity of the process, while reducing the overall capital cost. Initial testing with 2-ethylhexanol in ethanol-water separations indicated that lower solvent rates were feasible.

The critical fluid extraction process appears to have a promising future with the potential to save substantial amounts of energy in the separation of a variety of organics from aqueous solutions.

II. INTRODUCTION

The primary objective of this pilot plant program was to demonstrate the technical feasibility of this process and to gather the engineering data required for process evaluation. This volume of the report has been prepared to serve several purposes. Its first purpose is to describe the pilot plant program and present the results. This includes a description of the process, the pilot plant hardware and operation, and the resulting data. Second, it is to demonstrate that the critical fluid extraction of alcohols from aqueous solutions is technically feasible. Third, it is to present an analysis of the data collected for use in the preparation of detailed commercial system designs. Finally, an analysis of the system's performance has been made to indicate process improvements, both in the pilot plant and in commercial design.

The structure of this report includes the process design basis in section III. Section IV contains the process flow sheet for the pilot plant, along with its equipment list and operating procedure. It also includes a comparison with a commercial scale flowsheet. Section V contains a detailed description of each run and analysis of the data. Section VI deals with a preliminary program with cosolvents.

The pilot plant was continuously improved throughout the program. As a result the quality and quantity of the data collected improved and increased with successive runs; however, not all runs used the same equipment configuration.

Prior evaluations of this critical fluid process to extract organic components from aqueous solutions have been based on engineering analyses and designs which drew from a body of literature (Volume I). Our pilot plant represented the first effort to demonstrate the use of continuous counter-current critical-fluid-liquid extraction combined with solvent recovery utilizing a vapor recompression cycle. The pilot-plant equipment was designed to permit scale-up to industrial capacities. Thus, the information gathered from the pilot plant would be applicable to the preparation of a commercial design, and technical success of the pilot plant could be translated into technical feasibility of a commercial-scale plant.

The pilot plant provided data for economic evaluations based on feeds and conditions actually tested. In addition, if there were satisfactory agreement between pilot-plant data and engineering models, the models could be used with greater confidence for cases not studied in the pilot plant.

III. PILOT-PLANT DESIGN BASIS

The design basis for the pilot plant differed from full scale plants in that the intent was to demonstrate and collect engineering data for the critical-fluid extraction process, not to produce product. Therefore, a major aspect of the design was its flexibility to handle a wide variety of feed materials, to operate under a variety of conditions, to test process modifications, and to produce the data necessary to analyze the process.

A. Feed Specifications

The feed materials were aqueous solutions of alcohols, representative of potential commercial feeds to the process. The alcohols - ethanol, isopropanol, and sec-butanol - were tested in concentrations ranging from 2% to 70%. The feeds were prepared by blending pure alcohols with tap water with the exception of the two feeds obtained from the fermentation of corn and molasses. These were obtained from commercial sources.

The alcohols used were commercial-grade isopropanol and sec-butanol obtained in drum quantities. A variety of ethanol sources were used: in addition to the fermentation broths already mentioned, SDA-30 (a "Specially Denatured Alcohol" formulation consisting of a 90:10 volume blend of ethanol:methanol), 190 proof, and 200 proof grain alcohol were all used. Feed-rate capacity ranged from about 0.1 to 10 lbs/min. Feed solutions were prepared in batches of about 30 gal in 35-gal stirred feed tanks mounted on a weigh scale.

B. Solvent CO₂ Specifications

The solvent requirements were approximately 100 lbs/run to initially fill the system and a make-up rate of about 15 lbs of CO₂ per 100 lbs of aqueous feed. Food-grade CO₂ was used and stored in a 6-ton insulated and refrigerated tank maintained at 0°F and 300 psi. The CO₂ gas from both the raffinate and product receiving tanks were vented to atmosphere. The CO₂ recycle rate varied from 0.5 to 13 lbs/min.

C. Product Specifications

The product quality and quantity varied considerably. Since product recovery was about 50% of the alcohol in the feed the product rates ranged from about 0.3 to 75 lbs/hr. The quality change with the different feeds and conditions was one of the parameters to be measured. Although they were not actual process by-products, the raffinate and decanter drain streams were regularly sampled and analyzed.

D. Operation

All unit operations of the pilot plant were run on a continuous basis, with a start-up and shut-down procedure which allowed experiments to be completed within an eight-hour shift. Run durations were usually between two and eight hours.

E. Utilities

Because the pilot plant was small scale, the utility requirements were easily met. The utilities used were electricity, cooling water, and instrument air. Electricity demand was about 30 kw at 110, 220, and 440 volts. The compressor was the largest energy consumer, followed by the feed pumps and the instruments. About 10 SCFM of compressed air at 20 and 35 psi was needed for the pneumatic controllers and the control valves with pneumatic positioners. Cooling water was required for direct cooling of the compressor as well as for cooling the compressed gas; the total consumption was about 10 gpm.

F. Control

The process control was partially automated. Independent control loops were used in several places to control pressure, flowrates, and liquid levels. Pneumatic controllers and control valves were used although flow and liquid level were measured electronically.

G. Data Collection

Data were collected manually. Runsheets were used for recording temperatures, pressures, flowrates, and visual observations. Compositional analysis was done for all components using gas chromatographs (GC) with both on-line sample analysis as well as manual sample collection and injection.

H. Equipment

The primary process equipment items were the extractor, the decanter, the still, the reboiler, the compressor, and the feed pump.

1. Extractor

Since the primary operation in the process was the extraction, much of the design was centered around the extractor and its needs. The extractor performance characteristics to be investigated were:

1. Hydraulical characteristics as influenced by method of operation;
2. Configurations of column internals;
3. Mass-transfer efficiency.

The extractor design characteristics were:

1. Interchangeable internals;
2. Four-inch diameter, chosen for several reasons:
 - a. A diameter of eight times the packing or hole size was considered necessary to avoid wall effects that would have a significant impact on performance. A 1/2" hole was the largest sieve hole size considered.

Calculations showed that a 3/8 - 1/2" packing size would be sufficient for satisfactory packing performance.

- b. A column capacity was desired which allowed reasonably small quantities of feed material to be processed while providing several gallons of product in a relatively short time.
- c. The 4" diameter was considered large enough to scale up to a small commercial plant size: ten times the diameter, about 3', would be large enough to handle certain commercial applications.

An extractor height of 80" allowed use of approximately 5 - 10 sieve trays, an adequate number for evaluating stage performance. With fewer stages, performance would be overly dependent on variables unrelated to stage efficiency such as nozzle design, head space, residence time, interfacial area in the head spaces, and backmixing in the vessel. With a very tall extraction column, stripping of the organic from water would be nearly complete, and hence differences in performance with different internals would be difficult to discern.

The extractor controls were as follows:

- 1. Aqueous feed flow into the extractor was metered using a variable-output metering pump.
- 2. Solvent CO₂ flow was metered into the extractor with a flow-control loop on the carbon dioxide output from the compressor.
- 3. Extract flow from the extractor was dependent on the extractor pressure, and thus was controlled with a back-pressure control loop maintaining the extractor at a set pressure.
- 4. Raffinate flow from the extractor was to be controlled by a loop maintaining a constant interface level at the top of the extractor. In practice, the response time between changes in the raffinate flow and a resultant change in the interface level was too slow (15-30 minutes) and required an excessively large proportional band on the controller (approximately 1000%). Instead, raffinate flow control was maintained with a manual valve as an adequate substitute.

2. Decanter

The function of the decanter was to coalesce and remove any water-rich phase from the extract stream after pressure reduction. Both the flashed gas and liquid extract then went on to the still. The dimensions of

the decanter were 4"-diameter by 3'-length, in a horizontal pressure vessel. It was filled with a coalescer mesh-type packing of all-stainless-steel construction.

3. Still

For the distillation column, only a small stripping section and no rectifying section were required. A large turn-down ratio was important. Physically the still was 4" in diameter and 60" long with 8 sections of 6" wire mesh packing including a demister at the top. It was also equipped with six feed, sample, and/or thermocouple ports on its side.

4. Reboiler

The purpose of the reboiler was to boil up CO_2 from the alcohol product solution in the still bottoms. At the same time it had to desuperheat, condense, and subcool the compressed CO_2 . It also required a variable surface area so that heat transfer coefficients could be measured at different fluid velocities through the tubes. Physically it consisted of four coils in parallel, each with a shutoff valve and each about 10' long with a diameter of 0.5" and a wall thickness of 0.065". The reboiler pot was a horizontal kettle type, 6" in diameter by 40" long. All reboiler parts were 316 stainless steel.

5. Compressor

The primary function of the compressor was to recompress the CO_2 vapors from the still tops at any still operating pressure. In addition, it initially filled the system with high pressure CO_2 from the 300-psi storage tank. Finally, it required sufficient flow capacity to flood the 4"-diameter extractor under any set of conditions. The compressor was a two-stage oil-free piston compressor with a 250-psi suction and a 2000-psi discharge pressure at a rated capacity of about 20 lbs/min.

6. Feed Pump

The feed required a wide capacity range over which it could accurately and reproducibly meter a liquid feed solution from atmospheric pressure against a head as high as 2000 psi. The desired flow range was about 0.1 to 10 lbs/min.

IV. PROCESS FLOW DIAGRAM

The pilot-plant process flow was similar to that of a liquid-liquid extraction system. The alcohol-containing aqueous feed was contacted with the CO_2 solvent in a counter-current sieve tray extraction column. The raffinate stripped of alcohol was discharged from the bottom of the extractor. The extract stream containing solvent and extracted alcohol was sent to a solvent stripping column. The solvent vapor was recovered from the top of the still, with the bottoms being substantially enriched in the alcohol-product. The overhead vapor was compressed, then passed through the tubeside of the reboiler. There the vapor was condensed, giving up its latent heat to boil-up the shellside liquid. The condensed CO_2 on the tubeside was then recycled to the extractor.

A. Flowsheet

The pilot plant process flowsheet is shown in Figure IV-1. The primary operations are extraction, distillation, and vapor recompression.

Feed was prepared in open-top 35-gallon stirred stainless steel tanks. It was pumped from the tank to the extractor. The aqueous phase, which was the continuous phase, flowed from stage to stage through downcomers in the extractor. After passing through the extractor, the raffinate was flashed through a metering valve to atmospheric pressure, and the liquid was collected in a 35-gallon raffinate tank. The CO_2 vapor which flashed out of the liquid upon pressure reduction was vented.

The liquid CO_2 solvent bubbled up through the extractor, coalescing above the extractor's uppermost tray. The position of this aqueous- CO_2 interface is referred to as the "extractor interface" or the "upper extractor interface". A similar interface existed at the bottom of the extractor and between each set of sieve trays. This CO_2 -rich phase exited via the extract line and was regulated by a back-pressure control loop maintaining a set extractor pressure.

The pressure drop of the extract stream through control valve, CV-1, was accompanied by a temperature drop and a partial flashing of liquid CO_2 to vapor. Since the solubility of water in CO_2 decreases with decreasing temperature, it was expected that in addition to CO_2 -rich liquid and vapor phases a water-rich phase should form with the temperature drop and vapor formation. The decanter through which the extract passed before entering the still was intended to remove the H_2O -rich phase from the extract stream. In practice, the decanter also removed water which was inadvertently carried out of the extractor as entrained dense phase in the extract.

The CO_2 -rich liquid-vapor mixture was drawn off the top of the decanter and sent to the still. Because of the high volatility of CO_2 relative to the alcohol product, the still's major function was to vaporize CO_2 . A mixture of approximately 50 wt% CO_2 was maintained in the reboiler. The overhead vapor was at least 99% CO_2 .

The reboiler bottoms was drawn off to maintain a constant liquid level in the reboiler. This stream was flashed to atmospheric pressure through CV-5 then into the product collection tank. The CO_2 vapor resulting

PILOT-PLANT PROCESS FLOW SHEET

DESIGNED BY	DATE	APPROVED BY	DATE	PROJECT NO.	75629	PILOT PLANT	DIAGRAM
REVIEWED BY	DATE	APPROVED BY	DATE	PROJECT NO.	75629	PILOT PLANT	DIAGRAM

FIGURE IV-1

from the flash was vented. There was no meter to measure the volume of CO₂ vented.

Vaporized CO₂ from the top of the still passed through back pressure control valve, CV-2, flashing to the compressor's inlet pressure.

The CO₂ vapor was combined with make-up CO₂ and recompressed. The vapor leaving the compressor was at a higher temperature and pressure than required for recycle to the reboiler. The outlet vapor passed through a flow control valve, where its pressure was reduced to extractor pressure. Excess heat was removed in the trim heat exchanger, then the hot vapor entered the reboiler. The vapor was condensed in the reboiler tubes; however, since the pressure was in excess of the critical pressure there was no actual phase change, although there was a large density change. The CO₂ was then recycled to the extractor as fresh solvent.

Since the design intent was to have the pilot plant operation both simple and flexible, one compressor was used for all pilot plant services. This included pressurization of CO₂ during start-up, pressurization of make-up CO₂ and CO₂ recycle, as well as operation at high flows and pressures. Thus, the inlet pressure for the compressor was 250 psi, and the exit pressure 2000 psi. This resulted in the necessity of reducing the still tops pressure.

While the oversized compressor allowed flexibility of operation, a by-pass control loop was required in order to maintain desired flowrates. The compressor was run at full capacity and the discharge stream was split. One portion was flashed through a back-pressure control valve to the compressor inlet. The remainder of the stream went to the process.

Carbon dioxide was stored in a 6-ton capacity tank at 300 psi and 32°F. Both vapor and liquid draw offs were available, with vapor supplied to the compressor inlet surge vessel.

B. Comparison with Commercial Scale Flowsheet

There were many minor differences between the pilot and commercial scales of operation; however, the one major variation was in the compression scheme. While a typical commercial design has three or more compressors, each operating at a different pressure, the pilot plant had only one compressor. This required the still tops to be flashed to low pressure before being recompressed. Also, the raffinate stream and reboiler bottoms were flashed directly to atmospheric pressure, with CO₂ gas vented rather than recovered. The industrial process calls for these streams to be flashed to intermediate pressures, heated and then flashed to atmospheric pressure, with the CO₂ vapor collected and recompressed. No heat was supplied to any flashing stream in the pilot plant. The pilot plant was also designed for use under a wide range of conditions and capacities, and it was instrumented for collection of design data.

The pilot plant extractor was much shorter and had fewer sieve stages than an industrial unit. Space, handling, and availability considerations all contributed to the decision to limit the pilot plant extractor height to

approximately 7 ft. In most cases, this did not result in the high recovery which an industrial design demands. However, it was well suited for studying capacity and mass transfer efficiency.

C. Equipment List

The extractor specifications were as follows:

1. 4" diameter x 80" vertical vessel;
2. Design pressure: 1400 psi;
3. Design temperature: 125°F;
4. Stainless steel construction;
5. Windows full extractor length (a windowless extractor with a 2000 psi pressure rating was also used);
6. Interface level control;
7. Pressure control;
8. Removable sieve-tray stacks consisting of 4, 8, and 16 trays with spacings of 14, 7, and 3.5 inches respectively;
9. Each tray had approximately 90 0.125" holes which were on a 2.5 diameter center-to-center spacing on a triangular pattern.
10. The downcomers were 1.125" diameter with removable orifices; this allowed the downcomer diameter to be reduced down to 0.25".
11. The tray stacks were a combination of teflon and stainless steel.
12. There were temperature, pressure, and liquid-liquid interface indicators for the extractor; in addition, each sieve tray could be viewed through the extractor windows and its performance observed.

The distillation column specifications were:

1. 4" diameter x 60" vertical vessel;
2. Design pressure: 1400 psi;
3. Design temperature: 150°F;
4. Stainless steel construction;
5. 8 sections, each 6" long, of wire-mesh packing;
6. Stripping section only; no condenser or rectifying section;
7. Indicators included still pressure and 5 thermocouples along the length of the still;
8. Pressure control;
9. The still was mounted directly on the reboiler

The reboiler specifications were:

1. 6" diameter x 40" horizontal vessel;
2. Design pressure: 1400 psi shell side and 2000 psi tubeside;
3. Design temperature: 200°F;
4. Four heat-exchanger coils, each 0.5" stainless-steel tubing with a wall thickness of 0.065", and 10' long;
5. The coils were in parallel and each had its own shut off valve so that the active surface area within the heat exchanger could be varied for measurement of heat transfer characteristics;
6. Level was maintained in the reboiler by controlling the liquid bottoms product flow.

The compressor was a two-stage reciprocating, oil-free, carbon dioxide compressor:

1. 250 psi inlet pressure;
2. 700 psi interstage pressure;
3. 2000 psi discharge pressure;
4. Interstage and aftercoolers were water-cooled;
5. Capacity was about 20 lbs/min;
6. Discharge pressure was maintained with a back pressure bypass-to-suction control loop.

The decanter specifications were:

1. 4" diameter x 30" horizontal vessel;
2. Design pressure: 1400 psi;
3. Design temperature: 125°F;
4. Packing was a wire-mesh coalscer.

The feed-pump specifications were:

1. Maximum capacity: 100 gph, variable from 1-100% of capacity by adjusting stroke length;
2. Maximum discharge pressure: 2000 psi.

D. Operating Procedures

Due to its flexible design, the pilot plant could be operated in a variety of ways. The operating procedure given here was one which was frequently used. It was only one of many operating procedures.

1. Start-Up

Several items of preparation were performed routinely. The thermocouple indicator was re-zeroed using an ice-water bath and a reference thermocouple. All tanks and vessels were pressurized to low pressures (10-20 psi) with air or CO₂, in order to blow out any trapped liquids. Standards were run on the GC to ensure that accurate weighting factors were used.

The aqueous feed pump was turned on and set for a flowrate of 1 lb/min. When the extractor was roughly 3/5 full of aqueous solution, the CO₂ storage tank valve was opened, along with the CO₂ flow controller, to pressurize the system to 250-300 psi. At this time the raffinate and product flash control valves were both closed, as was the still-pressure control valve.

With the extractor 3/5 full and the pressure at 250 psi throughout the system, the cooling water to the compressor and the trim heat exchanger was turned on. The extractor and still pressure controllers were then set for the desired operating pressures. The raffinate control needle valve was opened slightly.

With the manual by-pass loop around the compressor fully open, the compressor was turned on.

With the extractor pressure control valve closed (because $P < P_{\text{set}}$), the pressure in the extractor increased rapidly from 250 psi to the saturation pressure at the extractor temperature, usually between 850 and 1000 psi. Liquid CO_2 began to condense in the extractor and the extractor pressure remained constant until the extractor was full of liquid CO_2 .

At this time the compressor manual by-pass control valve and the CO_2 -solvent flow control valve were adjusted so that approximately 1.0 lb/min of CO_2 was flowing into the extractor. When the extractor was full of liquid, the pressure again rose rapidly until it reached the 1200-psi setpoint, and the pressure control valve opened, allowing extract to flow out of the extractor.

During this pressurization, the extractor interface level was observed, and the raffinate control valve adjusted. The proper setting matched the feed and raffinate flows, such that the extractor interface level was constant. This adjustment could be made by either observing the interface level in the extractor window or using the capacitance level indicator.

As CO_2 started to enter the still, the still pressure rose to the set pressure, between 600 and 750 psi. As this pressure was approached, the still-pressure control valve opened, and CO_2 started flowing from the still back to the compressor inlet. The sight gauge in the still tops line was observed, ensuring that the still was not flooded and that only CO_2 vapor was in the still tops.

With the extractor and still operating at the desired pressures, flowrate changes could be made. The raffinate control valve was adjusted to match any change in feedrate. While these adjustments were made the compressor inlet, interstage, and outlet temperatures and pressures, as well as the extractor temperature, were observed and adjusted as necessary.

2. Operation

Once the set flowrates and hydraulic balance in the extractor had been obtained, the extractor began to approach mass-transfer or compositional steady-state. The time required to reach this steady-state condition depended on both the feed and solvent flowrates. Steady-state was determined by compositional analysis of raffinate samples on a frequent basis. Generally, 1.5 to 2 aqueous hold-up volumes had to be displaced before the raffinate concentration stabilized.

In addition to raffinate samples, analyses of samples from the product tank, decanter, and reboiler were taken regularly. Two gas chromatographs (GC) were used, one for the above-mentioned liquid samples, and the other for on-line sampling of solvent and extract streams. The on-line samples were taken through high pressure 0.125" tubing to a flash valves in a hot oil bath (380°F) with the line from the flash valve to the GC sample valve wrapped with heating tape.

While running, the liquid levels of the feed tank, the raffinate receiver, the reboiler, the product receiver, and the extractor interface were checked frequently, and adjustments made as needed. Any aqueous phase which collected in the decanter was manually removed and sampled. In addition all of the data required for the run sheets was recorded.

3. Shut-Down

The system was quite simple to shut down. The feed pump and the raffinate control valve as well as a valve in the feed line were shut off simultaneously. The CO_2 tank valve was closed. The flow of CO_2 through the extractor was reduced by partially closing the flow control valve and opening the manual by-pass valve. The power to the compressor was then turned off. When the compressor was turned off, to avoid a high pressure surge to the compressor inlet, which in turn activates a relief valve, the surge vessel pressure control valve was manually opened at the same time that compressor power was shut off. CO_2 in the system was also vented via the product flash vessel. After the raffinate tank had been drained, the residual aqueous solution in the extractor was drained. All raffinate, decanter, product, and extractor samples and residues were weighed to complete the mass balance.

V. EXPERIMENTAL

A. Program

The pilot plant experimental program consisted of extraction of feedstocks of aqueous solutions of ethanol, isopropanol, and sec-butanol. The ethanol feeds were prepared both synthetically by mixing ethanol and water, as well as by using commercial fermentation broths. The isopropanol and sec-butanol were prepared synthetically only. For each feed, the capacity and mass-transfer efficiency for the extraction were evaluated, as well as the overall system performance.

The process evaluation information required from the pilot program was that needed to design the major equipment items: the extractor, the reboiler, and the compressor. In a particular experiment a feedstock, feedrate, extractor temperature and pressure, and still pressure were selected. The alcohol content of the raffinate and of the alcohol product recovered were measured to determine the mass-transfer efficiency. Visual observation of the extractor and its outlet streams was used to determine the column capacity and hydraulic characteristics of the extraction. For thermodynamic and heat transfer characteristics of the process to be evaluated, measurements were taken of the reboiler temperature, pressure, liquid level, and composition, along with the tube-side temperatures in and out, pressure, flow rate, and the number of active coils. Although the compressor temperatures, pressures, amperage, and cooling water flowrate were measured, they were used primarily to warn of any compressor malfunction. Since pure CO_2 thermodynamic properties are well understood, it was not necessary to collect data on compression for design evaluation.

The program for each feed consisted of several experimental runs, with most runs lasting five to twelve hours. Among the various runs, the sieve-tray configuration and the feed concentration were varied. During any given run, the parameters varied were solvent-to-feed ratio, total flowrate, and still pressure. At each operating condition, the concentrations of alcohol in the raffinate, product, solvent, and extract

streams were determined. Temperatures and pressures throughout the system were recorded on a regular basis. Reboiler compositions were also obtained but on a less frequent basis.

Tables V-1, V-2, V-3, and V-4 list and briefly describe the ethanol E and W series, isopropanol, and sec-butanol runs, respectively. A description of the extractor and tray stack, the run number, a feed description and concentration, and the objectives and comments are given for each run.

The data collected on a run-by-run basis is presented in the next section, accompanied by a brief statement of objectives and observations for each run.

