DESIGN AND ECONOMIC ASSESSMENT OF LIQUID-LIQUID EXTRACTION FOR THE RECOVERY OF THE CLOSTRIDIUM FERMENTATION PRODUCTS

By

ALIREZA MEMARAN DADGAR

Bachelor of Science in Chemical Engineering
Oklahoma State University
Stillwater, Oklahoma
1981

Master of Science
Oklahoma State University
Stillwater, Oklahoma
1983

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Thesis Approved:

Gary L. Foutch
Thesis Adviser

J P Chandler

Robert A. Wills

Jan Wagner

Norman N. Durham
Dean of the Graduate College

PREFACE

The results of an experimental investigation for the recovery of Clostridium fermentation products by liquid-liquid extraction are presented. Forty-seven solvents were screened for their ability to extract butanol, acetone, and ethanol from water at concentrations similar to those found in fermentation broth. The criteria utilized for solvent selection include: distribution coefficient, selectivity, toxicity, physical extractive properties (i.e., density, viscosity, surface tension, boiling point, heats of vaporization, etc.), and cost. The classes of solvents which demonstrated desirable characteristics were aliphatic alcohols, ketones, esters, and halogenated hydrocarbons.

An improved separation technique which substantially reduces the energy consumption during the purification stage of the Clostridium fermentation process was designed and cost estimated. An economic evaluation of this process for a 200 MM lb/yr n-butanol plant is presented. Comparative economics of the improved separation process, distillation-fermentation process, and rhodium catalyst petrochemical process is discussed.

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TO MY FATHER AND THE LOVING MEMORIES OF MY MOTHER

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NOMENCLATURE

A	area per unit volume, ft^{-1}
B	number of impeller blades
D	column diameter, ft
d_i	impeller diameter, ft
E	extract flow rate, lb/min
E_m	molar extract flow rate, moles/(sec-ft^2)
E_{md}	Murphree dispersed-phase stage efficiency
F	feed flow rate, lb/min
f	liquid phase fugacity
ΔG	change in Gibbs energy
H_{eff}	effective column height, ft
HETS	height equivalent to theoretical stages
H_{ext}	extraction column height, ft
h_i	impeller height, ft
H_{mix}	height of mixing section of the column, ft
H_{packed}	height of packed section of the column, ft
HTU	height of the transfer unit
ISBL	inside battery limit
J	solute mass transfer flux, moles/(sec-ft^2)
K	distribution coefficient
K_E	extract phase overall mass transfer coefficient, mols/(sec-ft^2)

k_E	extract phase individual mass transfer coefficient, mols/(sec-ft^2)
K_R	raffinate phase overall mass transfer coefficient, mols/(sec-ft^2)
k_R	raffinate phase individual mass transfer coefficient, mols/(sec-ft^2)
M	slope of operating line
MM	quantity expressed in millions
N	number of actual stages
n	number of theoretical stages
n	number of moles in Equation II-12
n_T	total number of moles
OSBL	outside battery limit
P	power input requirement (lbf-ft)/sec
ΔP	pressure drop, psia
P/V	power per unit volume. lbf/(ft^2-sec)
Q	total column throughput, lb/min
R	raffinate flow rate, lb/min
R_m	molar raffinate flow rate, moles/(sec-ft^2)
S	solvent flow rate, lb/min
T	temperature, R
X_C	solute mole fraction
X_A	carrier mole fraction
Z	total column height, ft

Greek Letters

β	selectivity coefficient (separation factor)
γ	activity coefficient

Δ	operating point for graphical extraction ternary diagram
σ	surface tension, dy/cm
ρ	density, lb/ft^3

Superscripts

'	quantity in the aqueous phase
"	quantity in the