B. Data and Analysis

This section is organized into subsections according to the type of data collected. Their order is as follows:

1. Generalized run summaries
2. Mass balance
3. Extractor performance
4. Compositional analysis
5. Still and reboiler performance

While several runs were performed prior to those reported herein, the primary function of those initial runs was to establish pilot-plant operating procedures.

Tables V-5 through V-33 are data summaries for each run which give average pressures and temperatures for the extractor and still, feed compositions, tray-stack specification, feed and solvent flowrates (m_f and m_s), alcohol concentrations in the raffinate and product, comments on the operation, and a mass-balance summary. Tables V-34 through V-36 are the material balances for each of the alcohols, including the alcohol recoveries. Tables V-37 through V-39 are the calculated recoveries for each condition tested. Table V-40 has the tray efficiencies and theoretical height equivalent of a single stage. Reboiler compositional data, which is relevant to the still performance, are presented in Tables V-41 through V-43. Tables V-44 through V-46 give product compositions for each of the alcohols as a function of feed concentration and solvent to feed ratio. Table V-47 summarizes these compositions and compares them with the azeotropes for each of the alcohols. Tables V-48 through V-50 have the reboiler and still temperatures used in calculating heat-transfer coefficients and other reboiler characteristics. Table V-51 has the boiling-point elevations measured and the reboiler composition at the time of measurement. Finally, Tables V-52 through V-54 give both boiling-point elevations and heat-transfer coefficients.

1. Run Summaries

The data summaries giving a description of each run, its purpose and observations, are presented first for ethanol, then for isopropanol, and finally for sec-butanol.

Table V-1

ETHANOL RUN SCHEDULE

All "E" series runs were made in a windowless extractor, with nine teflon sieve trays with downcomers spaced 7" apart.

Run #	Feed Rate	Objective and Comments
E1	Synthetic 14% EtOH	Demonstrate system operability using a feed with which we were familiar. Increase solvent and feed rates (maintaining the design S/F = 10) until flooding, to determine extractor capacity, and mass transfer efficiency as a function of flowrate.
E2	Corn Broth 9% EtOH	Examine system operability and performance using a feed containing solids (~3%) and a trace organics. Repeat outline of E1, looking for a shift in capacity with the change in feed.
E3	Corn Broth 9% EtOH	Using a decanted broth, continue to investigate operability and concentrate on performance at a fixed set of flow rates, set at roughly 70-80% of those at which flooding was observed in E2.
E4 E5	Molasses Mash 9% EtOH	As with E2 and E3, substituting molasses mash for corn broth.
E6	Synthetic 5% EtOH	Operate with a low feed concentration to simulate the lower section of a taller extractor. A 5% EtOH feed was used to demonstrate that a lower raffinate concentration could be obtained.
E7	Synthetic 20% EtOH	Operate with a high feed concentration to simulate a process in which ethanol product is recycled, with the aim of obtaining a more concentrated product.

TABLE V-2
Ethanol Run Schedule
"W" Series

All "W" Series were made in a windowed extractor

Run#	Feed Rate	Tray Spacing	#Trays	Upcomer/ Downcomer Diameter	Tray Stack Configuration	Tray Construction	Objective and Comments
W1	10% Synthetic	7"	9	1/4"	Downcomer	Teflon	Establish capacity, tray efficiency at various flowrates. Trays did not disperse CO ₂ properly.
W2	2-1/2% Synthetic	7"	9	1/4"	Downcomer	Teflon	Determine tray efficiencies at lower concentrations
W3	10% Synthetic	7"	9	1/4"	Upcomer	Teflon	Evaluate feasibility of upcomer configuration. (1/4" upcomers proved too small.)
W4	10% Synthetic	14"	4	1-1/8"	Upcomer	Teflon	Evaluate feasibility of upcomer configuration. Performed satisfactorily.
W5	6% Molasses	14"	4	1-1/8"	Upcomer	Teflon	Evaluate potential of upcomer configuration in abating molasses foaming problem.
W6	10% Synthetic & Co-solvent	14"	4	1-1/8"	Upcomer	Teflon	Evaluate effect of co-solvent ethyl hexanol on distribution coefficient. None observed.
W7	10% Synthetic	7"	9	1/4"	Downcomer	Teflon & Stainless Steel	Test new sieve trays. Dispersed CO ₂ properly but solvent nozzle too close to downcomer.
W8	10% Synthetic	7"	8	1/4"	Downcomer	Teflon & Stainless Steel	New sieve trays perform as expected. Determine tray efficiency at various flowrates.
W9	14% Synthetic	7"	8	1/4"	Downcomer	Teflon & Stainless Steel	Look for change in product concentration with change in still pressure.
W10	10% Synthetic	14"	4	1/4"	Downcomer	Teflon & Stainless Steel	Look for change in tray efficiency with change in tray spacing.

Table V-3

ISOPROPANOL RUN SCHEDULE

All "I" series runs were made in a windowed extractor with eight teflon-stainless steel sandwich-type sieve trays with downcomers spaced 7" apart.

Run#	Feed Rate	Objective and Comments
I1	60%	Establish capacity, tray efficiencies, product quality for high concentration feeds.
I2	10%	Vary S/F ratio, keeping the sum of the solvent (M_s) and feed rates (M_f) at approximately 6 lbs/min. Also, determine capacity w/S/F = 3.
I3	10%	At a given S/F, vary M_s and M_f , and evaluate tray efficiency, recovery and product quality.
I4	2%	Attempt to obtain very low raffinate compositions to simulate the bottom section of a tall extraction column.
I5	20%	Attempt to produce higher product concentration via higher feed concentration.

Table V-4

SEC-BUTANOL RUN SCHEDULE

All 'B' series runs were made in a windowed extractor.

Run#	Feed Rate	Tray Spacing	Tray Construction	Purpose
B1	10%	14"	Teflon	Establish capacity and efficiency of upcomer tray system. "Shake-down" butanol handling.
B2	10%	7"	Teflon	Evaluate change in tray efficiency with increased tray spacing for upcomer systems.
B3	10%	7"	Teflon & Stainless Steel	Observe changes in performance with varying S/F.
B4	10%	7"	Teflon & Stainless Steel	Evaluate performance (tray efficiency butanol recovery, product quality) with S/F = 0.5.
B5	10%	7"	Teflon & Stainless Steel	Evaluate performance using S/F = 1.5.
B6	10%	14"	Teflon & Stainless Steel	Evaluate change in tray efficiency with increased tray spacing for downcomer system.
B7	2%	14"	Teflon & Stainless Steel	Evaluate ability to obtain very high recovery -- models lower section of tall extractor.
B8	70%	7"	Teflon & Stainless Steel	Evaluate ability to process high concentration feeds.

a. Ethanol

The ethanol (EtOH) experiments were conducted in two phases. During the first phase runs, designated E1 through E7 in Tables V-5 through V-10, a steel-walled extractor having no windows was employed. A windowed extraction vessel was employed for the second phase of the EtOH experiments, which were designated W1 to W10, summarized in Tables V-11 through V-20.

The same tray stack was used for E1 through E7. It consisted of nine teflon sieve trays spaced 7" apart. Each sieve tray had 88-1/8 inch sieve holes, and a 6"-long by 1-1/4"-outside diameter downcomer. Each downcomer had a teflon plug inserted in the last inch of its length, which effectively reduced its diameter to 1/4". Feeds used for these runs included synthetic mixtures of EtOH and water, and fermentation broths, both corn- and molasses-based. The alcohol used to prepare the synthetic feeds during this first phase was SDA-30, a 90/10 mixture of EtOH-MeOH. The fermentation broths were obtained from commercial sources but had preservatives added to them.

The second phase experiments utilizing the windowed extractor used synthetic feeds prepared from anhydrous grain alcohol and water, with the exception of W6, which used a molasses-based fermentation broth. Two tray stack configurations were tested in these runs, one used a standard downcomer, the other used an "upcomer" configuration (Figure V-1). In the standard downcomer configuration the CO₂-rich phase is dispersed in the aqueous phase, while in the upcomer configuration the aqueous phase is dispersed in a continuous CO₂-rich phase. Both teflon and teflon-stainless-steel "sandwich" sieve trays (Figure V-2) were tested. The latter were employed to get proper drop formation in the downcomer configuration. Downcomer (or upcomer) orifice sizes were varied as needed to provide the appropriate pressure drop across the column for formation of a 1/2" to 1" coalesced layer of the dispersed phase below (or above) each tray. Tray spacings of 7" and 14" were tested; variations in the tray stack are specified in the run summaries. The effect of varying still pressure between 600 and 750 psi was also investigated in this series of runs. Except as noted, all compositions, concentrations, and weights are on a CO₂-free basis.

In run E1, the extractor displayed an increase in efficiency as the flooding point was approached, contrary to our expectations. With a solvent-to-feed ratio of 10, flooding was observed when solvent flow exceeded about 10.5 lbs/min, or a superficial mass velocity of about 2 lbs/ft²-sec.

The corn broth used in run E2 had roughly 3% solids, and a higher viscosity than the synthetic feed. The solids clogged the raffinate needle valve, making control of the extractor interface level very difficult. Flooding occurred at a lower flowrate than that experienced with the synthetic feed, possibly due to its higher viscosity. The product was collected in two phases, both of which were predominantly EtOH. The heavy phase was oily, and on further analysis, was found to contain esters such as ethyl oleate. The source of these materials was most probably corn oil and its derivatives, which were extracted from the corn solids.

ETHANOL RUN E1 DATA SUMMARY

$$P \text{ (Extractor)} = 1200 \text{ psi}$$

P (Still) = 750 psi

Feed: Synthetic 13.86% (wt) EtOH, 1.65% MeOH (14.09% EtOH on MeOH-free basis)

11:00-12:00

Total Feed	=	282	lbs
Total Output	=	283	lbs
Decanter	=	5.9	lbs
Raffinate	=	241	lbs
Product	=	19.9	lbs
Extractor Residual	=	15.8	lbs
Reboiler Residual	=	0.45	lbs

- Operation was very smooth
- Flooding overhead was observed when M_s and M_f exceeded about 10.5 and 1.25 lb/min, respectively.

TABLE V-6

ETHANOL RUN E2 DATA SUMMARY

T (Extractor) = 81°F

T (Still) = 63°F

Feed: Corn Fermentation Broth: 9.7% EtOH, 3% solids, 1% Sodium Benzoate Preservative,

Viscosity 3-20 cp

Viscosity 3-20 cp			Solvent to-Feed Ratio	Ethanol Concentration (wt %)					
Time	Feed Rate	Solvent Rate		Raffinate			Product		
	(lbs/min)	(lbs/min)		Average	High	Low	Average	High	Low
12:00-1:00		Start-up							
1:00-2:40	0.275	3.33	12.1	4.4	4.7	4.2	74.0		
2:40-5:00	0.623	6.00	9.60	4.6	6.2	3.8	85.9	87.1	84.7

Mass Balance Summary:(CO₂-free basis)

Total Feed	=	169	lbs
Total Output		160	lbs
Decanter		5.7	lbs
Raffinate		146.9	lbs
Product		7.03	lbs

Notes:

- Operation was hindered by high solids content - A clogged raffinate valve left the extractor interface level controller inoperative.
- A two-phase product was collected, 7 lbs. of light phase, 0.9 lbs of dense phase, which contained high MW esters, e.g., oleates, presumably corn oil. Benzoc acid was present in both product phases.
- A distribution coefficient of 0.04 (wt basis) was measured in the laboratory for this feed.

TABLE V-7

ETHANOL RUN E3 DATA SUMMARY

T (Extractor) = 72°F

P (Extractor) = 1200 psi

T (Still) = 61°F

P (Still) = 750 psi

Feed: Corn Fermentation Broth: 8.77% EtOH (wt), low solids, 1% Sodium Benzoate

Time	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	Ethanol Concentration (wt %)					
				Raffinate			Product [*]		
				Average	High	Low	Average	High	Low
10:25-11:30		Start-up							
11:30-12:30	0.328	4.54	13.8	3.69	3.99	3.26	88.3	88.9	86.49
12:30-1:10	0.579	4.25	7.35	4.00	4.31	3.69	89.1	89.2	89.0
1:10-3:20	0.405	4.51	11.1	5.51	6.67	4.59	87.5	90.2	81.2

Mass Balance Summary: (CO₂-free basis)

Total Feed	= 143	lbs
Total Output	= 142.5	lbs
Decanter	= 3.0	lbs
Raffinate	= 112.8	lbs
Product	= 7.02	lbs
Extractor Residual	= 19.7	lbs

Notes:

* Some MeOH found in initial product, results reported on an MeOH-free basis.

- This feed has coarse solids removed by siphoning feed from top of a drum in which the solids had been allowed to settle. This solved most of the problems observed during E2.

ETHANOL RUN E4 DATA SUMMARY

T (Extractor) = 66°F P (Extractor) = 1200 psi
T (Still) = 64°F P (Still) = 750 psi
Feed: Molasses Fermentation Broth: 8.84% (wt) EtOH

Time	<u>Feed Rate</u> (lbs/min)	<u>Solvent Rate</u> (lbs/min)	<u>Solvent- to-Feed Ratio</u>	<u>Ethanol Concentration (wt %)</u>						
				<u>Raffinate</u>			<u>Product</u>			
				Average	High	Low	Average	High	Low	
2:30 - 3:30		Start-up								
3:30 - 4:30	0.126	2.69	21.4	6.69	-	-				
4:30 - 5:20	0.333	2.69	8.06	3.78	3.91	3.68	90			

Mass Balance Summary: (CO₂-free basis)

Total Feed	=	53.0 lbs
Total Output	=	46.9 lbs
	=	16.4 lbs
	=	30.2 lbs
	=	0.3 lbs

Notes:

- Molasses mash had a severe foaming problem
 - Much of the feed was carried over with the extract, but was separated in the decanter
- Cumulative decanter analysis was 8.11% EtOH.
- Foaming problem caused loss of extractor interface level control. This resulted in the interface varying from the top of the column to 1/2 empty.
 - The run was stopped early due to the foaming problem.
 - Run E5 was a repeat of E4, but with a silicone anti-foaming agent and increased EtOH concentration. This did not solve the foaming problem, so the run was discontinued.

TABLE V-9

ETHANOL RUN E6 DATA SUMMARY

T (Extractor) = 82°F
 T (Still) = 61°F

P (Extractor) = 1200 psi
 P (Still) = 750 psi

Time	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	Ethanol Concentration (wt % on a MeOH-free Basis)					
				Raffinate			Product		
				Average	High	Low	Average	High	Low
2:55-4:00		Start-up							
4:00-5:45	0.832	7.60	9.13	2.56	3.00	2.08	81.7	81.9	81.4

Mass Balance Summary: (CO₂-free basis)

Total Feed	=	138.5	lbs
Total Outputs	=	132.1	lbs
Decanter	=	0	lbs
Raffinate	=	115.8	lbs
Product	=	2.83	lbs
Extractor Residual	=	13.5	

NOTES: This run was used to simulate the bottom section of an extractor with many sieve trays, demonstrating that a low EtOH concentration in the raffinate would result from using a low feed concentration.

TABLE V-10

ETHANOL RUN E7 DATA SUMMARY

T (Extractor) = 73°F P (Extractor) = 1220 psi
 T (Still) = 61°F P (Still) = 764 psi
 Feed: Synthetic; 19.4% EtOH, 2.5% MeOH (19.9% EtOH on MeOH-free basis)

Time	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	Ethanol Concentration (wt % on an MeOH-free basis)					
				Raffinate			Product		
				Average	High	Low	Average	High	Low
10:15-11:05		Start-up							
11:05-11:35	0.284	2.69	9.46	8.68	8.69	8.67			
	0.625	5.92							
11:35- 2:35	0.332	3.45	10.4	8.90	9.91	7.95	89.53	90.78	88.28
	0.730	7.59							

Mass Balance Summary: (CO₂-free basis)

Total Feed = 179.5 lbs
 Total Output = 162.8 lbs
 Decanter = 2.0 lbs
 Raffinate = 130.5 lbs
 Product = 15.4 lbs
 Extractor Residual = 15.0 lbs

NOTES:

- This run was used to simulate partial reflux or recycle of extracted alcohol by using a high-alcohol feed concentration.
- A substantially higher product concentration was not obtained. However, it is possible that some water was left in the system from the previous run, or that alcohol was preferentially lost from the product in the product flash tank vent gas.

Table V-11

ETHANOL RUN W1 DATA SUMMARY

T(extractor) = 73°F P(extractor) = 1200 psi
 T(still) = 61°F P(still) = 750 psi
 Feed: Synthetic, 10.39% Ethanol
 Trays: 9 Trays, All-Teflon, 1/4" Downcomer

<u>Time</u>	<u>Feed Rate</u> (lbs/min)	<u>Solvent Rate</u> (lbs/min)	<u>Solvent- to-Feed Ratio</u>	<u>Ethanol Concentration (wt%)</u>				
				<u>Raffinate</u>			<u>Product</u>	<u>Solvent</u>
				<u>Average</u>	<u>High</u>	<u>Low</u>		
2:30-3:30	Start-up							
3:30-4:35	0.59	5.95	10.1	5.00	5.15	4.85	86.2	0.14
4:35-5:30	0.73	7.65	10.5	4.29	4.62	3.99	87.45	0.11
5:30-5:45	0.88	9.14	10.4				87.68	
5:45-6:10	0.92	12.3	13.4	3.19			84.15	0.13
			Cumulative -	4.69				

Mass Balance Summary: (CO₂-free basis)

Total Feed = 139.5 lbs
 Total Output = 130.9 lbs
 Raffinate = 94.0 lbs
 Decanter = 5.43 lbs
 Extractor Residual = 25.0 lbs
 Product = 6.51 lbs

Notes: Trays were not operating properly; CO₂ was oozing up through the holes, rather than jetting through and breaking off into droplets. This did not affect pilot plant operation, just extractor efficiency.

Table V-12

ETHANOL RUN W2 DATA SUMMARY

T(extractor) = 81°F P(extractor) = 1200 psi
 T(still) = 61°F P(still) = 750 psi
 Feed: Synthetic, 2.27% Ethanol
 Trays: 9 Trays, All-Teflon, 1/4" Downcomer

Time	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	Ethanol Concentration (wt%)				
				Raffinate			Product	Solvent
				Average	High	Low		
10:50-11:30	Start-up							
11:30- 1:40	0.51	5.68	11.1	1.03	1.12	0.92	80.9	0.03
1:40- 3:15	0.88	7.59	8.65	0.92	0.96	0.85	70.1	0.03
Cumulative - 1.10								

Mass Balance Summary: (CO₂-free basis)

Total Feed = 184.0 lbs
 Total Output = 155.0 lbs
 Raffinate = 121.65 lbs
 Decanter = 4.58 lbs
 Extractor Residual = 26.52 lbs
 Product = 2.10 lbs

Notes: Two extractor windows leaked, causing the larger than usual discrepancy in the mass balance. Same problem with tray performance as in W1, but tray efficiency seems roughly the same for the two runs, despite large difference in feed concentrations used.

Table V-13

ETHANOL RUN W3 DATA SUMMARY

T(extractor) = 73°F P(extractor) = 1200 psi
T(still) = 68°F P (still) = 750 psi
Feed: Synthetic, 10.23% Ethanol
Trays: 9 Trays, All-Teflon, 1/4" Upcomer

Time	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	Ethanol Concentration (wt%)			Product	Solvent
				Raffinate				
				Average	High	Low		
3:00-4:00	Start-up							
4:00-4:30	0.80	2.76	3.45	6.07			--	
4:30-4:55	0.19	4.70	24.7	5.82	6.24	5.41		
4:55-5:25	0.19	11.9	62.6	5.71			81.7	

No Mass Balance for this run.

Notes: Run was discontinued early. The 1/4" upcomer orifices presented too high a pressure drop for the solvent, and thus requiring a head of water on the trays almost greater than the tray spacing. Most water-phase flow was by-passing the trays around the windows. No window leaks during this run.

Table V-14

ETHANOL RUN W4 DATA SUMMARY

T(extractor) = 77°F P(extractor) = 1200 psi
 T(still) = 60°F P(still) = 750 psi
 Feed: Synthetic, 10.1% Ethanol until 5:35, 6.68% after 5:35
 Trays: 4 Trays, All-Teflon, 1 1/8" Upcomers

Time	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	Ethanol Concentration (wt%)				
				Raffinate			Product	Solvent
				Average	High	Low		
2:20-3:10	Start-up							
3:10-3:45	0.59	3.55	6.02	8.27	9.11	7.21		0.11
3:45-4:55	0.85	7.85	9.23	6.60	7.35	5.58	86.3	0.11
4:55-5:15	1.02	13.1*	12.9	5.38	--	--	--	--
5:15-5:50	2.31	10.2	4.41	8.06	--	--	87.0	--
5:50-6:00	3.82**	10.2	2.67	--	--	--	84.8	--

Notes: No mass balance for this run, since raffinate was re-used as feed. Tray spacing and upcomer size were increased, and the trays functioned properly. There was no problem with drop formation experienced in the downcomer configuration with these all-teflon trays.

The high solvent flow through the downcomers entrained drops of the water phase. The high feed rate led to a mixing of extract and feed into an emulsion, which was carried over with the extract.

One extractor window started to leak toward the end of the run.

Table V-15

ETHANOL RUN W5 DATA SUMMARY

T(extractor) = 62°F P(extractor) = 1200 psi
T(still) = 35°F P(still) = 590 psi
Feed: Distillers Molasses Mash, 6.15% Ethanol
Trays: 4 Trays, All-Teflon, 1 1/8" Upcomers

<u>Time</u>	<u>Feed Rate</u> (lbs/min)	<u>Solvent- Rate</u> (lbs/min)	<u>Solvent- to-Feed Ratio</u>	<u>Ethanol Concentration (wt%)</u>			<u>Product</u>	<u>Solvent</u>
				<u>Average</u>	<u>High</u>	<u>Low</u>		
10:55-11:45	Start-up							
11:45-12:40	0.32	1.68	5.33	4.7	4.9	4.4	86.4	0.02
12:40- 1:20	0.94	5.51	5.85	4.7	4.8	4.5	--	0.02
1:20- 3:05	0.53	5.51	10.3	4.5	5.0	3.5	85.9	0.03
				Cumulative - 4.7				

Mass Balance Summary: (CO₂-free basis)

Total Feed	=	126.0	lbs
Total Output	=	108.3	lbs
Raffinate	=	100.6	lbs
Decanter	=	0	
Extractor Residual	=	6.4	lbs
Product	=	1.28	lbs

Notes: At low flowrates, there were no foaming problems when the extractor interface levels were properly maintained. Poor extractor interface level control led to foaming. The second window from the top leaked severely throughout the run. This was repaired after the run by shimming the window with an extra gasket, 1/32" thick.

Table V-16

ETHANOL RUN W6 DATA SUMMARY

T(extractor) = 74°F P(extractor) = 1200 psi
 T(still) = 61°F P(still) = 750 psi
 Feed: Synthetic, 10.2% Ethanol Co-solvent was added as a separate feed.
 Trays: 4 Trays, All-Teflon, 1 1/8" Upcomers

<u>Time</u>	<u>Feed Rate</u> (lbs/min)	<u>Solvent Rate</u> (lbs/min)	<u>Solvent-to-Feed Ratio</u>	<u>Ethanol Concentration (wt%)</u>			<u>Product</u>	<u>Solvent</u>
				<u>Raffinate</u>	<u>Product</u>	<u>Solvent</u>		
				Average	High	Low		
3:00-3:45	Start-up							
3:45-5:30	0.607	5.93	9.76	6.14	6.77	5.82	85.0	0.12
5:30-6:55	0.607	5.93	9.76	6.57	7.61	5.71		0.12
	w/addition of 5% Co-solvent		Cumulative 6.22					

Next Day - 83.7

Mass Balance Summary: (CO₂-free basis)

Total Feed	=	129.5	lbs
Total Output	=	117.8	lbs
Raffinate	=	107.5	lbs
Decanter	=	1.07	lbs
Extractor Residual	=	3.76	lbs
Product	=	5.51	lbs

Notes: A co-solvent, ethyl hexanol, was injected during the second half of the run. There was no trace of the co-solvent in the raffinate, only in the product. There was no dramatic change in raffinate or product concentration. The water concentration in the extract seemed to be reduced (0.6% → 0.1%) during the co-solvent injection, but this number could be in error, as it was not confirmed by the product analysis.

Table V-17

ETHANOL RUN W7 DATA SUMMARY

T(extractor) = 54°F P(extractor) = 1200 psi
T(still) = 45°F P(still) = 600 psi
Feed: Synthetic, 10.0% Ethanol
Trays: 9 Trays, Teflon/Stainless Steel, 1/4" Downcomers

<u>Time</u>	<u>Feed Rate</u> (lbs/min)	<u>Solvent Rate</u> (lbs/min)	<u>Solvent-to-Feed Ratio</u>	<u>Ethanol Concentration (wt%)</u>			<u>Product</u>	<u>Solvent</u>
				<u>Average</u>	<u>High</u>	<u>Low</u>		
4:00-4:35	Start-up							
4:35-5:35	0.432	4.20	9.72	2.09	2.52	1.66		~0.10
5:45-6:45	0.246	1.06	4.31	3.65	4.05	2.74		0.10

53.6 (Next Day)

Notes: This run was to test the new teflon/stainless steel layered sieve trays. They operated properly, with good CO₂ droplet formation. However, the solvent nozzle was directly under the lowest downcomer, impeding raffinate flow. This resulted in column flooding overhead at all but very low solvent flowrates, e.g., 1.0 lb/min. This problem was corrected before Run W8 by removing the lowest sieve tray.

Table V-18

ETHANOL RUN W8 DATA SUMMARY

T(extractor) = 73°F P(extractor) = 1200 psi
T(still) = 52°F P(still) = varied
Feed: Synthetic, 9.97% Ethanol
Trays: 8 Trays, Teflon/Stainless Steel, 1/4" Downcomers

<u>Time</u>	<u>Feed Rate</u> (lbs/min)	<u>Solvent Rate</u> (lbs/min)	<u>Solvent-to-Feed Ratio</u>	<u>Still Pressure</u> (psi)	<u>Ethanol Concentration (wt%)</u>				
					<u>Raffinate</u>	<u>Product</u>	<u>Solvent</u>		
					Average	High	Low		
3:00-3:45	Start-up								
3:45-4:45	0.452	5.32	11.8	700	4.29	--	--	--	0.06
4:45-5:05	0.932	11.3	12.1	740	4.19	--	--	--	0.06
5:05-5:30	1.28	8.55	6.68		6.60	--	--	--	0.14
5:30-6:05	0.952	8.71	9.15	640	4.82	5.54	4.29	87.4	0.10
6:05-6:50	0.565	5.35	9.45	640	4.04	4.62	3.72	84.7	0.10

Mass Balance Summary: (CO₂-free basis)

Total Feed	=	178.0	lbs
Total Outputs	=	169.3	lbs
Raffinate	=	128.7	lbs
Decanter	=	5.9	lbs
Extractor Residual	=	25.9	lbs
Product	=	8.79	lbs

Notes: This run went very smoothly, with proper sieve tray operation. Flowrates were limited by still flooding at M = 12 lbs/min. This was probably due to excess cooling of the CO₂ prior to entering the reboiler tubes. The "low" figures given for raffinate composition are probably accurate, as they usually occurred toward the end of a run segment when steady state would most likely have been reached.

Table V-19

ETHANOL RUN W9 DATA SUMMARY

T(extractor) = 76°F P(extractor) = 1200 psi
T(still) = 46, 62°F P(still) = 600, 750 psi
Feed: Synthetic, 14.5% Ethanol until 5:00, then 13.5%
Trays: 8 Trays, Teflon/Stainless Steel, 1/4" Downcomers

<u>Time</u>	<u>Feed Rate</u> (lbs/min)	<u>Solvent Rate</u> (lbs/min)	<u>Solvent-to-Feed Ratio</u>	<u>Still Pressure</u> (psi)	<u>Ethanol Concentration (wt%)</u>				
					<u>Raffinate</u>			<u>Product</u>	<u>Solvent</u>
					Average	High	Low		
12:30-1:45	Start-up								
1:45-5:50	0.784	7.77	9.91	600	6.53	8.60	5.50	87.9	0.10
5:50-7:50	0.784	7.77	9.91	750	6.45	7.61	5.02	86.8	0.06

Mass Balance Summary: (CO₂-free basis)

Total Feed	=	307.0	lbs
Total Outputs	=	287.2	lbs
Raffinate	=	229.5	lbs
Decanter	=	4.25	lbs
Extractor Residual	=	27.60	lbs
Product	=	25.86	lbs

Notes: The objective of this run was to obtain higher product concentrations by increasing the feed alcohol concentration and decreasing the still pressure. The change in product quality observed with the change in still pressure was insignificant. The higher feed concentration also did not lead to a notably higher product concentration. However, CO₂-free samples removed directly from the reboiler were about 91.5% ethanol.

Table V-20

ETHANOL RUN W10 DATA SUMMARY

T(extractor) = 71°F P(extractor) = 1200 psi
T(still) = 45°F P(still) = 600 psi
Feed: Synthetic, 10.0% Ethanol
Trays: 4 Trays, Teflon-Stainless Steel, 1/4" Downcomers

Time	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	Ethanol Concentration (wt%)			Product	Solvent
				Raffinate	High	Low		
11:30-12:30	Start-up							
12:30- 2:50	0.838	7.73	9.22	5.17	5.48	4.90	--	0.05
2:50- 5:00	0.525	5.47	10.4	4.58	5.01	4.25	83.0	0.05

Mass Balance Summary: (CO₂-free basis)

Total Feed = 206.0 lbs
Total Outputs = 202.9 lbs
Raffinate = 163.3 lbs
Decanter = 0.10 lbs
Extractor Residual = 27.04 lbs
Reboiler -
Dense Phase = 1.79 lbs
Product = 8.59 lbs

Notes: This run's purpose was to evaluate the impact of increased drop rise time on tray efficiency.
"Light" phase samples from the reboiler had ethanol concentrations as high as 89.4%.
Increasing tray spacing to 14" from 7" increased tray efficiency.

UPCOMER VS DOWNCOMER SIEVE TRAY OPERATION

FIGURE V-1

SIEVE TRAY CONSTRUCTION

FIGURE V-2

The feed for run E3 used the same source of broth as E2; however, the liquid was carefully decanted, so as to leave behind most of the solids. This simple precaution eliminated most of the operating problems experienced during E2. In addition, only one product phase was observed.

The molasses mash used in run E4 was a viscous brown liquid. Since the molasses solids were very fine and well suspended, the problems encountered with the corn solids in E2 were not expected. However, the molasses mash and the CO_2 emulsified, leaving the extractor interface level indicator inoperable. Carryover of the feed in the extract stream was observed at all flow rates, and it was difficult to determine whether the extractor sieve trays were functioning properly. Without knowing how much of the extractor was active at any given time, the raffinate compositions obtained have limited value. Yet, it was reassuring that a high quality (90% EtOH) product was obtained, albeit in small quantities, indicating that the emulsion was broken by the decanter.

In run E5, we added a chemical defoaming agent, Dow Corning Antifoam Emulsion B, was added plus sufficient SDA 30 to boost the alcohol concentration to about 20%, hoping to overcome the emulsification problem. These treatments were tested successfully in the laboratory for breaking molasses mash-air foams. However, they were not effective in preventing emulsification with liquid CO_2 in the extractor. This run was aborted.

Run E6 was an attempt to simulate a section of a tall extraction column well below the feed point, by starting with a dilute feed (5% EtOH). As expected, a lower concentration was obtained in the raffinate.

Similarly, run E7 was to simulate an extractor with product recycle, by starting with a concentrated synthetic feed (20% EtOH). The objective was to obtain a final product with an EtOH concentration significantly greater than 90%, the highest concentration obtained thus far. However, the highest concentration measured in this run was only about 91% EtOH. The reason for the lack of higher product purity is uncertain. Some possible explanations are: 1) water may have been left in the system from the previous run, and diluted the product; 2) twenty percent is beyond the optimum feed concentration, and product purity may be decreasing; 3) the upper limit of product purity may be lower than theoretical estimates; 4) a separate water phase formed in the still (which has been observed in the still sight gauge in other runs) and carried out with the product, thus diluting it.

Run W1 was intended to be a base case against which future modifications would be compared. With a 10% EtOH feed, we obtained data at several flowrates as flooding was approached. The all-teflon sieve trays did not operate properly in the downcomer configuration. Instead of liquid CO_2 jetting up through the sieve holes and breaking off to form drops, the CO_2 hole velocity was low. This formed an unstable layer of CO_2 on top of the tray, from which irregular and uncontrollably large drops of CO_2 would break away, rising up to the next tray (Figure V-3). While this did not hamper pilot plant operation, it probably decreased tray efficiency. As modified sieve trays could not be fabricated immediately, operation was continued with these trays, with the recognition that the extractor was probably performing well below its potential.

**EXTRACTOR CROSS SECTIONAL VIEW SHOWING
SIEVE TRAY OPERATION WITH TEFLON AND
WITH TEFLON/STAINLESS SIEVE TRAYS**

FIGURE V-3

Nevertheless, the strategy for run W1 closely followed that of E1 and similar results were obtained. The raffinate concentration was seen to decrease as the flowrates were increased, maintaining a $S/F = 10$. It seemed that the extractor capacity was greater than previously determined using the solid extraction column, as the flooding which had been observed at $m_f = 1.2$ lbs/min and $m_s = 12$ lbs/min during the earlier runs was not observed as these flowrates were approached in W1. It is possible that better extractor interface level control, a result of the windowed extractor, forestalled flooding.

Run W2 was similar to W1, except that a feed concentration of 2.5% EtOH was used. This feed was selected to simulate the lower section of a tall extractor. The objective was to determine if tray efficiency would remain constant throughout the length of an extractor designed for high EtOH recovery. Although the same problem with tray operation existed, as in W1, a comparison of their efficiencies would be useful. If the tray efficiencies stayed the same for both a 10% and a 2-1/2% feed, it is likely that the same observation would be made for properly operating sieve trays.

An upcomer tray configuration was used in run W3. This was accomplished simply by inverting the tray stack used in the previous two runs. If the system operated properly the CO_2 solvent would flow up through the upcomers as the continuous phase with the aqueous phase dispersed as it passed through the sieve tray holes and then through the CO_2 -rich phase. However, the pressure drop of the CO_2 through the 1/4" upcomer orifice caused a large aqueous-phase head develop on each tray, making operation impractical because of the lack of continuous-phase holdup.

The tray stack was modified for run W4; the tray spacing was increased to 14" and the downcomer orifice diameter was increased to 1-1/8". The increased orifice diameter reduced the continuous-phase pressure drop through the column, reducing the dispersed-phase holdup. The tray spacing was increased in case a large head was required to initiate water flow through the sieve holes. With this configuration the extractor operation went smoothly. The drop formation problem encountered with the teflon trays in the downcomer configuration was not observed when the same trays were used with upcomers, since the teflon was wet by the CO_2 and not by the water.

A major observation made using the upcomer configuration was that the column capacity increased significantly over the downcomer configuration. As the flooding flowrates observed for downcomer systems were exceeded, entrainment of CO_2 droplets was observed in the upcomers, demonstrating the need for sieve trays with larger upcomers for this application. Although the sieve trays continued to operate properly when the feed rate was increased to 3.8 lbs/min, other problems limited operation: the pulsations of the feed stream mixed the aqueous and organic phases into an emulsion. The emulsion was then carried over into the extract stream. It appeared that the extractor capacity could be boosted considerably for EtOH-water systems by employing properly designed upcomer sieve trays and with pulsation dampening.

CO-SOLVENT INJECTION SYSTEM

FIGURE V-4

The same tray stack was used in run W5, with a molasses mash feed containing 6% EtOH. In previous runs using molasses-based feeds and the downcomer configuration, emulsification was a problem, resulting in the carryover of feed with extract (runs E4 and E5). With the upcomer configuration, the problem ranged from slight to non-existent. However, the molasses extraction was sensitive to proper level control, both at the upper and lower extractor interfaces. Most incidences of foaming in W5 occurred when level control was lost. The extractor capacity was lower with molasses feed, perhaps due to its high viscosity relative to synthetic EtOH feeds.

A co-solvent, 2-ethylhexanol, was used intermittently during run W6. A sketch of the equipment used to inject the co-solvent is given in Figure V-4. The co-solvent feed rate was approximately 5% of the EtOH feed rate. The injection system performed as desired, and the co-solvent was stripped from the raffinate by the upflowing solvent. However, no increase in the extent of henohol extraction was observed at the S/F of 10. The extract stream analyses indicated a suppression of water solubility during 2-ethylhexanol injection. However, this was not reflected in the product quality. Systematic testing of co-solvent is described in Section VI.

Runs W7, W8, W9, and W10 were made using a teflon-stainless steel layered sieve tray, as diagramed in Figure V-2. When the stainless steel trays were fabricated, the burr which was formed around each sieve hole was left in place. When the trays were assembled the steel layer was placed on top of the teflon with the burr directed upward. These trays were designed to prevent CO₂ from wetting the trays and covering the top of the tray, as had occurred with the all-teflon trays. The trays performed as desired, with proper drop formation, and jetting at higher flowrates.

Only low flowrates and S/F ratios were tested in run W7. The lowest downcomer was inadvertently located directly above the solvent inlet nozzle, impeding the aqueous-phase flow and resulting in flooding overhead at all but very low solvent flowrates. The problem was eliminated for subsequent runs by removing the bottom tray, such that the distance between the bottom of the column and the lowest tray was increased by 7", and directing the solvent nozzle away from the downcomer orifice.

Run W8 is comparable to W1, the only difference being the use of the "layered" tray construction in W8. A much greater surface area was generated with the new sieve trays, and thus higher tray efficiencies were expected.

During the six hour duration of Run W9 only one change in operating conditions was made: the still pressure was changed from 600 to 750 psi after four hours. The long duration at one condition allowed steady-state to be reached in the still while the extractor conditions remained unchanged. A 14% EtOH feed was used in this run. The product quality at these conditions was 88 and 87% EtOH at 600 and 750 psi, respectively.

The tray spacing was increased to 14" for run W10, with the number of trays reduced to four. The objective was to examine the effect of tray spacing on tray efficiency.

With the exception of runs W3 and W7, the "W" series of runs went smoothly, with no mechanical or operational problems. However, larger control valves, and larger feed and raffinate tanks would be required to run at the highest flowrates achievable using the upcomer tray configuration.

b. Isopropanol

The isopropanol (IPA) experiments ("I" series) were run in the same windowed extractor used for the "W" series EtOH runs. Eight teflon-stainless steel layered sieve-tray assemblies spaced 7" apart were employed. Only the downcomer configuration was used, with the orifices varied for different operating conditions. All feeds were synthetically prepared from anhydrous IPA and water. These runs are summarized in Tables V-21 through V-25.

A high concentration feed, 60% IPA, was used in run I1. Since a large change in volumetric flowrate of the water-rich phase was expected due to the transfer of IPA to the CO₂-rich phase, the downcomer orifice size was decreased from 0.5" at the top of the column to 0.25" at the bottom of the column. IPA recovery in the product was high, even at the lowest S/F tested. This run was difficult to control, as the column frequently "blacked out". This phenomena is apparently due to operating near saturation where a slight change in conditions results in instantaneous formation of a second phase of fine size which blocks out light. This prevented control of the extractor interface level during the run.

During run I2, an unobstructed downcomer with a 1.12" diameter was used. A feed rate of 1 lb/min of 9% IPA was maintained, while the solvent rate was varied from 1 - 10 lbs/min. As expected the raffinate concentration decreased with increasing S/F. A S/F of about 5 worked well for this extraction. In the last half-hour of run I2 the feed rate was increased to determine column capacity. At aqueous feed rates of 3 - 6 lbs/min and a solvent rate of 10.2 lbs/min operation became unstable, with periodic flooding. With the large downcomers the coalesced CO₂ head under each tray was only about 0.5 - 0.25".

The downcomer orifice was reduced to 0.5" for run I3. The smaller orifice increased the CO₂ head height to roughly 1". With a 9.7% IPA feed, the S/F was varied from 3.5 - 6 to gather more data under probable commercial operating conditions.

A feed concentration of 2.7% IPA was tested in run I4 to simulate the lower portion of a tall extractor. Recovery increased with increasing flowrates, while maintaining a constant S/F. A decrease in product quality was observed; however, this has no impact on actual product quality which is dependent on the aqueous phase composition in the feed at the top of the extractor.

The effect of a 20% IPA feed concentration was tested in run I5. A slight increase in the IPA concentration of the product was observed. While the

TABLE V-21

ISOPROPANOL RUN 11 DATA SUMMARY

T (extractor) = 66°F

P (extractor) = 1200 psi

T (still) = 49°F

P (still) = 600 psi

Feed: 59.8% IPA until 3:00, 60.6% after 3:00

Trays: 8 Trays, Teflon-Stainless Steel, Downcomer
size decreasing from 1/2" at top to 1/4"
at bottom of extractor.

Time	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	Isopropanol Concentration (wt %)						Solvent
				Raffinate			Product			
				Average	High	Low	Average	High	Low	
				10:45-12:20	Start-up					
12:20- 3:30	0.958	1.50	1.56	12.6	17.1	2.50	83.5	85.8	81.1	0.20
3:30- 5:00	0.985	2.18	2.28	3.40	4.31	2.66	86.4	86.8	85.3	0.20

Mass Balance Summary (CO₂-free basis)

Total Feed	=	277.0	lbs
Total Output	=	262.1	lbs
Raffinate	=	63.37	lbs
Decanter	=	4.04	lbs
Extractor Residual	=	28.39	lbs
Product		166.3	lbs

Notes: The objective of this run was to investigate operation at high feed concentrations. The large variations in raffinate composition result from large swings in extractor interface level. Extract compositions averaged 03.5 and 26.0% IPA at the two sets of conditions, respectively. Of the IPA fed, 84.8% was recovered in the product.

Table V-22

ISOPROPANOL RUN 12 DATA SUMMARY

T(extractor) = 77°F P(extractor) = 1200 psi
T(still) = 46°F P(still) = 600 psi*
Feed: 8.81% IPA until 1:25, 8.46% after 1:25
Trays: 8 Trays, Teflon-Stainless Steel, 1 1/8" Downcomers

<u>Time</u>	<u>Feed Rate</u> (lbs/min)	<u>Solvent Rate</u> (lbs/min)	<u>Solvent- to-Feed Ratio</u>	<u>Isopropanol Concentration (wt%)</u>				
				<u>Raffinate</u>			<u>Product</u>	<u>Solvent</u>
				Average	High	Low	(Reboiler)	
10:45-11:30	Start-up							
11:30-12:45	1.05	0.965	0.922	7.45	7.96	7.16	--	0.17
12:45- 2:20	1.05	1.63	1.56	6.13	6.86	4.08	(94.0)	0.14
2:20- 3:40	1.05	4.98	4.76	2.37	2.71	2.00	(94.5)	0.12
3:40- 4:30	1.05	10.2	9.71	1.52	1.62	1.44	--	0.14
4:30- 4:45	2.00	10.2	5.09	2.29	--	--	--	--
4:45- 4:55	3.10	10.2	3.28	3.64	--	--	--	--
4:55- 5:00	4.1	10.2	2.48	4.28	--	--	--	--
5:00- 5:05	6.2	10.2	1.64	--	--	--	--	--

End Run 94.2

Mass Balance Summary: (CO₂-free basis)

Total Feed	= 483.6 lbs
Total Outputs	= 463.7 lbs
Raffinate	= 415.0 lbs
Decanter	= 5.9 lbs
Extractor Residual	= 19.3 lbs
Product	= 16.8 lbs
Reboiler Samples	= 4.7 lbs

Notes: Extract compositions fell from 2.85% to 1.18% IPA in CO₂ as the S/F was increased from 0.922 to 9.71. Overall recovery of IPA in the product was 48.7%. Smooth operation was difficult to maintain at the highest flow rates.
*Still pressure increased to 760 psi when the solvent rate was increased to 10.2 lbs/min. Still temperature then rose to 65°F, and the extractor temperature increased to 93°F.

Table V-23

ISOPROPANOL RUN 13 DATA SUMMARY

T(extractor) = 34°F P(extractor) = 1200 psi
 T(still) = 46°F P(still) = 600 psi*
 Feed: 9.74% IPA until 4:15, 9.62% after 4:15
 Trays: 8 Trays, Teflon-Stainless Steel, 1/2" Downcomers

Time	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	Isopropanol Concentration (wt%)				
				Raffinate			Product	Solvent
				Average	High	Low	(Reboiler)	
1:45-2:30	Start-up							
2:30-4:05	1.11	4.05	3.65	3.03	3.82	2.56	--	0.16
4:05-5:00	1.11	5.04	4.54	2.15	2.59	2.01	93.4	0.14
5:00-5:45	1.11	6.49	5.85	1.38	2.11	1.05	94.6	0.13
5:45-6:25	1.86	9.15	4.92	1.98	2.56	1.64	--	--
End Run 94.3								

Mass Balance Summary: (CO₂-free basis)

Total Feed = 320.3 lbs
 Total Output⁺ = 331.1 lbs
 Raffinate⁺ = 283.32 lbs
 Decanter = 1.14 lbs
 Extractor Residual = 24.52 lbs
 Product = 13.39 lbs
 Reboiler Samples = 3.70 lbs
 (+) Raffinate in error by 10-20 lbs, see text.

Notes: *At the highest solvent rate, the still pressure and temperature rose to 730 psi, and 60°F respectively, and the extractor temperature then increased to 90°F. Extract compositions decreased from 3.14 to 2.37% IPA in CO₂ with increasing S/F. Of the IPA fed, 67.2 was recovered in the product.

Table V-24

ISOPROPANOL RUN I4 DATA SUMMARY

T(extractor) = 75°F P(extractor) = 1200 psi
T(still) = 47°F P(still) = 600 psi*
Feed: 2.69% IPA
Trays: 8 Trays, Teflon-Stainless Steel, 1/2" Downcomers

Time	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	Isopropanol Concentration (wt%)				
				Raffinate			Product	Solvent
				Average	High	Low	(Reboiler)	
1:30-2:40	Start-up							
2:40-3:50	0.995	4.96	4.98	1.02	1.45	0.75	--	0.04
3:50-4:50	0.995	6.05	6.08	0.75	0.84	0.67	--	0.05
4:50-5:50	1.81	8.99	4.97	0.87	1.17	0.66	(88.7)	0.07
5:50-6:30	1.51	8.99	5.95	0.55	0.58	0.47	(90.5)	0.08
End Run 83.8								

Mass Balance Summary: (CO₂-free basis)

Total Feed	=	356.9	lbs
Total Output	=	344.6	lbs
Raffinate	=	306.6	lbs
Decanter	=	3.72	lbs
Extractor Residual	=	25.96	lbs
Product	=	5.97	lbs
Reboiler Samples	=	2.42	lbs

Notes: Extract compositions ranged from 0.75 to 0.60% IPA. Of the IPA fed, 74.8% was recovered in the product. Still pressure was difficult to control -- it was later learned this was due to a leak in the solvent line.
*At the highest solvent rate, still pressure rose to 780 psi, with T (still) increasing to 65°F and T (extractor) increasing to 85°F.

Table V-25

ISOPROPANOL RUN 15 DATA SUMMARY

T(extractor) = 87°F P(extractor) = 1200 psi
T(still) = 65°F P(still) = 750 psi
Feed: 20.1% IPA
Trays: 8 Trays, Teflon-Stainless Steel, 1/2" Downcomers

<u>Time</u>	<u>Feed Rate</u> (lbs/min)	<u>Solvent Rate</u> (lbs/min)	<u>Solvent- to-Feed Ratio</u>	<u>Isopropanol Concentration (wt %)</u>				
				<u>Raffinate</u>			<u>Product</u>	<u>Solvent</u>
				Average	High	Low		
12:00-2:15	Start-up							
2:15-5:00	1.02	5.54	5.43	2.69	5.12	1.89	94.8	0.32
5:00-6:00	1.60	8.07	5.04	2.48	2.96	2.18	95.0	0.34
6:00-6:30	1.25	8.07	6.46	2.47	2.88	1.77	94.7	0.36

Mass Balance Summary: (CO₂-free basis)

Total Feed = 342.5 lbs.
Total Output = 334.5 lbs.
 Raffinate = 246.3 lbs.
 Decanter = 3.36 lbs.
 Extractor Residual = 25.64 lbs.
 Product = 55.73 lbs.

Notes: Investigating effect of higher feed concentration on product concentration. Extract compositions ranged from 4.42 to 6.09% IPA. 81.4% of the IPA fed was recovered in the product.

10% feeds gave product with an average IPA concentration of 94.2% and a maximum of 94.6%, the 20% feed had average and maximum product concentrations of 94.8% and 95.0, respectively. Although the raffinate concentration is low and the recovery high for this high feed concentration, it is not completely unexpected. As the feed concentration is increased, the difference between the S/F at the bottom of the extractor and the overall S/F increases; the 20% feed has in effect a 20% higher S/F, which is significant. Also, the distribution coefficient may increase with increasing feed concentration.

c. Sec-Butanol

In the sec-butanol (SBA) experiments ("B" series, in Tables V-26 through V-33) the same extractor and pilot plant system were used as in the "W" and "I" series of experiments. Since the distribution coefficient for SBA between CO₂ and water is greater than that of EtOH or IPA, lower S/F were used with SBA. Solvent-to-feed ratios in the range of 0.3 - 3 were planned based on measured distribution coefficients of 0.8 - 2. The lower S/F allows higher feed throughput; therefore, the size of the downcomers was increased to 1-1/8". In addition, a larger valve was installed for controlling raffinate flow.

The program for SBA included varying S/F, tray spacing, upcomer vs. downcomer configuration, and varying feed concentrations. There is limited miscibility of SBA in water; mixtures containing between 12 and 65% SBA separate into two phases. Therefore, the feeds were kept below 12% or above 65% SBA to remain single-phase.

Run B1 used an upcomer tray stack configuration with four trays spaced 14" apart. Flooding was observed at a feedrate of about 9 lbs/min, with a solvent rate of 4.5 lbs/min. While this capacity (on a total throughput basis) is similar to that observed with EtOH and IPA systems, the capacity to process aqueous feed is significantly higher with SBA than with the other alcohols. The SBA concentration in the product was high, in the 94-95% range. Recovery, on the other hand, was below 50% at a S/F of 0.5. At the higher feedrates, greater than 3 lbs/min, the pulsed aqueous feed agitated the top of the extractor. However, this did not result in any carry-over of feed with the extract. When flooding occurred, solvent was carried out with raffinate at the bottom of the extractor.

Eight upcomer trays spaced 7" apart were employed in run B2. Due to the high feedrates employed, raffinate was blended with product for re-use as feed. Unfortunately, this resulted in poor accounting of material flow. Product compositions ranged from 91.6 - 93.6%. With the S/F ranging from 0.5 - 1.8, 67% of the SBA in the feed was recovered as product.

Run B3 utilized 8 teflon-stainless-steel-layered trays in a downcomer configuration. With a 10% feed, the feedrate was kept constant at 2.74 lbs/min, while the solvent flowrate was varied between 1.92 and 0.875 lbs/min. This gave a S/F range of 0.865 - 0.319. Overall, 77% of the SBA fed to the extractor was recovered in the product. The product analyses indicated much lower SBA concentrations than the previous runs. This is probably an indication of extractor and decanter flooding that went unrecorded.

TABLE V-26

sec-BUTANOL DATA SUMMARYRUN B-1

T (Extractor) = 67°F

P (Extractor) = 1200 psi

T (Still) = 53°F

P (Still) = 600 psi

Feed: 10.2% sec-Butanol until 5:05, 7.7% after 5:05

Trays: 4 Trays, all-Teflon, 1-1/8" Upcomers

TIME	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	sec-Butanol Concentration (Wt %)				
				Raffinate			Product (Reboiler)	Solvent
				Average	High	Low		
2:00-2:50	Start-up							
2:50-3:20	0.603	1.22	2.02	3.1	4.1	2.1	----	---
3:20-3:40	0.929	1.19	1.28	2.8	3.1	3.1	----	---
3:40-4:30	1.46	1.00	0.685	4.8	5.2	4.4	----	---
4:30-4:50	2.61	0.978	0.375	6.0	---	---	94.4	---
4:50-5:45	2.61	1.48	0.567	5.5	5.9	5.0	(94.0)	0.13
5:45-6:00	3	1.6	0.53	5.8	---	---	----	0.12
6:00-7:20	3-11	1.6-16	see notes	5.6	---	2.5	94.3 (95.2)	---
							Next day: 94.4	

NOTES: Extract composition varied between 3.8 and 12.6% sec-butanol in CO₂. At the end of the run very high flow rates were used and we lost track of the mass balance. As flows became high, the top of the extractor "black-out", but no carry-over was observed. Finally, we observed flooding out the raffinate line when m_F was about 9 lbs/min and m_S about 4.5 lbs/min.

TABLE V-27

sec-BUTANOL DATA : SUMMARY

RUN B-2

$T_{\text{Extractor}} = 72^{\circ}\text{F}$

P (Extractor) = 1200 psi

T (Still) = 50°F

P (St111) = 600 psi

Feed: 9.79% sec-Butanol until 12:30, 10.37% from 12:30 to

1:20, 9.90% from 1:20 to 2:20 and 10.52% after 2:20

Trays: 8 Trays, all Teflon, 1-1/8" Upcomers

TIME	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	sec-Butanol Concentration (Wt %)				
				Raffinate			Product (Reboiler)	Solvent
				Average	High	Low		
10:15-11:05	Start-Up							
11:05-11:40	0.946	1.73	1.83	1.21	1.44	1.05	----	0.06
11:40-12:05	2.07	1.22	0.589	3.33	3.99	2.99	----	----
12:05- 1:20	5.66	2.99	0.528	4.53	4.81	4.25	(91.6)	0.11
1:20- 2:40	4.11	2.21	0.538	4.59	5.65	3.55	93.6	0.12
2:40- 3:30	4.11	3.44	0.837	3.63	4.24	3.19	(92.3)	----

Mass Balance Summary (CO₂-free basis)

Total Feed = 724 lbs

Total Output = 565 lbs(?)

Raffinate = 537 lbs

Extractor

Residual = 6 lbs

Product = 52 lbs

NOTE: Extract compositions ranged from 3% to 13.5% sec-butanol in CO₂. Poor mass balance closure is probably due to error in raffinate collection. Approximately 67% of the sec-butanol fed to the extractor was recovered in the product.

TABLE V-28

sec-BUTANOL DATA SUMMARYRUN B-3

T (Extractor) = 75°F

P (Extractor) = 1200 psi

T (Still) = 52°F

P (Still) = 600 psi

Feed: 9.51% sec-Butanol before 3:50, 9.51% after 3:50

Trays: 8 Trays, Teflon-Stainless Steel, 1-1/8" Downcomers

TIME	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	sec-Butanol Concentration (Wt %)				
				Raffinate			Product	Solvent
				Average	High	Low		
1:50-3:10	Start-up							
3:10-4:10	2.74	1.92	0.701	2.87	3.18	2.00	---	0.05
4:10-5:00	2.74	0.875	0.319	4.76	5.61	3.88	≈20(?)	--
5:00-5:50	2.74	2.37	0.865	1.95	3.07	1.26	≈82.5	0.05

Mass Balance Summary (CO₂-free basis)

Total Feed = 524.9 lbs
 Total Output = 494.6 lbs
 Raffinate = 401.2 lbs
 Decanter = 14.33 lbs
 Extractor
 Residual = 35.64 lbs
 Product = 43.40 lbs

NOTES: Extract compositions ranged from 6.25 to 16.4% sec-butanol in CO₂ or 17 to 85% on a CO₂-free basis. There was a pressure pulsation in the column of about 50 psi apparently caused by the piston pump. Approximately 77% of the sec-butanol fed to the extractor was recovered in the product.

TABLE V-29

sec-BUTANOL DATA SUMMARYRUN B-4

T (Extractor) = 75°F

P (Extractor) = 1200 psi

T (Still) = 52°F

P (Still) = 600 psi

Feed: 9.82% sec-Butanol until 3:10, 9.95% after 3:10

Trays: 8 Trays, Teflon-Stainless Steel, 1-1/8" Downcomers

TIME	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	sec-Butanol Concentration (Wt %)			Product	Solvent
				Average	High	Low		
10:45-12:00	Start-up							
12:00- 1:55	0.995	0.586	0.589	2.91	3.60	1.60	----	0.05
1:55- 3:30	2.10	0.969	0.461	3.98	4.64	2.27	----	0.06
3:30- 4:25	2.92	1.56	0.534	4.22	4.57	3.90	----	0.03
End Run 93.7								

Mass Balance Summary (CO₂-free basis)

Total Feed = 507 lbs
 Total Output = 484 lbs
 Raffinate = 413 lbs
 Decanter = 12.71 lbs
 Extractor
 Residual = 29.52 lbs
 Product = 29.03 lbs

NOTES: Extract composition ranged from 10.5 to 17.1% sec-butanol in CO₂, about 92% on a CO₂-free basis. 54% of the sec-butanol introduced as feed was recovered in the product. We attempted to vary both solvent and feed ratios while maintaining a constant S/F of about 0.5. At higher flows, pressure pulsations in the column, caused by the feed pump, caused a pulsed jetting of solvent through the sieve holes.

TABLE V-30

sec-BUTANOL DATA SUMMARYRUN B-5

T (Extractor) = 76°F

P (Extractor) = 1200 psi

T (Still) = 52°F

P (Still) = 600 psi

Feed: 9.61% sec-Butanol until 1:50, 10.3% after 1:50

Trays: 8 Trays, Teflon-Stainless Steel, 1-1/8" Downcomers

TIME	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	sec-Butanol Concentration (Wt %)				
				Raffinate			Product (Reboiler)	Solvent
				Average	High	Low		
11:15-12:15	Start-up							
12:15- 2:05	1.05	1.52	1.45	1.12	1.38	0.86	----	0.11
2:05- 3:45	2.05	3.03	1.48	1.31	1.56	1.01	(95.0)	0.11
3:45- 4:35	3.13	4.51	1.44	1.31	1.64	1.01	(95.5)	0.11
End Run 95.9								

Mass Balance Summary (CO₂-free basis)

Total Feed = 480.5 lbs
 Total Output = 485.4 lbs
 Raffinate = 410.4 lbs
 Decanter = 1.43 lbs
 Extractor
 Residual = 25.9 lbs
 Product = 44.3 lbs
 Reboiler
 Samples = 3.41 lbs

NOTES: Extract composition varied from 7.29 to 8.47% sec-butanol in CO₂, which was about 92% on a CO₂-free basis. 87.4% of the sec-butanol input was recovered in the product. We attempted to maintain a S/F of 1.5, while varying the solvent and feed rates. At the lowest of flow rates not all the sieve holes were active. At intermediate rates, all of the holes became active. At the highest rates, steady jetting occurred.

TABLE V-31

sec-BUTANOL DATA SUMMARYRUN B-6

T (Extractor) = 72°F

P (Extractor) = 1200 psi

T (Still) = 46°F

P (Still) = 600 psi

Feed: 9.77% sec-Butanol until 2:30, 9.38% after 2:30

Trays: 4 Trays, Teflon-Stainless Steel, 1-1/8" Downcomers

TIME	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	sec-Butanol Concentration (Wt %)			Product (Reboiler)	Solvent
				Average	High	Low		
11:15-12:15	Start-up							
12:15- 2:00	1.05	1.49	1.42	2.47	3.52	1.80	(94.1)	0.07
2:00- 3:30	2.05	3.06	1.49	1.94	2.79	1.45	(79.1)	0.09
3:30- 4:30	3.04	4.40	1.45	1.40	1.76	1.23	(95.4)	0.10
4:30- 5:10	2.07	5.92	2.86	0.62	0.73	0.55		0.09
End Run 95.7								

Mass Balance Summary (CO₂-free basis)

Total Feed = 579.8 lbs
 Total Output = 573.7 lbs
 Raffinate = 491.1 lbs
 Decanter = 1.7 lbs
 Extractor
 Residual = 27.3 lbs
 Product = 48.3 lbs
 Reboiler
 Samples = 5.3 lbs

NOTES: Extract compositions ranged from 5.73 to 7.54% sec-butanol in CO₂ or about 90% on a CO₂-free basis. Of the sec-butanol fed, 918% was recovered in the product. The object of the run was to examine recovery at various feed rates, maintaining a S/F of 1.5. The "Low" raffinate concentrations measured are usually closest to the steady state values; usually the raffinate samples taken early, during the approach to steady-state, bias the average raffinate.

TABLE V-32

sec-BUTANOL DATA SUMMARYRUN B-7

T (Extractor) = 68°F

P (Extractor) = 1200 psi

T (Still) = 45°F

P (Still) = 600 psi

Feed: 1.91% sec-Butanol until 1:45, 1.87% after 1:45

Trays: 4 Trays, Teflon-Stainless Steel, 1-1/8" Downcomers

TIME	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	sec-Butanol Concentration (Wt %)			Product (Reboiler)	Solvent
				Raffinate Average	High	Low		
12:00-1:00	Start-up							
1:00-2:20	2.07	3.20	1.55	0.79	0.86	0.78	---	--
2:20-3:30	2.66	4.06	1.53	0.74	0.81	0.61	---	0.03
3:30-3:50	2.66	1.54	0.579	1.35	1.38	1.34	---	--
3:50-4:00	4.1	3.5-9.0	see notes	----	----	----	---	0.04
End Run 93.5								

Mass Balance Summary (CO₂-free basis)

Total Feed = 496.0 lbs
 Total Output = 481.9 lbs
 Raffinate = 464.1 lbs
 Decanter = 0.5 lbs
 Extractor Residual = 12.46 lbs
 Product = 4.86 lbs

NOTES: Extract compositions ranged from 0.40 to 1.45% sec-butanol. Of the sec-butanol fed, 47.7% was recovered in the product. The object of this run was to investigate recovery at low feed concentrations. At very high feed and high solvent rates (the end of the run), an emulsion formed throughout the extractor, which resulted in CO₂ being carried out with the raffinate.

TABLE V-33

sec-BUTANOL DATA SUMMARYRUN B-8

T (Extractor) = 73°F

P (Extractor) = 1200 psi

T (Still) = 64°F

P (Still) = 750 psi

Feed: 69.9% sec-Butanol until 4:20, 67.5% after 4:20

Trays: 8 Trays. Teflon-Stainless Steel, Downcomer
size decreasing from 1/2" at top to 1/4" at
bottom of extractor.

TIME	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent- to-Feed Ratio	sec-Butanol Concentration (Wt %)				
				Raffinate	Product			Solvent
					Average	High	Low	
1:30-2:00	Start-up	---	-	---	---	--	-	--
2:00-5:45	0.932	1.51	1.62	---	91.0	9.17	89.2	0.33

Cumulative-10.3

Mass Balance Summary (CO₂-free basis)

Total Feed = 201.3 lbs
 Total Output = 193.7 lbs
 Raffinate = 52.54 lbs
 Product = 135.8 lbs
 Decanter = 5.39 lbs

NOTE: The objective was to test operation with a high concentration feed. Level control in the extractor was difficult to monitor and maintain. Extract concentrations averaged 34.7% sec-Butanol and 3.5% H₂O in CO₂. Of the sec-Butanol fed, 89.2% was recovered in the product.

Run B4 used the same tray stack and feed as B3. The plan for this run was to operate at several different flowrates while maintaining a S/F of 0.5. Product concentration was similar to that observed in B1 and B2, about 94%. At this S/F, 54% of the SBA fed to the extractor was recovered in the product. Contrary to earlier results with the other alcohols, tray efficiency apparently decreased with increasing flowrates.

Run B5 was similar to B4, except that the S/F was maintained at 1.5. Tray efficiency decreased only slightly with decreasing flowrates in this run. Relatively high product concentrations were obtained, ranging from 95 to 96% SBA. Nearly 90% of the SBA feed was recovered in the product.

Four downcomer trays were used in run B6, in order to evaluate the impact of tray spacing on tray efficiency for the downcomer configuration. A 10% SBA feed solution and a S/F of 1.5 were used with several different flowrates. The raffinate compositions ranged from 1.4 - 2.5%, with tray efficiency increasing with increasing flowrate. When the S/F was changed to 2.9 at the end of the run the raffinate concentration dropped to 0.6%.

A low concentration feed, 1.9% SBA, was tested in run B7. Running with S/F of 1.5 and 0.5, raffinate concentrations of 0.75 and 1.36 were obtained, respectively. Therefore, the recovery of SBA in this run was only about 60% at S/F of 1.5, compared to an 80% recovery with a 10% feed under otherwise similar circumstances in B6. As indicated in run I5, several explanations are possible for the apparent dependence of recovery on feed concentration; a dependence of the distribution coefficient on feed concentration; and an effectively higher S/F (particularly near the bottom of the extractor) due to a substantial portion of the aqueous solution being extracted from high-concentration feeds. Also, a low raffinate concentration allows the operating line to approach the solvent-raffinate equilibrium line, thus reducing recovery potential.

A feed containing 70% SBA, just within the upper solubility limit, was tested in run B8. A high-concentration feed solution introduces special problems; decreased product quality; a large decrease in the volume of the water-rich phase as it passes through the column; and the possibility of the two phases approaching the isopicnic point.

The product concentration was lower than that obtained with lower concentration feeds. A 91% product was collected versus the 93-96% obtained in most runs with 10% SBA feeds. The lower concentration could be due either to carry-over of small amounts of water or to a reduction in selectivity at the high feed concentrations. At the same time, a seven-fold reduction from the feed concentration was obtained giving an average raffinate concentration of 10.3% SBA.

The volume of the water-rich phase flowing through the column decreased by about 75% from feed point to raffinate discharge. Therefore, a tray stack with a single downcomer orifice size would have resulted in different heads of coalesced CO₂ under each tray. To maintain similar head heights, downcomer orifices were installed which decreased in size going down through the extractor. Thus, the top two sieve trays had downcomer orifices of 1/2", the next two 13/32", then 11/32", with the bottom two

having 1/4" orifices. This variation of downcomer size worked satisfactorily.

Solutions of high SBA concentration in water have densities which are quite close to the density of liquid CO₂. If the difference in density between the two phases is insufficient, then separation of the phases can be a problem. During run B8 it was difficult to distinguish the two phases in the upper portion of the extractor as a result of the similarity in density. In addition, the extract-line sight gauge was "blacked-out". Thus it was difficult to maintain a phase interface at the top of the extractor.

2. Material Balances

The overall system material balance was a gauge of the quality of measurements: when the balance closed, all materials were accounted for. Because the pilot plant was not equipped to measure the amount of CO₂ fed to and vented from the system, the overall material balance accounted for liquids (water and alcohol) only. The overall material balances are given for each run in the "Mass Balance Summary" portion of each "Data Summary", Tables V-5 through V-33.

The material balances were also used to determine alcohol recovery and loss. An alcohol material balance around the extractor was used to evaluate extractor performance. This alcohol balance also gave a check on the alcohol concentration in the extract, one of the more difficult streams to sample and analyze directly and accurately. The loss of material overall, and for alcohol alone, have been calculated as a percentage of the total feed and the alcohol feed, respectively. These losses are shown in Tables V-34, V-35, and V-36 for ethanol, isopropanol, and sec-butanol, respectively.

The calculations for the overall material balance were as follows:

$$\text{total input } (M_i) = \text{total output } (M_o) + \text{losses}$$

$$M_i = M_f = M_{f,a} + M_{f,w}$$

$$M_o = M_{r_M} + M_p + M_{\text{extractor residue}} + M_{\text{samples}}$$

$$\text{Overall Loss (\%)} = \frac{M_i - M_o}{M_i} \times 100$$

The material balance for the alcohol component was made, both overall as well as around the extractor only, with similar calculations.

One gauge of overall system performance is the recovery, which can be obtained directly from the material balance. It is defined as the fraction of alcohol fed to the system which is recovered in the product:

$$\text{Product Alcohol Recovery} = \frac{x_{p,a} \times M_p}{x_{f,a} \times M_{f,a}}$$

TABLE V-34
MATERIAL LOSSES AND RECOVERIES

Ethanol Runs

Run Number	Overall Loss (%, CO ₂ -free basis)	Ethanol Loss (%)	Product Tank (%)	Ethanol Recovery (%)	
				Extractor Run Average	Extractor Instantaneous (S/F)
E1	+	10	43	-	46.6 (10.1) 51.2 (11.1) 58.2 (11.3)
E2	5.3	19	37	49.7	54.6 (12.1) 52.6 (9.60)
E3	0.5	2	50	-	57.9 (13.8) 54.4 (7.35) 37.2 (11.1)
E4	11.5	34	4.9	55.8	24.3 (21.4) 57.2 (8.06)
E6	4.6	14	34	48.8	49.3 (9.13)
E7	9.3	19	38	56.6	56.4 (9.46) 55.5 (10.4)
W1	6.4	16.7	38.4	54.9	51.9 (10.1) 58.7 (10.5) 69.3 (13.4)
W2	15.8	18.6	35.0	51.5	54.6 (11.1) 59.5 (8.65)
W4	-		27.8	-	18.1 (6.02) 34.7 (9.23) 46.7 (12.9)
W5	14.1	21.2	13.3	23.6	23.6 (5.33) 23.6 (10.3) 26.8 (10.3)
W6	9.0	11.4	35.0	39.0	39.8 (9.76) 35.6 (9.76)
W8	4.9	5.4	41.8	-	56.9 (11.8) 57.9 (12.1) 33.8 (6.68) 51.7 (9.15) 59.5 (9.45)
W9	6.4	2.3	52.6	-	54.3 (9.91)
W10	1.5	-	34.3	-	48.3 (9.22) 54.2 (10.2)

- Insufficient data were collected.

+ A slight rain was measured.

TABLE V-35
MATERIAL LOSSES AND RECOVERIES
Isopropanol Runs

Run Number	Overall Loss (%, CO ₂ -free basis)	Isopropanol Loss (%)	Isopropanol Recovery (%)		
			Product Tank (%)	Extractor Run Average	Extractor Instantaneous (S/F)
I1	5.4	8.50	84.8	89.1	78.9 (1.56) 94.4 (2.28)
I2	4.1	+	48.7	40.7	15.4 (.922) 30.4 (1.56) 72.0 (4.76) 82.0 (9.71)
I3	+	1	67.2	68.5	68.9 (3.65) 77.9 (4.54) 85.7 (5.85) 79.4 (4.92)
I4	3.4	+	74.8	62.1	62.2 (4.98) 72.1 (6.08) 67.7 (4.97) 79.6 (5.95)
I5	2.3	0	81.4	85.4	86.6 (5.43) 87.7 (5.04) 87.7 (6.46)

+ A slight gain was measured.

TABLE V-36
MATERIAL LOSSES AND RECOVERIES
sec-Butanol Runs

<u>Run Number</u>	<u>Overall Loss (%, CO₂-free basis)</u>	<u>sec-Butanol Loss (%)</u>	<u>sec-Butanol Recovery (%)</u>		
			<u>Product Tank (%)</u>	<u>Extractor Run Average</u>	<u>Extractor Instantaneous (S/F)</u>
B1	-	-	-	-	69.6 (2.02) 72.6 (1.28) 52.9 (.685) 41.2 (.375)
B2	22	-	66.7	-	87.6 (1.83) 66.0 (.589) 55.1 (.528) 53.6 (.538) 65.5 (.837)
B3	5.8	-	-	76.6	70.0 (.701) 50.2 (.319) 79.6 (.865)
B4	4.5	-	54.1	-	70.5 (.589) 59.7 (.461) 57.2 (.534)
B5	+	-	87.4	-	88.3 (1.45) 87.3 (1.48) 87.3 (1.44)
B6	1.1	+	91.8	80.0	74.7 (1.42) 80.1 (1.49) 85.1 (1.45) 93.4 (2.86)
B7	2.8	5.0	47.7	50.3	58.6 (1.55) 60.4 (1.83) 27.3 (.579)
B8	3.8	3.5	89.2	85.0	- (1.62)

- Insufficient data were collected.
+ A slight gain was measured.

The product alcohol recovery usually differed from the extractor alcohol recovery, which was based on the yield loss of alcohol from the water-rich phase during extraction. It was calculated as:

$$\text{Extractor Alcohol Recovery} = \frac{X_{f,a} - X_{r,a}}{X_{f,a}} \text{ or } 1 - \frac{X_{r,a}}{X_{f,a}}$$

where $x_{r,a}/x_{f,a}$ is the yield loss in the extractor. This calculation assumes that the feed and raffinate flows do not differ significantly. This is a reasonable assumption when $x_{f,a} < 0.1$; however, at $x_{f,a} = 0.6$ a significant error is introduced by the large difference between M_f and M_r .

This extractor recovery represents the amount of product alcohol available if there were no losses from sampling; from the decanter, still, or product flash; or from unaccounted losses.

The prime reason for the large overall material loss during Runs W2, W4, W5, and B2, was gasket leakage at some of the extractor windows. Runs W3 and W7 were cut short, as the tray stacks were not performing well. Therefore, no attempt was made to close these material balances. A "+" has been used to indicate situations in which a gain was recorded. In all cases this gain was small, less than one percent in runs E1 and B5. In run I3, the three-percent gain is due to improper weighing of a portion of collected raffinate. In other cases, these slight gains are probably due to small errors in weighing, or possibly from material which had remained in the system from the previous run.

Comparing the overall and the alcohol-loss data in the early ethanol runs, the loss of alcohol was significantly larger than the overall loss. In most of these cases, the product recovery was substantially lower than the extractor alcohol recovery. This indicated that the loss of ethanol took place in the decanter-still-reboiler-product flash section of the process. It is possible that the ethanol was lost with CO_2 vented from the product flash vessel, either as ethanol vapor or mist.² The operation and equipment were modified for later runs. The rate at which reboiler-bottoms liquid was flashed to the product tank was kept low to minimize misting. In addition a demister was installed before run B3, and no mist problem was observed during the sec-butanol or the isopropanol runs.

The alcohol product recovery, which exceeded extractor recovery during runs I2, I4, and B6, may be explained by alcohol hold-up in the reboiler or product tank from a previous run, or by errors in the analysis of solutions.

3. Extractor Performance

The performance of the pilot plant extractor is based on its hydraulic characteristics, its capacity, and its mass-transfer efficiency. Each of these three responses were evaluated under a variety of conditions with each of the three alcohols tested. Hydraulic characteristics were based primarily on visual observation of the sieve trays. Capacity was usually considered the highest flowrates obtained before flooding, although at times steady state operation was not attained at those flowrates. Mass

transfer efficiency was measured both as tray efficiency and as the height equivalent of a theoretical plate (HETP).

The capacity tests were usually run by increasing solvent and feed rates while maintaining a constant S/F, in an effort to determine flooding limits for that S/F. During these tests changes in mass transfer efficiency were also measured as the capacity limit was approached. Changes in both the equilibrium and the mass-transfer efficiency were tested with changes in the aqueous feed concentration. Variations in tray spacing were made to determine the effect on tray efficiency. For ethanol and sec-butanol, the tray stack configuration was inverted, such that the CO₂-rich phase was continuous, and the aqueous phase dispersed. The trays were inverted to determine the capacity increase obtained particularly with ethanol, and at the same time to examine changes in tray efficiency.

a. Equilibrium, Mass Transfer Rates, and Efficiency

The alcohol-water-CO₂ equilibrium, combined with the material balance and compositional analyses of the four streams entering and leaving the extractor, allow a McCabe-Thiele type (M-T) graphical analysis or an analytical solution similar to a M-T analysis known as the Kremser-Brown-Soudier equation (KBS). For a given set of extractor conditions, the number of theoretical plates required to perform the observed separation is determined and the efficiency of the actual extractor sieve trays calculated. The information needed to perform this analysis include the equilibrium and four of the following five terms:

- (1) solvent-to-feed ratio (S/F)
- (2) feed composition (x_f)
- (3) raffinate composition (x_r)
- (4) solvent composition (y_s)
- (5) extract composition (y_e)

Typically the S/F , x_f , and x_r were measured accurately, and while y_s and y_e were measured, the same degree of accuracy was not obtained.^s The S/F and three of the compositions were used to determine the N_{th} and the fourth concentration.

Flowrate measurements for the pilot plant are reasonably accurate (about $\pm 1\%$) as are most aqueous feed and raffinate compositional data. However, there is considerably less accuracy in the analysis of the CO₂-rich streams, such as the solvent and extract compositions. Knowledge of the process allows reasonably tight limits to be put on the concentration of alcohol in the solvent stream, y_s , much closer bounds than are possible with the extract concentration, y_e . Thus, in performing a M-T analysis for a given run setting, S/F , x_f , x_r , and y_s are used to determine y_e and N_{th} .

The tray efficiency, n , is then calculated as N_{th}/N_{act} . In this case the value of n can be used to predict the separation achievable for the same system, while varying other parameters such as feed concentration.

An example of the M-T method is shown in Figure V-5 for the extraction of SBA from water with CO₂. An SBA concentration of 7% in the feed and

MCCABE-THIELE SAMPLE ANALYSIS
FOR SEC-BUTANOL

FIGURE V.5

0.1% in the solvent, and S/F of 2 were assumed. The resulting extract and raffinate compositions were 2.0 and 2.9%, and 3.2 and 1.4% SBA for one and four theoretical trays, respectively.

As previously noted, the value $(1-x_r/x_f)$ is the recovery of solute from the feed. This value is bounded between 0.0 (no recovery) and 1.0 (complete recovery). The yield loss, x_r/x_f , contains the same data but varies inversely, from 1.0 (no yield) to 0.0 (100% yield). Yield loss has been graphed as a function of S/F because its approach to the X-axis allows easy comparison and measurement of slight improvements in yield or recovery.

Figures V-6, V-7, and V-8 give a series of plots of x_r/x_f vs the S/F. These plots were generated based on equilibrium data, using a feed concentration of 10% and a solvent concentration of 0.1%. Values of N_{th} of 1, 2, 4, and 8 were then selected and the S/F was varied. The concentrations x_r and y_e were determined for each set of conditions, and the yield loss, x_r/x_f , was calculated and then plotted against S/F on lines of constant N_{th} .

Isopropanol and sec-butanol laboratory equilibrium data were used in this analysis. The SBA equilibrium data was closely fit by the following expression of distribution coefficient (mass basis), $m = 22.5 x_b$. The IPA equilibrium data showed m ranging from about 0.1 at low concentrations to about 0.25 at 10% concentrations of IPA in the aqueous phase. There was scatter in the ethanol laboratory equilibrium data and a constant value of $m = 0.1$ was used. The use of a linear equilibrium line allowed the KBS equation to be used. This equation analytically performs the equivalent of a M-T graphical analysis:

$$N_{th} = \frac{\log \left[\left(\frac{x_f - y_{s/m}}{x_r - y_{s/m}} \right) X(1-1/Q) + 1/Q \right]}{\log Q}$$

where $Q = S/F \times m$. The graphical M-T method was used with isopropanol and sec-butanol.

Tables V-37, V-38, and V-39 tabulate feed and raffinate concentration, solvent-to-feed ratio, yield loss, and the actual number of extractor sieve trays. The yield loss versus S/F is plotted in Figures V-9, V-10, and V-11, superimposed on the same equilibrium based plots of Figures V-6, V-7, and V-8.

While the equilibrium curves are for the case of a 10% feed concentration, several different feed concentration ranges are indicated in these plots. Each plot also represents several tray stack configurations, including changes in the number of trays and whether an upcomer or downcomer was used.

The range of solvent-to-feed ratios investigated was widest for IPA and SBA (Figures V-10 and V-11). Thus, the trend of the data is more clearly developed for these two feeds, and the general conclusions arrived at using the equilibrium data appear to hold. A similar trend is not as

ETHANOL

CALCULATED YIELD LOSS VS SOLVENT TO FEED RATIO
FOR VARIOUS NUMBERS OF THEORETICAL RATES

FIGURE V-6

ISOPROPANOL

CALCULATED YIELD LOSS VS SOLVENT TO FEED RATIO
FOR VARIOUS NUMBERS OF THEORETICAL RATES

FIGURE V-7

SEC - BUTANOL

CALCULATED YIELD LOSS VS SOLVENT TO FEED RATIO FOR VARIOUS
NUMBERS OF THEORETICAL RATES

FIGURE V-8

TABLE V-37

EXTRACTOR PERFORMANCE RAW DATA

Ethanol Runs

Run Number	Feed Concentration (X_f)	Raffinate Concentration (X_r)	Yield Loss (X_r/X_f)	Solvent to Feed Ratio (S/F)	Number of Actual Sieve Trays (N_{actual})
E1 a	.1409	.0753	.514	10.1	9
b		.0688	.488	11.1	9
c		.0589	.418	11.3	9
E2 a	.0970	.044	.454	12.1	9
b		.046	.474	9.60	9
E3 a	.0877	.0369	.421	13.8	9
b		.0400	.456	7.35	9
c		.0551	.628	11.1	9
E4 a	.0884	-	-	21.4	9
b		-	-	8.06	9
E6 a	.0505	.0256	.507	9.13	9 -
E7 a	.1990	.0868	.436	9.46	9 +
b		.0821	.413	10.4	9
W1 a	.1039	.0485	.4668	10.1	9
b		.0418	.4023	10.5	9
d		.0319	.3070	13.4	9
W2 a	.0227	.0103	.4537	11.1	9
b		.0092	.4053	8.65	9
W3	-				
W4 a	.1010	.0720	.713	6.02	4-II
b		.0660	.654	9.23	4-U
c		.0538	.533	12.9	4-U
d		-	-	4.41	4-U
W5 a	.0615	.047	.764	5.33	4-U
b		.047	.764	5.85	4-U
c		.045	.732	10.3	4-U
W6 a	.1020	.0614	.602	9.76	4-U
W7 a	.1000	.0209	.209	9.72	9
b		.0365	.365	4.31	9
W8 a	.0997	.0429	.430	11.8	8
b		.0419	.420	12.1	8
c		.0660	.662	6.68	8
d		.0440	.441	9.15	8
e		.0385	.386	9.45	8
W9 a	.143	.0653	.457	9.91	8
b	.135	.0646	.479	9.91	8
W10 a	.100	.0517	.517	9.22	4
b		.0458	.458	10.4	4

TABLE V-38

EXTRACTOR PERFORMANCE RAW DATA

Isopropanol Runs

Run Number	Feed Concentration (X_f)	Raffinate Concentration (X_r)	Yield Loss (X_r/X_f)	Solvent to Feed Ratio (S/F)	Number of Actual Sieve Trays (N_{actual})
I1 a	.598	.1260	.211	1.56	8
b		.0340	.056	2.28	8
I2 a	.0881	.0725	.823	.922	8
b	.0881	.0635	.721	1.56	8
c	.0846	.0225	.266	4.76	8
d	.0846	.0152	.180	9.71	8
e	.0846	.0229	.271	5.09	8
f	.0846	.0364	.430	3.28	8
g	.0846	.0428	.506	2.48	9
I3 a	.0974	.0275	.282	3.65	8
b	.0962	.0215	.224	4.54	8
c	.0962	.0119	.124	5.85	8
d	.0962	.0198	.206	4.92	8
I4 a	.0269	.0092	.342	4.96	8
b		.0075	.279	6.08	8
c		.0087	.323	4.97	8
d		.0055	.205	5.95	8
I5 a	.201	.0228	.113	5.43	8
b		.0278	.138	5.04	8
c		.0247	.123	6.46	8

TABLE V-39
EXTRACTOR PERFORMANCE RAW DATA
sec-Butanol Runs

Run Number	Feed Concentration (X_f)	Raffinate Concentration (X_r)	Yield Loss (X_r/X_f)	Solvent to Feed Ratio (S/F)	Number of Actual Sieve Trays (N_{actual})
B1 a	.102	.0235	.230	2.02	U-4
b	.102	.031	.304	1.28	U-4
c	.102	.048	.471	.685	U-4
d	.102	.060	.588	.375	U-4
e	.077	.050	.649	.567	U-4
B2 a	.0979	.0121	.124	1.83	U-8
b	.0979	.0375	.383	.589	U-8
c	.1037	.0453	.437	.528	U-8
d	.0990	.0459	.464	.538	U-8
e	.1052	.0343	.326	.837	U-8
B3 a	.0961	.0287	.299	.701	D-8
b		.0476	.495	.319	D-8
c		.0195	.203	.865	D-8
B4 a	.0982	.0291	.296	.589	D-8
b	.0982	.0447	.456	.461	D-8
c	.0995	.0398	.400	.534	D-8
B5 a	.0961	.0112	.117	1.45	D-8
b	.103	.0131	.127	1.48	D-8
c	.103	.0131	.127	1.44	D-8
B6 a	.0977	.0190	.195	1.42	D-4
b	.0977	.0194	.199	1.49	D-4
c	.0938	.0140	.149	1.45	D-4
d	.0938	.0062	.066	2.86	D-4
B7 a	.0191	.0079	.414	1.55	D-4
b	.0187	.0074	.396	1.53	D-4
c	.0187	.0136	.727	.579	D-4
B8 a	.699	.103	.147	1.62	D-8

FIGURE V-9

ISOPROPANOL :
YIELD LOSS VS SOLVENT TO FEED RATIO WITH DATA FROM THE
"I" SERIES OF RUNS

FIGURE V-10

SEC-BUTANOL
YIELD LOSS VS SOLVENT TO FEED RATIO WITH DATA FROM THE
"B" SERIES OF RUNS

FIGURE V-11

clear with the ethanol data (Figure V-9). While this is partially due to the narrow range of S/F tested, it is probably primarily due to the fact that ethanol was the first alcohol tested, and that the greatest refinement of operating procedures and analysis systems occurred during the ethanol experiments. Thus, it would be expected that some of the scatter results from earlier, less accurate data.

1. Ethanol

The ethanol runs are divided into two categories of feeds and three categories of extractor internal configuration. A standard feed concentration of approximately 10% was used when other parameters were being varied and tested. The second category of feed is all other feeds tested, which included ethanol concentrations higher and lower than 10% and fermentation broths. The extractor configurations tested were 8 or 9 downcomer trays, 4 downcomer trays, and 4 upcomer trays. The tray stack with 8 or 9 downcomer trays was the standard used in tests with lower and higher concentration feeds.

From Figure V-9, it is observed that the upcomer tray stack operated with poorer tray efficiency (equivalent of less than one theoretical plate) than the downcomer tray stacks. The points with the highest yield loss (lowest efficiency) were obtained during run W5 (Table V-37), which used a molasses-based fermentation broth as feed. Thus, the presence of suspended solids and other dissolved components in this feed appears to have had an impact on the mass-transfer efficiency and/or the ethanol equilibrium distribution, although this may have been due in part to poorer control with the opaque molasses solution.

Although the yield-loss curves generated from the equilibrium curve shift with changing feed concentration, the shift is small in the case of a constant equilibrium distribution coefficient. This is in fact observed with the pilot plant data: data points from runs W2, E6, and E7, with feeds of 2, 5, and 20% respectively, lie within the data obtained with 10% feeds (Table V-37 Figure V-9).

Comparing data points in Figure V-9 obtained with 4 and with 8 downcomer trays, the number of theoretical plates did not vary significantly. It seems that the increased tray spacing resulted in a higher tray efficiency, and the same recovery resulted. However, it is also possible that the extractor tray stack is not operating as desired.

For most cases, excluding the upcomer tray-stack configuration, a separation equivalent to about 1.5 theoretical trays is obtained. This represents a tray efficiency of about 20% for the eight tray stack, and 37% for the four tray stack. Alternatively, for either tray stack the height equivalent of a theoretical plate (HETP) is about 3 ft.

The yield losses calculated from equilibrium were based on an ethanol concentration in the solvent stream of 0.1%. This was in fact the average value of y_g measured by the on-line gas chromatograph (GC) system.

A solvent-to-feed ratio of 10 to 12 appears to be best for ethanol extraction. This is based on the pilot plant data (Figure V-9) which

shows increases in the S/F beyond 12 gave little or no improvement in yield. Figure V-9 also demonstrates that at a S/F of 10 to 12 the best way to improve yield is to increase the number of theoretical plates.

From the equilibrium-based calculations (Figure V-6) it is further shown that to improve yield beyond that obtained by increasing the number of theoretical trays to 8 the purity of the solvent, y_s , entering the extractor should be improved. That would most likely be accomplished by partially refluxing the CO_2 at the still top. Since the pilot-plant still did not have a reflux condenser, this option was not tested.

ii. Isopropanol

All isopropanol runs were performed with eight downcomer sieve trays spaced 7" apart. The alcohol feed concentrations tested were roughly 2.7, 10, 20, and 60%. A wide range of solvent-to-feed ratios was investigated with the 10% feed. Pilot plant operating procedures and GC analysis techniques were well developed for these runs, this is reflected by the relatively small amount of scatter in the data obtained using a 10% feed.

The plots of yield loss, x_r/x_f , versus solvent-to-feed ratio (Figure V-7) generated from the equilibrium data show a substantial shift with changing feed concentration. This is caused by the non-linearity of the equilibrium distribution. The pilot plant results obtained with the lower feed concentration are shifted to higher values of x_r/x_f than observed for the 10% feed. Similarly, the x_r/x_f values for a 20% feed are shifted downward, and the 60% feed values shifted downward even further. A standard M-T graphical analysis was used to evaluate these runs. From Figure V-10 it is seen that the eight-tray stack functioned as three to four theoretical plates, giving an efficiency of 38 to 50%. This is equivalent to a 1.5 to 1.2 ft. HETP.

iii. Sec-Butanol

In the sec-butanol runs, both feed concentration and sieve tray configuration were varied. A 10% feed was tested with both the upcomer and downcomer configuration, and both of these were tested at 7" and 14" tray spacings. A 1.9% SBA feed was run in the extractor with four downcomer trays spaced 14" apart. A 70% SBA feed was tested with eight downcomer trays.

As observed with ethanol, doubling the tray spacing while halving the number of trays did not measurably affect the overall extractor performance. This is seen in Table V-39 and Figure V-11, where the data points generated by runs B4, B5, and B6 fall close to the equilibrium-based line for $N_{th} = 4$. This gives a 50% tray efficiency for the 7" tray spacing, and about 100% efficiency for the 14" tray spacing. In both cases, the value for the HETP is the same, about 1.2 feet. The yield loss for run B7 (low alcohol feed) increased as was observed with isopropanol. The yield loss in run B8, which employed a 70% SBA feed, is not shifted downward as was experienced with the high concentration run made with IPA. This run was quite difficult to control, and it is possible that the data is not representative of steady-state.

A decrease in tray efficiency was observed with the upcomer tray configuration, although it was not as dramatic as observed with ethanol. Eight upcomer trays performed as the equivalent of three to four theoretical trays. The four upcomer tray stack performed as only two theoretical trays. Thus, for upcomer trays spaced 7" apart, the tray efficiency, n , varies from 38 to 50%, versus 50% for the downcomer trays. For 14" upcomer trays, n was approximately 50%, versus 100% for similar downcomer trays. Therefore, HETP varied from 1.5 to 1.2 feet for upcomers spaced 7" apart, and was roughly 2.3 feet for upcomers 14" apart.

The tray efficiencies (n) and height equivalent of a theoretical plate (HETP) are summarized in Table V-40 for all three alcohols.

b. Extractor Capacity

Extractor capacity is defined as the maximum set of flowrates for which, at a given solvent-to-feed ratio, the column is hydraulically functional. While the extractor mass transfer efficiency may be diminished at these maximum flowrates, they were still considered to represent the column capacity. Flooding is defined as the point at which the raffinate or extract stream has a second phase entrained in it. When the extractor is operating at capacity, increasing either solvent or feed flowrate causes the extractor to flood.

Another limit to extractor capacity is the entrainment of dispersed phase by the continuous phase. If the linear velocity of the continuous phase is anywhere greater than the droplet rise velocity of the dispersed phase, droplets are entrained. This was observed in the downcomer tube on one occasion.

1. Ethanol:

The solvent-to-feed ratio for ethanol extraction is about ten. The capacity of the extractor was measured with a S/F of 10, sieve trays spaced 7" apart, and 6" downcomers. Each sieve tray had 88 one-eighth inch holes, and a downcomer opening of 1/4". This gave a downcomer area of 3.4×10^{-4} ft², or 0.4% of the column cross-sectional area, and a sieve-hole area of 7.5×10^{-5} ft², or 8.6% of column area.

Early efforts to determine flooding limits were made in runs A6 (not previously reported) and E1, both using an unwindowed column. During run A6, two phases were observed in both the extract and raffinate sight gauges, indicating flooding, when the feed rate, m_f , exceeded 1.1-1.3 lbs/min and the solvent flowrate, m_s , exceeded 11 lbs/min. M_f and m_s values of about 1.1 and 11 lbs/min were attained in run E1 without flooding. A solvent rate of 12.3 lbs/min was run with a feedrate of 0.92 lbs/min in run W1. This was the first run for which the windowed extractor was used, and the tray action observed. As previously noted, tray performance was poor and no further attempts were made to measure capacity with downcomer trays until new sieve trays were fabricated and installed for run W8.

During run W8, with $m_s = 11.3$ lbs/min and $m_f = 1.28$ lbs/min, there was only minor flooding overhead. A solvent head of roughly 1" was observed below the sieve trays. At these high flowrates the extractor contents were highly agitated. Based on these observations, the total flow capacity for the extractor operating at a S/F of 10 was about 12 lbs/min.

TABLE V-40

EXTRACTOR MASS TRANSFER EFFICIENCY

<u>Alcohol</u>	<u>Feed Concentration</u> $\frac{x_f}{x_f}$	<u>Tray Spacing (in)</u>	<u>n (%)</u>	<u>HETS (ft)</u>
Ethanol	0.10	7"	19	3
		14"	37	3
		14"-upcomer	10	12
Isopropanol	0.10	7"	38-50	1.5-1.2
sec-Butanol	0.10	7"	50	1.2
		14"	100	1.2
		7"-upcomer	38-50	1.5-1.2
		14"-upcomer	50	2.5

The extractor capacity with corn-based fermentation broths in runs E2 and E3 was lower. This feed contained approximately 3% suspended corn solids, 9% ethanol, and a variety of dissolved chemicals. The total flow capacity was approximately 7 lbs/min with $S/F = 10$.

Molasses-based fermentation broths were tested in runs E4 and E5. With the downcomer tray stack, these feeds formed an emulsion with the liquid CO_2 , preventing operation. This problem was overcome by the use of an upcomer tray stack in run W5 which was carried out without emulsion problems. Capacity of the extractor was diminished to roughly 6 lbs/min total flow with S/F of 10.

Several other runs were made with inverted tray stacks, or "upcomer" tray stacks. In these cases, the aqueous phase was dispersed, and the CO_2 -rich phase was continuous. The upcomer allowed the dispersion of the phase with the lower volumetric flowrate and an increase in capacity. The same sieve trays were used, having $88\frac{1}{8}$ " holes, but the tray spacing was increased to 14" and the downcomer orifice diameter was increased to $1\frac{1}{8}$ ". Runs W4, W5, and W6 were performed in this manner. In run W4, it was observed that when the solvent rate exceeded 14 lbs/min, drops of aqueous solution were entrained in the upcomers. This indicated that the droplet terminal velocity was less than the solvent velocity through the upcomer. At this point, the feedrate was roughly 1 lb/min. By further increasing the upcomer cross-sectional area, a substantial gain in column capacity could be achieved. The increase in capacity with upcomers must be weighed against the decrease in efficiency.

ii. Isopropanol

All isopropanol runs were made using eight sieve trays spaced 7" apart. Each sieve tray had $88\frac{1}{8}$ " holes. Each downcomer was 6" long. The downcomer orifice size was varied from $\frac{1}{2}$ " to $\frac{1}{4}$ " in run I1, $1\frac{1}{8}$ " for I2, and $\frac{1}{2}$ " for later runs. The desired solvent-to-feed ratio for isopropanol ranged from 4 to 6. Feed rates of 2 lbs/min with solvent rates of 8 to 10 lbs/min could be run. Higher m_0 could not be tested; at the time of the IPA experiments, 10 lbs/min was the maximum CO_2 flowrate which was available to the extractor. Therefore, higher feedrates were tested at low S/F . During run I2, m_f was increased from 2.0 lbs/min to 3.1 lbs/min, 4.1 lbs/min, and 6.2 lbs/min, while maintaining a solvent flowrate of 10.2 lbs/min. With $m_f = 3.1$ lbs/min, there was no flooding, but the solutions between the trays were very turbulent, with the CO_2 droplets rising in swarms. Because of the turbulent action, it was impossible to determine if a distinct region of coalesced CO_2 existed under the trays. When feedrate was increased to 4.1 lbs/min, and later to 6.2 lbs/min, it became very difficult to maintain control of the extractor. Intermittent flooding overhead was observed, although this might have been due in part to difficulty with raffinate flow control at these high rates. Thus, the highest flowrates which allowed stable operation were $m_f = 3.1$ lbs/min and $S = 10.2$ lbs/min.

iii. Sec-Butanol

Both upcomer and downcomer tray stacks were tested, and both were tested with eight and four trays in the stack. Because of the low

solvent-to-feed ratio requirement about 1.5 with SBA, it was anticipated that high feedrates could be achieved. Based on the EtOH and IPA runs, a total flowrate capacity of 12 lbs/min was expected without flooding. At $S/F = 1.5$, this would be about $m_f = 5$ lbs/min and $m_s = 7$ lbs/min. During run B7, with a feedrate of approximately 4.0^s lbs/min, the solvent rate was varied from 1.5 to 9 lbs/min. However, with a feedrate of 4.0 lbs/min, there was a pressure pulsation in the column of as much as 50 psi with each pump stroke. For this reason, feedrates higher than 4 lbs/min were not tested.

As the solvent rate was pushed to 9.0 lbs/min, the action within the extractor was turbulent. No coalesced region of dispersed droplets was observed. After a few minutes of this turbulence, the two phases emulsified. The CO₂-rich phase was being entrained through the downcomers and in the raffinate. This capacity limit, while different from that observed with EtOH and IPA, occurred at a similar total flowrate at 13 lbs/min. The same limit was observed during run B1, using four upcomer trays spaced 14" apart.

In summary, the limit of extractor capacity was roughly 12 lbs/min, regardless of solvent-to-feed ratio. This capacity for downcomer sieve tray stacks is equivalent to 2.5 lbs/ft²-sec. The upcomer tray stack configuration shows promise of increasing extractor capacity for high S/F systems. Corn-based fermentation broths had a capacity reduction of approximately 50%.

4. Reboiler and Product Compositions

Samples from the reboiler were analyzed, using a gas chromatograph, for two primary purposes. The compositions were used in determining the product quality expected under various operating conditions; they were also used in obtaining the thermal characteristics of the reboiler, such as the heat-transfer coefficients and boiling-point elevations.

These samples were obtained in one of two ways. The method used in earlier runs was to draw a sample from the reboiler by flashing it from the still to atmospheric pressure, and collecting a liquid sample at room temperature. This method gave the reboiler composition on a CO₂-free basis. The more complex method, used in later runs, was to flash the reboiler liquid down to atmospheric pressure, trap the liquid in a cold U-tube sampler, and measure the amount of gas evolved from the liquid sample with a dry test meter (DTM). This method allowed calculation of the reboiler composition on a CO₂-included basis.

These data are presented in Tables V-41, V-42, and V-43 for ethanol, isopropanol, and sec-butanol, respectively.

Tables V-44, V-45, and V-46 give the concentration of alcohol in samples obtained from the "product receiver" for each of the three alcohols tested. The feed concentration, x_f , and the solvent-to-feed ratio, S/F , are also listed for each run. A summary of these data along with each of the alcohol water azeotropes is shown in Table V-47.

The product composition is dependent on feed concentration. However, because of scatter in the compositional data, the precise effect of changes in feed composition on the product are not known. For example

TABLE V-41

REBOILER COMPOSITIONS DURING ETHANOL RUNS

<u>Run Number</u>	<u>Time</u>	<u>Feed Rate (lbs/min)</u>	<u>Solvent Rate (lbs/min)</u>	<u>Reboiler Composition (wt %)</u>			
				<u>EtOH</u>	<u>CO₂</u>	<u>H₂O</u>	<u>EtOH (CO₂-free)</u>
W4	4:30	0.85	7.85				90.5
W5	12:00	0.315	1.68	-	-	-	87.6
	12:30	0.315	1.68	-	-	-	85.2
W6	4:35	0.607	5.93	-	-	-	87.3
W9	7:15	0.784	7.77	5.3	94.2	0.5	91.4
W10	3:00	0.525	5.47	35.4	58.9	5.7	86.1
	4:00	0.525	5.47	52.5	38.1	9.4	84.8
	4:45	0.525	5.47	17.9	79.9	2.2	89.4

TABLE V-42

REBOILER COMPOSITIONS DURING ISOPROPANOL RUNS

<u>Run Number</u>	<u>Time</u>	<u>Feed Rate (lbs/min)</u>	<u>Solvent Rate (lbs/min)</u>	<u>Reboiler Composition (wt %)</u>			
				<u>IPA</u>	<u>CO₂</u>	<u>H₂O</u>	<u>IPA (CO₂-free)</u>
I1	3:05	.958	1.50	59.7	28.1	12.2	83.0
I2	3:05	1.05	4.98	49.2	48.0	2.8	94.6
I3	4:30	1.11	5.04	62.4	33.2	4.4	93.4
	5:40	1.11	6.49	60.9	35.6	3.5	94.6
I4	5:00	1.81	8.99	27.4	69.1	3.5	88.7
	5:40	1.81	8.99	30.7	66.2	3.1	90.7
	6:25	1.51	8.99	22.9	74.6	2.5	90.2
I5	3:05	1.02	5.54	49.1	46.6	4.3	92.0
	4:30	1.02	5.54	49.9	46.9	3.2	94.0
	5:30	1.60	8.07	49.8	47.3	2.9	94.5
	6:30	1.25	8.07	51.3	45.9	2.8	94.8

TABLE V-43

REBOILER COMPOSITIONS DURING SEC-BUTANOL RUNS

Run Number	Time	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Reboiler Composition (wt %)			
				SBA	CO ₂	H ₂ O	SBA (CO ₂ -free)
B1	5:15	2.61	1.48	-	-	-	94.0
	6:15	3.00	1.48	-	-	-	95.2
B2	12:25	5.66	2.99	-	-	-	91.6
	2:50	4.11	3.44	-	-	-	92.3
B3	5:00	2.74	2.37	62.7	24.1	13.2	82.5
B5	2:40-3:50	2.05	3.03	67.1	29.2	3.7	94.8
	4:30	3.13	4.51	63.8	33.3	2.9	95.6
B6	2:00	1.05	1.49	52.3	44.5	3.2	94.2
	3:20	2.05	3.06	42.4	46.4	11.2	79.1
	4:30	3.04	4.40	70.7	25.9	3.4	95.4

TABLE V-44

PRODUCT CONCENTRATIONETHANOL

<u>Run Number</u>	<u>Ethanol Concentration in the Feed</u> (wt %)	<u>Solvent to Feed Ratio</u>	<u>Ethanol Concentration in the Product</u> (%)
E1	0.1409	10.1	85.9
		11.1	88.9
		11.3	84.0
E2	0.0907*	12.1	74.0
		9.6	85.9
E3	0.0877*	13.8	88.3
		7.35	89.1
		11.1	87.5
E4	0.0884**	21.4	88.5
		8.06	--
E6	0.0505	9.13	81.7
E7	0.199	9.46	89.53
W1	0.1039	10.1	86.2
		10.5	87.5
		10.4	87.7
		13.4	84.2
W2	0.0227	11.1	80.9
		8.65	70.1
W4	0.1010	9.23	86.3
W5	0.0615**	5.33	86.4
		10.3	85.9
W6	0.102	9.76	85.0
W8	0.0997	9.15	87.4
		9.45	84.7
W9	0.143	9.91	87.5
W10	0.100	10.4	83.0
			89.4

* corn fermentation broths

**molasses fermentation broths

TABLE V-45

PRODUCT CONCENTRATIONISOPROPANOL

<u>Run Number</u>	<u>Isopropanol Concentration in the Feed (wt %)</u>	<u>Solvent to Feed Ratio</u>	<u>Isopropanol Concentration in the Product (%)</u>
I1	0.60	1.56 2.28	83.5 86.4
I2	0.088 0.088 0.85	1.56 4.98 1.6-9.7	94.0 94.5 94.2
I3	0.097	4.54 5.85 4.92	93.4 94.6 94.3
I4	0.027	4.98 5.95	88.7 90.5 83.8
I5	0.201	5.43 5.04 6.46	94.8 95.0 94.7

TABLE V-46

PRODUCT CONCENTRATIONsec-BUTANOL

<u>Run Number</u>	<u>sec-Butanol Concentration in the Feed</u> (wt %)	<u>Solvent to Feed Ratio</u>	<u>sec-Butanol Concentration in the Product</u> (%)
B1	.102 .077	.4-2	94.4
B2	0.10	.53 .53 .84	91.6 93.6 92.3
B4	0.098	.53	93.7
B5	0.099	1.46	95.5
B6	0.098 0.094 0.094	1.42 1.45 2.86	94.1 95.4 95.7
B7	0.019	0.6-1.5	93.5
B8	0.68	1.62	91.0

TABLE V-47
PRODUCT CONCENTRATION
SUMMARY

<u>Feed Alcohol</u> (Azeotrope Comp.) @ 1 atm.	<u>Feed Alcohol Concentration</u> <u>Range or Type</u>	<u>Average Alcohol Concentration</u> <u>in the Product</u> (%)
Ethanol (95.6)	$0 < X_f < 0.05$	77.6 ± 6.5
	$0.05 < X_f < 0.14$	86.1 ± 1.9
	$0.14 < X_f < 0.20$	87.2 ± 2.2
	Corn Broth	84.3 ± 7.0
	Molasses Broth	87.1 ± 1.2
Isopropanol (87.9)	$0 < X_f < 0.05$	87.7 ± 3.5
	$0.05 < X_f < 0.15$	94.2 ± 0.2
	$0.15 < X_f < 0.50$	94.8
	$0.50 < X_f < 0.70$	85.0 ± 2.0
sec-Butanol (87.9)	$0 < X_f < 0.05$	93.5
	$0.05 < X_f < 0.15$	94.2 ± 1.4
	$0.50 < X_f < 0.70$	91.0

while a 20% ethanol feed gave a higher average product concentration than the 10% feeds there was overlap of measured product concentration between the two sets of products. For ethanol, the general trend was that with increasing ethanol concentration in the feed (at least up to the highest feed concentration tried, 20%) the product quality improved. In the cases of isopropanol and sec-butanol, where feed concentrations in excess of 50% were tested, the product concentration passed through a maximum as a function of feed concentration.

The product concentrations exceeded the azeotropic compositions for SBA and IPA with water (1 atm). The EtOH product concentration fell short of the azeotrope with water.

The reboiler, extract, and product compositions should have been equivalent on a CO_2 -free basis; however, that was not necessarily observed due to alcohol vaporization with CO_2 .

5. Still and Reboiler Performance

The still and reboiler performance, including the boiling-point elevation for mixtures of CO_2 and alcohol, were monitored for the three alcohols. These data are presented as the boiling-point elevations, BPE, the heat-transfer coefficients, U_o , and the purity of the distillate, which is recycled to the extractor as solvent.

a. Boiling Point Elevation

The BPE is defined as the increase in temperature required to boil a mixture of carbon dioxide, alcohol, and water over the temperature required to boil pure liquid CO_2 at the same pressure. When the distillation column is operating at a constant pressure and the overhead vapor is nearly pure CO_2 , the temperature difference between the boiling liquid in the reboiler and the overhead vapor is approximately equal to the boiling point elevation. This approximation is reported as the BPE in this section.

Still and reboiler temperatures along with some run conditions are tabulated in Tables V-48, V-49, and V-50 for EtOH, IPA, and SBA, respectively. These data were used in the calculation of BPE and U_o . Reboiler sample compositions and BPE are given in Table V-51. Values of BPE averaged 3 °F for ethanol-water- CO_2 mixtures, in which the ethanol concentration was as high as 52.5%. Unfortunately, only a few reboiler compositions are available for EtOH- CO_2 mixtures; the reboiler sampling technique was not operational until the last two ethanol runs.

The boiling-point elevation observed with isopropanol is considerably higher than that for ethanol, and shows a stronger dependence on solution composition. For example BPE of 6 - 7 °F are observed for solutions which are 20 - 30% IPA, and 12 - 13 °F at about 60% IPA.

Boiling point elevations for sec-butanol ranged from 4 °F to 9 °F, with SBA concentrations ranging from 42.4% to 67.1%. A very high value of BPE, 18 °F, was observed with an SBA concentration of 62.7% in run B3.

TABLE V-48

REBOILER AND STILL TEMPERATURES
Ethanol

RUN NUMBER	FEED CONCENTRATION	FEED RATE (lbs/min)	SOLVENT RATE (lbs/min)	SOLVENT-TO- FEED RATIO	REBOILER SHELLSIDE	STILL (MINIMUM)	TUBESIDE In	TUBESIDE Out
E1	0.1409	0.500	5.06	10.1	65	61	101	72
		0.700	7.82	11.1	65	62	112	81
		0.861	9.78	11.3	66	63	116	86
E2	0.0907	0.275	3.33	12.1	65	61	104	71
		0.623	6.00	9.60	66	63	114	85
E3	0.0877	0.328	4.54	13.8	65	61	104	
		0.579	4.25	7.35	65	61	107	72
		0.405	4.51	11.1	65	61	105	72
F4	0.0884	0.126	2.69	21.4	62	60	100	65
		0.333	2.69	8.06	64	61	108	66
E6	0.0505	0.832	7.60	9.13	63	60	113	83
E7	0.199	0.204	2.69	9.46	64	60	98	74
		0.332	3.45	10.4	64	61	104	74
W1	0.1039	0.59	5.95	10.1	64	61	108	73
		0.73	7.65	10.5	65	62	116	78
		0.88	9.14	10.4	66	63	118	84
		0.92	12.3	13.4	65	62	112	90
W2	0.0227	0.51	5.68	11.1	63	61	111	82
		0.88	7.59	8.65	64	61	118	90
W4	0.1010	0.59	3.55	6.02	64	61	110	79
		0.85	7.05	9.23	64	60	116	82
		1.07	13.1	12.9	--	--	---	--
		2.31	10.2	4.41	62	59	113	85
		3.82	10.2	2.67	--	--	---	--
W5	0.0615	0.32	1.68	5.23	52	31	85	66
		0.94	5.51	5.85	38	37	99	49
		0.53	5.51	10.3	36	36	99	43
W6	0.1020	0.607	5.93	9.76	64	61	103	76
W8	0.0997	0.452	5.32	11.8	57	56	105	66
		0.932	11.3	12.1	67	63	125	82
		1.28	8.55	6.68	--	--	---	--
		0.952	8.71	9.15	55	52	123	83
		0.565	3.31	9.45	52	48	114	81
W9	0.143	0.784	7.77	9.91	psi 600+47 750+65	43	113	72
						63	114	86
W10	0.100	0.838	7.73	9.22	48	46	119	76
		0.525	5.47	10.4	46	43	119	75

TABLE V-49
REBOILER AND STILL TEMPERATURES
Isopropanol

Run Number	Feed Concentration	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent to Feed Ratio	Average Temperatures (°F)			
					Reboiler Shellside	Still (Minimum)	Tubeside In	Tubeside Out
I1	0.60	0.958	1.50	1.56	54	49	94	58
		0.958	2.68	2.28	59	49	101	67
I2	0.086	1.05	0.965	0.922	59	47	93	64
		1.05	1.63	1.56	58	46	98	67
		1.05	4.98	4.76	55	46	109	79
		1.05	10.2	9.71	74	65	121	94
		2.00	10.2	5.09	77	65	116	96
I3	0.097	1.11	4.05	3.65	58	46	105	82
		1.11	5.04	4.54	58	45	110	82
		1.11	6.49	5.85	58	46	116	86
		1.86	9.15	4.92	71	60	121	92
I4	0.027	0.995	4.96	4.98	49	45	108	71
		0.995	6.05	6.08	56	50	113	74
		1.81	8.99	4.97	70	64	123	85
		1.51	8.99	5.95	72	65	123	91
I5	0.201	1.02	5.54	5.43	73	65	109	85
		1.60	8.07	5.04	76	66	121	94
		1.25	8.07	6.46	76	65	118	93

TABLE V-50

REBOILER AND STILL TEMPERATURES
sec-Butanol

Run Number	Feed Concentration	Feed Rate (lbs/min)	Solvent Rate (lbs/min)	Solvent to Feed Ratio	Average Temperatures (°F)			
					Reboiler: Shellside	Still (Minimum)	Tubeside In	Tubeside Out
B1	0.1020	0.603	1.22	2.02	50	45	76	59
		0.929	1.19	1.28	49	51	79	62
		1.46	1.00	0.685	50	49	88	52
		2.61	0.978	0.375	50	50	119	53
		2.61	1.48	0.567	54	47	125	58
B2	0.10	0.946	1.73	1.83	48	46	85	56
		2.07	1.22	0.589	48	46	75	53
		5.66	2.99	0.528	50	48	95	59
		4.11	2.21	0.538	51	47	92	54
		4.11	3.44	0.837	50	47	96	56
B3	0.0951	2.74	1.92	0.701	67	49	112	82
		2.74	0.875	0.319	66	49	101	70
		2.74	2.37	0.865	62	44	137	82
B4	0.099	.995	0.506	0.589	49	48	86	55
		2.10	0.969	0.461	53	49	96	59
		2.92	1.56	0.534	68	49	108	77
B5	0.099	1.05	1.52	1.45	51	46	89	56
		2.03	3.03	1.48	53	46	98	61
		3.13	4.51	1.44	54	46	101	73
B6	0.096	1.05	1.49	1.42	50	46	92	59
		2.05	3.06	1.49	51	47	98	59
		3.04	4.40	1.45	52	46	100	65
		2.07	5.92	2.86	53	45	105	73
B7	0.019	2.07	3.20	1.55	46	44	98	54
		2.66	4.06	1.53	48	46	101	54
		2.66	1.54	0.579	48	46	92	52
B8	0.699	0.932	1.51	1.62	68	64	96	71

TABLE V-51

REBOILER BOTTOMS COMPOSITION AND BOILING POINT ELEVATIONS (BPE)

Run		Reboiler Composition (wt %)			BPE (°F)
Number		Alcohol	CO ₂	H ₂ O	
<u>Ethanol</u>					
W9	b	5.3	94.2	0.5	2
W10	b	35.4	58.9	5.7	3
	b	52.5	38.1	9.4	3
	b	17.9	79.9	2.2	3
<u>Isopropanol</u>					
I1	a	59.7	28.1	12.2	5
I2	c	49.2	48.0	2.8	11
I3	b	62.4	33.3	4.4	13
	c	60.9	35.6	3.5	12
I4	c	27.4	69.1	3.5	7
	c	30.7	66.2	3.1	7
	d	22.9	74.6	2.5	6
I5	a	49.1	46.6	4.3	8
	a	49.9	46.9	3.2	8
	b	49.8	47.3	2.9	10
	c	51.3	45.9	2.8	11
<u>sec-Butanol</u>					
B3	b	62.7	24.1	13.2	18
B5	b	67.1	29.2	3.7	7
	c	63.8	33.3	2.9	9
B6	a	52.3	44.5	3.2	4
	b	42.4	46.4	11.2	4
	c	70.7	25.9	3.4	6

These data have been plotted as boiling-point elevation versus weight-fraction CO_2 in the reboiler in Figure V-12.

The pilot plant data indicate that maintaining a reboiler composition of about 40% CO_2 would be appropriate for ethanol and sec-butanol. An optimum composition is not apparent for isopropanol; further analysis of energy requirements as a function of composition would be required.

b. Reboiler Heat Transfer Coefficient

The heat transfer coefficient for the pilot plant reboiler has been calculated under a variety of conditions. The log-mean temperature difference around the reboiler was calculated from the temperature data in Tables V-52, V-53, and V-54. From the temperature change on the tubeside and the tubeside pressure the change in enthalpy of the CO_2 was found. The product of the enthalpy change times the solvent mass flowrate is the heat transfer rate, Q , which was calculated for each run setting. Then the overall heat transfer coefficient was calculated for each run setting as follows:

$$\begin{aligned} Q &= U_o \times A \times T_{LM} \\ Q &= \dot{m} \times dH \\ \text{so } U_o &= \dot{m} \times dH / (A \times T_{LM}) \\ \text{and } A_o &= 6 \text{ ft}^2 \end{aligned}$$

These values are tabulated in Tables V-52, V-53, and V-54, for EtOH, IPA, and SBA, respectively. These values of U_o have been plotted against the solvent flowrate in Figures V-13, V-14, and V-15. The velocity of the fluid entering and leaving the tubes is given beneath the mass flowrate. A dependence of U_o on the velocity through the tubes is observed. This would indicate that most of the heat transfer resistance is on the tubeside. By maintaining tube velocities in excess of 2.5 ft/sec at the inlet, heat transfer coefficients on the order of 200 BTU/hr-ft²-°F can be achieved.

It should be noted that conditions in the pilot plant varied from conditions for which a full-scale plant would be designed. The tubeside pressure in the pilot-plant was 1200 psi, whereas a tubeside pressure of 960 psi is planned for a full-scale plant. While no phase change occurs at 1200 psi, the density change of the fluid is quite similar to that of condensing CO_2 at 960 psi.

c. Solvent Purity

The solvent purity was measured with an on-line GC. It varied from 0.02 - 0.14%, 0.04 - 0.36%, and 0.03 - 0.33% alcohol for ethanol, isopropanol, and sec-butanol, respectively. The alcohol concentration increased with increasing feed concentration of alcohol and with decreasing S/F.

BOILING POINT ELEVATION
VERSUS WEIGHT FRACTION CO₂ IN
REBOILER

FIGURE V-12

TABLE V-52
REBOILER HEAT TRANSFER COEFFICIENTS AND BOILING POINT ELEVATIONS

<u>Ethanol</u>				
<u>Run Number</u>	<u>Solvent Flowrate (lbs/min)</u>	<u>T_{RB}-T_S* (°F)</u>	<u>ΔT_{LM}** (°F)</u>	<u>Heat Transfer Coefficient (Btu/hr, ft², °F)</u>
E1	5.06	4	17.7	153
	7.82	3	28.8	169
	9.78	3	32.7	181
E2	3.33	4	17.6	112
	6.00	3	31.3	116
E3	4.54	4	20.5	127
	4.25	4	19.5	136
	4.51	4	18.9	139
E4	2.69	2	13.8	110
	2.69	3	13.6	137
E6	1.60	3	32.7	143
E7	2.69	4	19.6	61
	3.45	3	21.6	90
W1	5.95	3	22.1	168
	7.65	3	27.8	186
	9.14	3	32.0	184
	12.3	3	34.9	177
W2	5.68	2	31.3	108
	7.59	3	38.3	112
W4	3.55	3	27.7	79
	7.85	4	32.0	160
	13.1	-	----	----
	10.2	3	35.2	172
	10.2	-	----	----
W5	1.68	21	22.2	12
	5.51	1	29.2	116
	5.51	0	25.5	139
W6	5.93	3	22.9	138
W8	5.32	1	23.3	145
	11.3	4	31.8	254
	8.55	-	----	----
	8.71	3	45.1	132
	5.31	4	43.4	79
W9	7.77	2	42.9	108
		2	33.0	137
W10	7.73	2	46.2	129
	5.47	3	47.7	82

*T_{RB}-T_S is the reboiler shell side temperature minus the lowest temperature recorded in the still at the same time. This temperature difference is referred to as the boiling point elevation.

**ΔT_{LM} is the log mean temperature difference.

TABLE V-53

REBOILER HEAT TRANSFER COEFFICIENTS AND BOILING POINT ELEVATIONSIsopropanol

<u>Run Number</u>	<u>Solvent Flowrate (lbs/min)</u>	<u>T_{RB}-T_S* (°F)</u>	<u>ΔT_{LM}** (°F)</u>	<u>Heat Transfer Coefficient (Btu/hr, ft², °F)</u>
I1	1.50	5	15.6	39
	2.68	10	20.5	72
I2	.965	12	15.1	22
	1.63	12	20.8	39
	4.98	11	37.0	81
	10.2	9	31.6	149
	10.2	12	27.8	137
I3	4.05	12	34.2	62
	5.04	13	36.2	83
	6.49	12	41.2	94
	9.15	11	33.4	152
I4	4.96	4	37.5	85
	6.05	6	33.8	123
	8.99	6	30.1	198
	8.99	7	32.4	171
I5	5.54	8	21.8	138
	8.07	10	29.5	129
	8.07	11	27.6	132

*T_{RB}-T_S is the reboiler shell side temperature minus the lowest temperature recorded in the still at the same time. This temperature difference is referred to as the boiling point elevation.

**Δ_{LM} is the log mean temperature difference.

TABLE V-54

REBOILER HEAT TRANSFER COEFFICIENTS AND BOILING POINT ELEVATIONSsec-Butanol

<u>Run Number</u>	<u>Solvent Flowrate (lbs/min)</u>	<u>T_{RB}-T_S* (°F)</u>	<u>ΔT_{LM}** (°F)</u>	<u>Heat Transfer Coefficient (Btu/hr, ft², °F)</u>
B1	1.22	5	16.0	9.2
	1.19	5	20.3	8.3
	1.00	1	12.2	26.4
	.978	0	21.0	40
	1.48	7	23.3	57
B2	1.73	2	18.9	21
	1.22	2	13.0	14
	2.99	2	22.4	56
	2.21	4	14.5	54
	3.44	3	19.6	85
B3	1.92	18	27.3	33
	.875	17	14.3	33
	2.37	18	41.6	45
B4	.586	1	17.0	8.3
	.969	4	18.8	24
	1.56	19	20.8	59
B5	1.52	5	16.3	26
	3.03	7	21.4	76
	4.51	9	30.9	75
B6	1.49	4	21.4	22
	3.06	4	22.0	76
	4.40	6	26.8	89
	5.92	8	33.5	101
B7	3.20	2	23.5	78
	4.06	2	21.6	117
	1.54	2	16.7	33
B8	1.31	4	11.2	52

*T_{RB}-T_S is the reboiler shell side temperature minus the lowest temperature recorded in the still at the same time. This temperature difference is referred to as the boiling point elevation.

**ΔT_{LM} is the log mean temperature difference.

Figure V-13

ISOPROPANOL

FIGURE V-14

SEC-BUTANOL

FIGURE V-15

VI. CO-SOLVENT STUDIES

A. Introduction

The foregoing discussion of experimental studies and the engineering analysis of critical-fluid extraction showed that relatively high solvent-to-feed ratios are required for ethanol recovery. For a 10% ethanol feed, a ratio of 11.5 (weight per weight) of solvent to feed is required (Part I, Table IV-18). While this results in a reduction in energy consumption compared to distillation, it is apparent that there could be a significant improvement if the solvent-to-feed ratio could be decreased.

Several reports in the literature (1,2) describe the use of co-solvents, or entrainers, to improve the extraction of a given component with supercritical solvents. Co-solvents are usually ordinary organic liquids, such as acetone (2). Based on these reports, it was proposed that certain liquids may serve to improve the distribution coefficient for ethanol, when added to the CO₂ solvent.

Increasing the distribution coefficient by the addition of a co-solvent could decrease the overall capital and operating costs of the extraction system in the following way. The major equipment items are the extractor, the reboiler, and the compressor. The primary utility cost is power for the compressor. With the addition of a co-solvent, the solvent requirement, or solvent-to-feed ratio, to perform the same amount of ethanol extraction from the aqueous feed is decreased. Since the extractor tower diameter, reboiler surface area, and compressor capacity and power consumption are all related to the solvent-to-feed ratio, a decrease in the required solvent-to-feed ratio decreases both the capital and operating cost of the process.

Co-solvent would be introduced into the extractor at a point several stages above the bottom solvent feed point; this is to allow acceptably complete stripping of residual co-solvent from the aqueous phase for exit of the raffinate stream. The only additional unit operation relative to the co-solvent-free process is a still to separate product and co-solvent from the vapor-recompression evaporator bottoms product. This represents a relatively small addition of energy and capital because the product-co-solvent still capacity is small compared to the major equipment items.

Based on these apparent advantages, a series of laboratory tests with several candidate materials was carried out. The results of these are summarized in Table VI-1. Because of analytical difficulties in high-pressure samples drawn from the bench-scale equilibrium apparatus, absolute values of the distribution coefficient may not be meaningful. For example, with no co-solvent, the dc value was 0.03-0.06, lower than the value for ethanol given previously (0.10). However, the quantitative improvement in dc with the use of certain co-solvents was evident. On the basis of these results, 2-ethylhexanol was chosen for further study.

TABLE VI-1
COSOLVENT DATA ON ETHANOL-WATER-CO₂ SYSTEM

	<u>No</u> <u>Cosolvent</u>	<u>2-Ethyl</u> <u>Hexanol</u>	<u>Hexanol</u>	<u>Ethyl</u> <u>Hexanediol</u>	<u>n-Amyl</u> <u>Alcohol</u>	<u>tert-Amyl</u> <u>Alcohol</u>	<u>n-</u> <u>Butanol</u>
% Cosolvent (in total volume)	-	2.9%	1.4%	1.9%	1.7%	0.4%	1.7%
% Ethanol in Feed (cosolvent-free)	10%	9%	10%	13%	11%	9%	9%
% EtOH in product (cosolvent-free)	73%	56%	81%	78%	61%	64%	75%
D.C.	.03-.06	.2-.4	.1	.01-.07	.12	.1	.07
D.C. of cosolvent	-	> 10	> 10	.75	> 10	> 10	.89

An initial pilot-unit program was undertaken to be followed by a test program to obtain detailed process data. These initial studies reported herein were carried out as a first phase to build and test modifications to the existing pilot unit. The major objective was to determine the effectiveness of co-solvent addition in improving extractor performance.

The pilot plant co-solvent program consisted of ten experimental runs. Compositions of the feed, raffinate, solvent, extract, and product streams were determined. Temperatures and pressures throughout the system were recorded on a regular basis. During each run, the aqueous feed rate, the co-solvent feed rate, and the solvent-to-feed ratio could be varied.

Table VI-2 lists the experimental runs in chronological order. Solvent-to-feed ratios, feed concentrations, and objectives are given for each run. Co-solvent concentrations in the CO₂ phase were varied. Feed concentrations were changed in later runs to evaluate the extractor performance with dilute feeds. Comparison of pilot-unit data with and without co-solvents were made by estimating the change in distribution coefficient due to the presence of co-solvents.

B. Unit Equipment and Operation

The critical-fluid extraction pilot unit was modified to include a co-solvent feed and recovery system. In this flowscheme, co-solvent, mixed with liquid CO₂, contacted the ethanol-containing aqueous feed in a counter-current extraction column. The co-solvent was carried along with CO₂ in the extract, and together were sent to the CO₂ recovery still. The CO₂ was vaporized and taken off as overhead, leaving a bottoms product rich in ethanol and co-solvent. A new recovery system was designed and tested to separate and recover the co-solvent and the ethanol product. A flow schematic is given in Figure VI-1.

1. Extractor and CO₂ Recovery/Recycle

The extractor was a windowed vessel constructed of 316 stainless steel designed for counter-current operation. It was 80 inches in height, with an internal diameter of 4 inches. The aqueous feed solution was prepared in two open-top 35 gallon tanks connected in parallel. The feed was pumped from the tanks to the top of the extractor and passed counter-currently to a liquid CO₂-co-solvent stream. After passing through the extractor, the raffinate was flashed to atmospheric pressure across a valve and sent to a receiving tank.

The CO₂ solvent was recycled through the extraction system. It exited the compressor as a superheated fluid and was cooled to room temperature as it passed through the CO₂-recovery still reboiler coils, giving its latent heat to boil-up the shellside liquid. A portion of the liquid CO₂ stream was metered through a valve and mixed with the co-solvent in a sight gauge, with the remainder of the CO₂ going directly to the bottom of the extractor. The co-solvent was pumped to the sight gauge from a closed-top 35 gallon tank. The metering pump used was 1/3 hp, rated to 2000 psi discharge pressure, and 4.9 gph flow with variable stroke-length adjustment for 10:1 turndown ratio. The CO₂-co-solvent mixture was fed to the extractor just below the bottom sieve tray. It was injected directly into the coalesced CO₂ phase through a tube extending two inches in from the wall of the extractor column.

TABLE VI-2
COSOLVENT EXTRACT EXPERIMENTS

<u>RUN #</u>	<u>FEED</u>	<u>SOLVENT-TO-FEED RATIO</u>	<u>OBJECTIVE OF RUN</u>
CSE-1	Synthetic 10% EtOH	5	Test the operation of the co-solvent feed system.
CSE-2	Synthetic 10% EtOH	5	Establish if cosolvents affect extractor performance.
CSE-3	Synthetic 10% EtOH	2	Investigate how the cosolvent concentration affects the extractor performance.
CSE-4	Synthetic 10% EtOH	2	Further investigate the effect of the cosolvent concentration on the extractor performance.
CSE-5	Synthetic 1% EtOH	1	Operate with a low feed concentration to simulate the lower section of an extraction column.
CSE-6	Synthetic 1% EtOH	2	As in CSE-5.
SCE-7	Synthetic 0.05% EtOH	2	Extend knowledge of the extractor performance with more dilute feed solution.

TABLE VI-2
COSOLVENT EXTRACT EXPERIMENTS
continued

<u>RUN #</u>	<u>FEED</u>	<u>SOLVENT-TO-FEED</u> <u>----- RATIO -----</u>	<u>OBJECTIVE OF RUN</u>
CSE-8	Synthetic 0.05% EtOH	2	As in CSE-7.
CSE-9	Synthetic 0.5% EtOH	2	Operate with a low feed concentration, a low extraction temperature, and a lower concentration of cosolvent in CO ₂ (about 10%) to try to eliminate foaming problems.
SCE-10	Synthetic 14.5% EtOH	2	Investigate the extractor performance with a more concentrated feed, cosolvent concentration of about 20% in CO ₂ , and a low extractor operating temperature.

FIGURE VI-1. EXTRACTION UNIT FLOW SCHEMATIC

The CO₂-co-solvent mixture bubbled up through the extractor contacting the aqueous feed and finally coalesced under the top flange of the extractor. The position of the liquid interface was maintained by manual control of a metering valve regulating the raffinate flowrate. The extract flowrate was regulated by a back-pressure control loop. The extract stream was flashed to the operating pressure of the CO₂-recovery still and sent to the decanter.

The CO₂-co-solvent ethanol liquid-vapor mixture was drawn off the top of the decanter and sent to the CO₂ recovery still. An almost pure CO₂ stream was taken out of the still tops, leaving approximately 50 wt % CO₂ mixture in the reboiler. The reboiler liquid was drawn off to maintain a liquid level just above the coils in the reboiler and was sent to the reboiler sampling system. The reboiler sampling system consisted of two sight gauges connected in series, the first acting as a liquid vapor separator, and the second as a liquid-liquid separator. This system allowed the separation and sampling of a dense and a light liquid phase when two liquid phases were present. The light liquid phase was drawn off from the second sight gauge, flashed to 30 psig, and sent to a flash vessel where most of the CO₂ was vaporized from the liquid. The liquid, primarily ethanol and co-solvent and CO₂-lean, was then sent to the co-solvent product recovery system.

2. Co-Solvent/Product Recovery

The co-solvent/product recovery system flow schematic is shown in Figure VI-2. The system design was based on a feed rate to the still of 0.4 lb/min, and 50 wt % co-solvent. All process equipment was oversized and designed for easy turn-down with high turn-down ratios to allow for flexibility in the operation of the system.

The feed to the co-solvent recovery still was drawn off the bottom of the flash vessel and the flowrate was regulated by manual control of a metering valve. The flash vessel was a closed-top 35-gallon stainless steel tank. The operating pressure in the flash vessel was maintained at 30 psig by regulating the flow of CO₂ vapor out the top of the vessel. The CO₂ vapor flashed from the liquid mixture as the mixture passed from the still at 750 psi to the flash vessel at 30 psig. The feed stream was sent through the feed preheater and brought to its boiling point before entering the still. The feed preheater was a heat exchanger with the feed passing on the tube side counter-currently to hot oil in the shell.

The still was a 94-inch column of 2-1/2-inch 316 stainless-steel pipe. The column consisted of three sections. The top section housed a water-cooled partial-reflux condenser coil made of 2-1/2 feet of 1/4-inch 316 stainless-steel tubing. The condensing coil had 3 coils and 3-inch leads, giving a surface area of 0.16 ft². The water flowrate was regulated using a flowmeter rated to 100 cc/min with a manual valve.

FIGURE VI-2. PILOT-PLANT COSOLVENT/PRODUCT RECOVERY SYSTEM

The middle section of the co-solvent recovery still consisted of a feed disperser and two 12-inch sections of Metex stainless steel mesh packing. One 12-inch section of packing supplied the equivalent of about 5 theoretical trays by providing contact area between the vapor upflow and the liquid downflow in the distillation column. One section of packing was placed above the feed point and acted as a rectifying section, while the other section of packing was placed below the feed point, providing a stripping section. The feed disperser was a 1/4-inch 316 stainless-steel tube which extended 1-1/2 inches into the column. The end of the tube was capped and ten radial slits were cut 0.08 inches deep into the underside of the tube to disperse the feed in a spray over the bottom section of packing.

The bottom section of the co-solvent recovery still housed the reboiler coils. There were 17-1/2 feet of 3/8-inch 316 stainless-steel tubing wrapped in a coil 30 inches long and 1-3/4 in diameter which provided 1.72 ft^2 of surface area. Hot oil was the tube-side fluid which supplied the latent heat of vaporization of the shell-side liquid. The co-solvent-enriched shell-side fluid was drawn off to maintain a liquid-vapor interface just above the reboiler coils. A sight glass on this section of the still was used for manual control of the liquid level. The bottoms liquid was then sent through the shell side of a 20-foot water-cooled heat exchanger before storage in the co-solvent tank.

The overhead product, rich in ethanol, was metered through a valve sized to maintain a constant still pressure of 5 to 10 psig. The overhead product was sent through the shell side of a water-cooled condenser and cooler and then to the ethanol product tank.

Hot oil was the heating medium for both the still reboiler and the feed preheater. The oil was drawn from the heating-fluid storage and surge tank and pumped to the circulation heater by a high-temperature centrifugal circulation pump rated to 500°F, with a capacity of 4 gpm at 17 psi pressure head. The circulation heater was rated at 18 kW. When the oil temperature reached 475°F, the voltage to the heater was decreased from 480 volts to 208 volts, which decreased the power from 18kW to 3.4kW. This enabled less cycling of the oil temperature, and thus better temperature control. The hot oil exited the circulation heater and passed first through the tube side of the reboiler coils and then the shell side of the feed preheater. The cooled oil was then recycled to the circulation heater.

3. Operating Procedures

A procedural checklist was assembled for start-up, operation, and shut-down for the modified pilot system. In addition, an emergency shut-down procedure was written for the co-solvent recovery system.

Once the extractor and still reached the desired operating pressures and the flowrates were set and balanced, the extractor approached a mass-transfer steady-state. A standard run sheet (Appendix III) was utilized in recording the operating conditions throughout a run. Attainment of steady-state was monitored by frequently sampling and analysis of the raffinate. Raffinate samples were taken after the pressure let-down valve but before the raffinate entered the storage tank.

Feed samples were taken from the feed line valve just after the feed pump, giving an in-line sample of the feed to the extractor. Samples of the extract and of the solvent entering the extractor flowed directly to a gas-chromatograph sampling valve. This sampling technique required a simultaneous pressure let-down and sample vaporization, which was achieved by immersing the flash valves in a hot-oil bath, and wrapping the line from the valve to the GC with heating tape.

For the case of three-phase mixtures in the reboiler, a reboiler sampling system was built to separate and sample each liquid phase. In this system the samples were flashed across a valve and liquid was coalesced and collected, while the vapor phase was passed through a dry test meter to determine the liquid-to-vapor ratio.

A porapak Q column was used with a thermal conductivity detector in the GC analyses. A Spectra Physics Minigrator was used to integrate peak areas and calculate concentrations. Samples were injected into the GC twice, once at a low temperature (about 90°C) to obtain peak separation between the water and ethanol and again at a higher temperature (200°C) to separate the co-solvent peak from the combined ethanol-water peak. This technique was used for all reboiler, product, raffinate, and decanter samples. To establish a baseline for comparison, ethanol water standard solutions (0.02 wt % - 15 wt %) were injected at the low temperature setting (90°C) and co-solvent ethanol standard solutions (0.1 wt % - 60 wt %) were injected at the higher temperature (200°C).

The co-solvent/product recovery system was viewed as two separate systems during the start-up operation: the hot oil system and the recovery system per se. The majority of the control system was manual. A standard run sheet is given in Appendix IV.

C. Results

1. Extraction Runs

A summary of results of pilot-unit co-solvent runs is given in Tables VI-3 through VI-12. Listed are compositions, solvent-to-feed ratios, pressures, temperatures, co-solvent concentrations in the CO₂ phase, observations on system performance, and comments on the results.

All runs were performed in the windowed extraction column. A tray stack of eight teflon-stainless steel sieve trays spaced 7" apart was used for the series of runs CSE-2 through CSE-10. Each sieve tray had 88 1/8-inch sieve holes, and a 3-1/2-inch-long downcomer with 1/2-inch internal diameter. The feeds for these runs were mixtures prepared with 190-proof ethanol and water. Run CSE-1 used water mixed with SDA 30, a 90/10 blend of ethanol and methanol.

TABLE VI-3

RUN CSE-1

T (Extractor) = 70°F

P (Extractor) = 1180 psi

T (Still) = 49°F

P (Still) = 620 psi

Feed: SDA #30, 8.52 WT% EtOH

Clock Time	Feed (lbs/min)	Solvent (lbs/min)	Cosolvent Concentration in CO ₂ (Wt %)	Solvent-to- Feed Ratio	Ethanol Concentration (Wt %)					
					Raffinate			Product		
					Average	High	Low	Average	High	Low
5:10-6:00	1.18	4.97	-0-	4.21	6.21	6.26	6.16			
6:00-6:30	1.18	5.00	-0-	4.24	6.27	6.28	6.26			
6:30-7:15	1.21	5.14	1.53	4.25	5.01	6.28	4.32			

NOTES: Column performance with 16 tray design was erratic with frequent flooding. Cosolvent injection and premixing system operated well. Cosolvent mixing was clearly visible in CO₂ phase under first couple of trays. Density gradients in CO₂ phase were less noticeable as CO₂ moved up the column. Raffinates appear devoid of cosolvent.

TABLE VI-4

RUN CSE-2

T (Extractor) = 68°F

P (Extractor) = 1210 psi

T (Still) = 50°F

P (Still) = 630 psi

Feed: 9.93 Wt % EtOH

Clock Time	Feed (lbs/min)	Solvent (lbs/min)	Cosolvent Concentration in CO ₂ (Wt %)	Solvent-to- Feed Ratio	Ethanol Concentration (Wt %)					
					Raffinate			Product		
					Average	High	Low	Average	High	Low
12:35-3:10	1.06	5.06	-0-	4.77	7.31	7.89	6.79			
3:10-3:30	1.00	5.06	2.23	5.06	6.90	7.14	6.66			
3:30-5:17	1.02	4.94	5.38	4.84	5.50	5.91	5.17	83.39	85.00	81.77

NOTES: The raffinate concentration began to change almost instantaneously with the injection of cosolvent to the system. Extract composition decreased slightly from 71.2 to 70.3 Wt % EtOH on a CO₂-free basis. There were no problems with cosolvent feed system or injection port. Cosolvent mixed easily with CO₂, but more than one liquid phase was observed in the reboiler sight gauge.

TABLE VI-5

RUN CSE-3

T (Extractor) = 65°F

P (Extractor) = 1200 psi

T (Still) = 47°F

P (Still) = 610 psi

Feed: 10.24 Wt % EtOH

Clock Time	Feed (lbs/min)	Solvent (lbs/min)	Cosolvent Concentration in CO ₂ (Wt %)	Solvent-to- Feed Ratio	Ethanol Concentration (Wt %)					
					Raffinate			Product		
					Average	High	Low	Average	High	Low
12:40-2:30	2.10	4.02	-0-	1.91	9.55	9.91	9.39			
2:30-3:40	2.02	4.06	2.32	2.01	9.09	9.49	8.84	87.23	87.32	87.13
3:40-4:50	2.02	4.09	5.39	2.02	8.29	8.57	7.90	86.89	86.94	86.85
4:50-5:40	2.02	4.13	11.22	2.04	6.71	6.51	6.61	86.06	86.90	85.23

NOTES: As cosolvent concentration in CO₂ was increased, the amount of ethanol extracted increased. At high concentrations of cosolvent, frothing in the top section of the extractor was noticed. Product ethanol content decreased with an increase in the cosolvent concentration in CO₂.

TABLE VI-6

RUN CSE-4

T (Extractor) = 67°F

P (Extractor) = 1190 psi

T (Still) = 62°F

P (Still) = 730 psi

Feed: 9.78 Wt % EtOH

<u>Clock Time</u>	<u>Feed (lbs/min)</u>	<u>Solvent (lbs/min)</u>	<u>Cosolvent Concentration in CO₂ (Wt %)</u>	<u>Solvent-to- Feed Ratio</u>	<u>Ethanol Concentration (Wt %)</u>					
					<u>Raffinate</u>			<u>Product</u>		
					<u>Average</u>	<u>High</u>	<u>Low</u>	<u>Average</u>	<u>High</u>	<u>Low</u>
11:30-1:55	.48	.98	-0-	2.04	8.51	8.82	8.30			
1:55-3:30	.48	.97	12.91	2.02	6.06	6.24	5.82			
3:30-4:00	.48	.96	22.44	1.99	4.67	5.06	4.34			

NOTES: Raffinate ethanol concentrations continued to decrease with increasing cosolvent concentration in CO₂. A forced shutdown resulted from cosolvent carry-over to the compressor.

Table VI-7

RUN CSE-5

T (Extractor) = 6C°?
T (Still) = 48°F
Feed: 1.29 Wt % EtOH

P (Extractor) = 1120 psi
P (Still) = 630 psi

<u>Clock Time</u>	<u>Feed (lbs/min)</u>	<u>Solvent (lbs/min)</u>	<u>Cosolvent Concentration in CO₂ (Wt %)</u>	<u>Solvent-to- Feed Ratio</u>	<u>Ethanol Concentration (Wt %)</u>					
					<u>Raffinate</u>			<u>Product</u>		
					<u>Average</u>	<u>High</u>	<u>Low</u>	<u>Average</u>	<u>High</u>	<u>Low</u>
2:40-3:20	0.83	0.94	33.80	1.18	1.04	1.13	1.00			
3:20-4:20	0.80	1.27	29.90	1.55	.59	.66	.52	None		

NOTES: A dilute feed was used to attempt to simulate the bottom section of an extraction column. CO₂ phase in extractor was emulsified, which led to more difficult hydraulic control in the extractor. The bubble rise velocity was slower than usual, and bubbles were large, spherical, and opaque. Forced to shut-down because of cosolvent carry-over to the compressor. The still was not flooded based on the volume of liquid removed from the reboiler at the end of the run.

TABLE VI-8

RUN CSE-6

T (Extractor) = 77°F

P (Extractor) = 1170 psi

T (Still) = 70°F

P (Still) = 620 psi

Feed: 1.33 Wt % EtOH 11:00-1:30
 .98 Wt % EtOH 1:30-2:50
 .84 Wt % EtOH 2:50-3:15
 .31 Wt % EtOH 3:15-3:40

Clock Time	Feed (lbs/min)	Solvent (lbs/min)	Cosolvent Concentration in CO ₂ (Wt %)	Solvent-to- Feed Ratio	Ethanol Concentration (Wt %)				
					Raffinate			Product	
					Average	High	Low	Average	Decanter
11:00-1:30	1.09	1.89	19.28	1.74	.65	.68	.62	24.30	17.88
1:30-2:50	1.09	1.98	22.25	1.82	.52	.58	.48	25.95	19.05
2:50-3:15	1.50	2.72	17.24	1.81	.50	.52	.49		
3:15-3:40	1.50	2.72	17.24	1.81	.46	.46			

NOTES: This run was performed to collect further data on the extractor performance with a dilute feed. System ran smoothly; however, the cloudiness and opacity changes in the extractor were still present. At 3:40 the extract sight glass gasket blew and forced a shut-down. Steady-state operation at the last run condition was never reached.

TABLE VI-9

RUN CSE-7

T (Extractor) = 68°F

P (Extractor) = 1180 psi

T (Still) = 27°F

P (Still) = 460 psi

Feed: .05 Wt % EtOH

Clock Time	Feed (lbs/min)	Solvent (lbs/min)	Cosolvent Concentration in CO ₂ (Wt %)	Solvent-to- Feed Ratio	Ethanol Concentration (Wt %)					
					Raffinate			Product		
					Average	High	Low	Average	High	Low
12:30-1:20	1.73	1.73	20.17	1.0	---	--	-	----	--	-

NOTE: A feed concentration 6 times lower than in Run CSE-6 was used. Initial feed was contaminated with residual 15 Wt % ethanol solution in the extractor, despite attempts to flush the system clean. Steady state operation was never reached, and the system was shut down due to the presence of organics at the compressor inlet.

TABLE VI-10RUN CSE-8

T (Extractor) = 72°F

T (Still) = 37°F

Feed: .5 Wt % EtOH

P (Extractor) = 1200 psi

P (Still) = 530 psi

<u>Clock Time</u>	<u>Feed (lbs/min)</u>	<u>Solvent (lbs/min)</u>	<u>Cosolvent Concentration in CO₂ (Wt %)</u>	<u>Solvent-to- Feed Ratio</u>	<u>Ethanol Concentration (Wt %)</u>					
					<u>Raffinate</u>			<u>Product</u>		
					<u>Average</u>	<u>High</u>	<u>Low</u>	<u>Average</u>	<u>High</u>	<u>Low</u>

NOTE: No data were collected. System never reached steady-state operation and was shut down due to carry-over of organics to the compressor inlet.

*TABLE VI-11

RUN CSE-9

T (Extractor) = 70°F

P (Extractor) = 1180 psi

T (Still) = 49°F

P (Still) = 620 psi

Feed: SDA #30, 8.52 Wt % EtOH

<u>Clock Time</u>	<u>Feed (lbs/min)</u>	<u>Solvent (lbs/min)</u>	<u>Cosolvent Concentration in CO₂ (Wt %)</u>	<u>Solvent-to- Feed Ratio</u>	<u>Ethanol Concentration (Wt %)</u>					
					<u>Raffinate</u>			<u>Product</u>		
					<u>Average</u>	<u>High</u>	<u>Low</u>	<u>Average</u>	<u>High</u>	<u>Low</u>
2:00-4:45	1.11	1.98	10.32	1.78	0.044	0.049	0.040	8.71	11.28	5.31

NOTE: The purpose of the run was to operate with a feed concentration of 0.05 Wt % ethanol. A lower extractor temperature and cosolvent concentration in CO₂ was used to avoid the frothing problem which shut down earlier runs. No clouding in extractor was observed. At a solvent-to-feed ratio of 1.78 and a cosolvent concentration in CO₂ of 10 Wt %, 20% of the ethanol was extracted from the feed. At the same cosolvent concentration in CO₂ and a solvent-to-feed ratio of 2, 30% of the ethanol was extracted from the feed.

TABLE VI-12RUN CSE-10

T (Extractor) = 59°F
 T (Still) = 59°F
 Feed: 14.46 Wt % EtOH

P (Extractor) = 1190 psi
 P (Still) = 690 psi

<u>Clock Time</u>	<u>Feed (lbs/min)</u>	<u>Solvent (lbs/min)</u>	<u>Cosolvent Concentration in CO₂ (Wt %)</u>	<u>Solvent-to- Feed Ratio</u>	<u>Ethanol Concentration (Wt %)</u>					
					<u>Raffinate</u>			<u>Product</u>		
					<u>Average</u>	<u>High</u>	<u>Low</u>	<u>Average</u>	<u>High</u>	<u>Low</u>
12:00-12:30	1.13	2.00	21.57	1.77	6.63	7.08	6.18	79.67	79.67	78.64
12:30-3:15	1.00	2.00	20.95	2.00	6.45	6.91	6.11	87.63	89.52	85.49

NOTE: System ran smoothly with no foaming present in the extractor or still. Because the extractor temperature was low, the still feed was mostly liquid phase. There was cosolvent present in raffinate sight glass throughout run.

2. Co-solvent/Product Recovery System

A distillation column was constructed for separation of co-solvent from ethanol. Initially, the still was run as a batch operation, followed by several continuous runs. These runs were carried out separately from the extraction runs described above.

The co-solvent recovery system runs (designated CSR) were performed to test the system design, provide data to evaluate the recovery process, and initiate improvements in the system operation. Concentrated alcohol and co-solvent could thus be recycled in the pilot unit. Temperatures and pressures throughout the system were recorded on a regular basis, along with the flowrates of the overhead and bottoms products, and all cooling water streams. Total feed used in a run and the time duration of the run were used to calculate an overall average feed rate.

Run CSR-1 tested the operation of the co-solvent recovery system as a batch process. Compositions measured for the feed, overhead, and bottoms product are presented in Table VI-13. The overhead product composition measured 75 wt % EtOH from a 20.4 wt % EtOH feed. High concentrations of ethanol in the product resulted from a very high reflux rate, due to condensation occurring on the still column walls.

Run CSR-2 ran on a continuous basis. The CO₂-recovery still was pressurized to 300 psi, and this pressure was used to drive the feed solution from the flash vessel to the co-solvent recovery still. A liquid-level indicator was placed on the reboiler section to measure the liquid-vapor interface in the still bottoms. A feed rate of 2.40 lb/hr was used.

Table VI-14 presents the stream analysis. It should be noted that the boiling point of pure co-solvent was not achieved, and as a result the recovery of ethanol was only 58.38%. The condensation occurring due to the uninsulated column, however, provided a co-solvent recovery of 96.56-99.46%.

An important point to note is the enrichment of the overhead ethanol product. On a co-solvent-free basis, the feed in Run CWR-2 entered at about 15 wt % ethanol, and the overhead product composition reached 86.3 wt % ethanol. The maximum extent of this enrichment was not determined, because a galled valved forced a premature shutdown before a steady-state overhead composition could be reached.

Run CSR-3 (Table VI-15) was performed to reach a steady overhead product composition, to evaluate the performance of the reboiler, and to collect pressure-temperature-composition data with the still insulated. Previously a thermosyphoning effect resulted due to the uninsulated column, and a constant liquid-vapor interface in the boiler was not maintained.

Run CSR-3 ran as a batch distillation from 10:20 to 11:00. An ethanol solution of 76.63% (co-solvent-free basis) was fed to the still, and an ethanol concentration in the overhead product of 91.07 was realized. The still feed line was opened further at 11:00, and a decrease in the product-concentration resulted. The feed rate in Run CSR-3 was 24 lb/hr, close to the flooding capacity of the column. Flow control of all streams was minimal and the overhead and bottoms products compositions were essentially the same as the feed.

TABLE VI-13

RUN CSR-1

<u>TIME</u>	<u>SAMPLE</u>	<u>STILL PRESSURE</u> <u>(psig)</u>	<u>STILL TEMPERATURE (°F)</u>		<u>Concentration (Wt %)</u>		
			<u>Tops</u>	<u>Bottoms</u>	<u>Ethanol</u>	<u>Water</u>	<u>Cosolvent</u>
3:45	Overhead	9	72	195	14.96	84.69	0.35
4:25	Overhead	8	168	206	15.16	84.53	0.31
4:35	Overhead	0	220	220	75.99	20.38	3.63
----	Bottoms	--	---	---	12.22	87.39	0.39
4:35	Bottoms	0	220	220	12.73	85.59	1.68
Average Still Residual					4.08	95.49	0.43
Post-Run Feed					20.41	78.67	0.92

TABLE VI-14RUN CSR-2

<u>TIME</u>	<u>SAMPLE</u>	<u>STILL PRESSURE</u> <u>(psig)</u>	<u>STILL TEMPERATURE (°F)</u>		<u>Concentration (Wt %)</u>		
			<u>Tops</u>	<u>Bottoms</u>	<u>Ethanol</u>	<u>Water</u>	<u>Cosolvent</u>
1:50-3:20	Overhead	6-9	66-208		32.96	65.53	1.51
3:20-3:30	Overhead	0-9	183-208		64.40	29.09	6.51
3:00-4:00	Overhead	0-14	183-208		77.38	20.53	2.09
4:00-End	Overhead	0	173-188		86.29	13.56	0.15
1:50-3:20	Bottoms	6-9		198-237	14.39	4.78	80.83
3:20-3:30	Bottoms	0-9		237-312	9.83	3.93	86.24
3:30-4:00	Bottoms	0-14		275-312	5.78	3.63	90.59
4:00-End	Bottoms	0		275-312	5.60	3.32	91.08
Average Still Residual					6.72	3.92	89.36
Post-Run Feed					16.84	5.63	77.53

TABLE VI-15

RUN CSR-3

TIME	SAMPLE	STILL PRESSURE (psig)	STILL TEMPERATURE (°F)		Concentration (Wt %)		
			Tops	Bottoms	Ethanol	Water	Cosolvent
10:35	Overhead	15	215	320	88.01	11.17	0.82
11:00	Overhead	0-3	186	279	90.45	9.40	0.15
11:30	Overhead	10	190	264	23.51	6.77	69.72
12:23	Overhead	16	226	268	30.87	9.05	60.08
12:35	Overhead	10	190	256	27.69	7.80	64.52
11:30	Bottoms	10-30	190	264	13.95	6.19	79.86
11:45	Bottoms	10	190	264	13.45	5.39	81.16
12:00	Bottoms	22	189	252	14.48	4.10	81.42
12:45	Bottoms	16	226	268	14.13	3.90	81.96
Average Still Residual					19.28	5.80	74.92
12:30	Feed				18.01	5.51	76.41

The main difficulty encountered in controlling still performance was the control of the circulation heater. Oil temperature fluctuations of 250°F resulted in cyclic boil-up in the reboiler shell-side-fluid. The partial-reflux condenser could not handle the high boil-up rates and caused co-solvent to exit in the overhead stream. The temperature-sensing probe in the circulation heater was relocated and a switch was installed to decrease the voltage to the heater.

Run CSR-4 tested these modifications made to the circulation heater. Better temperature control was observed, but only because the cycle time was decreased. The cycle limits still were still about 150°F above the set point.

The purpose of Run CSE-5 was to attain a co-solvent-rich bottoms product for recycle and to determine if the system could be operated by a single operator. No attempt was made to collect data on a regular basis. Samples of the still bottoms only were taken and analyzed. Co-solvent compositions in the bottoms product of >99% were achieved over a 4-1/2-hour period. The still pressure averaged 20 psig, with an overhead temperature of 280°F, and a bottoms temperature of 410°F.

Runs CSE-6 and CSE-7 were designed to clean up waste solutions containing co-solvent. No engineering data were collected.

D. Analysis of Extractor Performance

The major objective of these studies was to determine the effect of co-solvent on extractor performance. Specifically, the effect of 2-ethylhexanol added to CO₂ was studied, varying co-solvent levels and ethanol feed concentrations. Thus, the co-solvent runs fell into two categories. Runs CSE 1-4 studied the effect of co-solvent level on the extractor performance; runs CSE 5-10 evaluated co-solvent in systems with different ethanol concentrations. Extractor performance was evaluated in terms of efficiency, by measuring degree of ethanol extraction under given conditions, and capacity, by visual observation of column hydraulics.

Runs CSE 2-4 compared the extractor performance in the absence and presence of co-solvent. Run CSE-1 was non-productive because of control and hydraulic problems. The system was initially run without co-solvent at fixed operating conditions. When steady-state operation was established as measured by the ethanol concentration in the raffinate, co-solvent was added to the system. The change in the extractor performances due to the co-solvent was monitored by measuring the ethanol concentration in the raffinate.

The raffinate concentration of ethanol as a function of time and co-solvent concentration in CO₂ for Runs CSE 2-4 is plotted in Figures VI-3, VI-4 and VI-5. An increase in co-solvent concentration in CO₂ resulted in a distinct decrease in the raffinate ethanol concentration. The co-solvent feed rate was increased to the limiting capacity of the equipment to determine the effect over a wide range of co-solvent concentrations. The degree of extraction appeared to be directly related to the co-solvent concentration in CO₂ for a given solvent-to-feed ratio. This relationship is plotted in Figure VI-6.

WEIGHT PERCENT ETHANOL IN RAFFINATE
AS A FUNCTION OF TIME AND COSOLVENT FOR
RUN CSE II

FIGURE VI-3

WEIGHT PERCENT ETHANOL IN THE RAFFINATE
AS A FUNCTION OF TIME AND COSOLVENT FOR
RUN CSE III

FIGURE VI-4

**WEIGHT PERCENT ETHANOL IN THE RAFFINATE
AS A FUNCTION OF TIME AND COSOLVENT
FOR RUN CSE IV**

Figure VI-6 ETHANOL CONCENTRATION REDUCTION VS. COSOLVENT LEVEL

Only qualitative conclusions can be drawn from the results at more dilute ethanol concentrations. In Run CSE-6, raffinate concentration was reduced to 0.46 wt % from a feed concentration of 1.33 wt % ethanol, a ratio of 0.35 at a solvent-to-feed ratio of 1.81 and a co-solvent concentration of 17.2%. This is somewhat better than the value of about 0.55 that would be predicted from the data in Figure VI-6 for 10 wt % ethanol feeds and a solvent-to-feed ratio of 2. Thus, dilute feeds may respond to the addition of co-solvent at least as well as 10% ethanol feeds.

In Run CSE-10, the extractor performance was investigated with concentrated feed (co-solvent concentration of about 20% in CO₂) and a low extractor operating temperature. No foaming was observed in the extractor, or the still; this may have been due to the higher ethanol concentrations in the system. Ethanol concentrations in the product reached 89.52%; this may have been due to the concentrated feed and/or the low extraction temperature. Figure VI-7 presents the ethanol concentration in extract and reboiler streams as a function of time. It should be noted that the decanter provides an enrichment in ethanol of 4-5%.

A quantitative measure of the extractor performance is the stage efficiency. This may be calculated from an estimate of the number of theoretical stages required for a given separation divided by the actual number of stages. The number of theoretical stages for zero co-solvent concentration was calculated from the Kremser-Brown-Souders equation given below.

$$\lim_{Q \rightarrow \infty} (X_r/X_f) = \frac{Y_s}{X_f M}$$

where,

X_F = feed composition

X_R = raffinate composition

Y_S = solvent composition

M = distribution coefficient of ethanol (solvent/water)

Q = solvent-to-feed ratio

An assumption was then made that adding co-solvent to the extractor would not change the number of theoretical stages if all other operating conditions remain unchanged. This assumption allowed a new distribution coefficient to be calculated for ethanol in the presence of co-solvent.

FIGURE VI-7 PRODUCT ETHANOL CONCENTRATION IN EXTRACT AND REBOILER

As shown in Figure VI-8, the DC was found to increase by as much as a factor of 20. This indicated that the co-solvent addition significantly enhanced the overall extractor performance.

Certain hydraulic problems caused by the presence of co-solvent remained unresolved. At co-solvent concentrations in CO₂ above 20%, the extractor became difficult to control: the solvent-co-solvent phase darkened and appeared emulsified and tray hydraulics were no longer visually detectable. In this concentration range, the co-solvent level may be close to the saturation limit, and thus reduced the critical temperature to the extractor operating temperature.

FIGURE VI-8 DISTRIBUTION COEFFICIENT OF ETHANOL VS. COSOLVENT LEVEL

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APPENDIX I

NOMENCLATURE

T	temperature
P	pressure
EtOH	ethanol
IPA	isopropanol
SBA	sec-butanol
MeOH	methanol
CO ₂	carbon dioxide
H ₂ O	water
S/F	solvent-to-feed ratio
S	solvent
F	feed
R	raffinate
E	extract
m	mass flow rate
x	concentration in the liquid phase
TFE	teflon
SS	stainless steel
wt	weight
psi	pounds per square inch
lbs	pounds
T _{LM}	log mean temperature difference
Q	heat transfer rate
GC	gas chromatograph
H	enthalpy
dH	enthalpy change
A	area
dia.	diameter
gpm	gallons per minute
K-B-S-eq	Kremser-Brown-Souder-eq.
M-T	McCabe-Thiele
DTM	dry test meter
HETP	height equivalent of theoretical plate
n	tray efficiency
N _{th}	number of theoretical trays
N _{act}	number of actual trays
min	minute
sec	second
hr	hour
"	inches
'	feet
m	distribution coefficient
M	mass
h	tray efficiency
gal	gallon

SUBSCRIPTS

s	solvent
f	feed
r	raffinate
e	extract
p	product
a	alcohol
w	water
i	input
o	output

SECOND SUBSCRIPT

e	ethanol
i	isopropanol
b	sec-butanol

APPENDIX II

PILOT PLANT

COSOLVENT FEED SYSTEM

RUN SHEET HEADINGS

CONTROLLERS

Pressure Indicator Controller, Extractor
Pressure Indicator Controller, Still
Flow Indicator Controller, Solvent flow to reboiler
Level Indicator Controller, Reboiler level
Pressure Indicator Controller, Surge vessel

FLOW

Solvent (lbs/min)
Total solvent (lbs)
Solvent reading time
Raffinate (lbs/min)
Total raffinate (lbs)
Raffinate reading time

SCALE WEIGHTS

Raffinate, scale weight (lbs)
Raffinate reading time
Pump, setting and time
Feed, (lbs)
Lewa pump, setting and time
Cosolvent feed, (lbs)

Pressure, flash vessel (psi)

Trim heat exchanger, water setting

Raffinate, valve setting

TEMPERATURE (^oF)

Still feed
Reference probe
Still tops, after flash
Ambient
CO₂ in, heat exchanger
CO₂ out, heat exchanger
H₂O in, heat exchanger
H₂O out, heat exchanger
Compressor, in
Compressor, interstage
Compressor, out
Control valve-5 (before flash)
Control valve-5 (after flash)
Reboiler, bottom
Reboiler, coil in
Reboiler, coil out

TEMPERATURE (°F)
(continued)

Still tops
Still top middle
Still middle
Still middle
Still bottom middle
Still bottom
Extractor, top
Extractor, bottom
Compressor room
Feed tank

Compressor power (amps)

COMPRESSOR PRESSURES (psig)

In
Interstage
Out

SIGHT GAUGES

Extractor
Extract
Raffinate still feed from decanter
Reboiler level

Notes

APPENDIX III

PILOT-PLANT

COSOLVENT/PRODUCT RECOVERY SYSTEM

RUN SHEET HEADINGS

PRESSURES (psig)

Flash vessel
Cosolvent still
Hot oil pump

FLOW METERS

Feed to cosolvent still
Water to reflux condenser
Water to condenser, heat exchanger A
Water to condenser, heat exchanger B

SIGHT GAUGES

Flash vessel
Cosolvent still bottoms

TEMPERATURES (°F)

Pump inlet
Oil pump outlet
Oil heater outlet
Preheater oil, in
Preheater oil, out
Preheater feed, in
Preheater feed, out
Flash temperature, before control valve-5
Flash temperature, after control valve-5
Top of cosolvent still
Cosolvent still, feed product
Cosolvent still, bottoms
EtOH product
Cosolvent product
Reference probe

Oil heater, thermostat setting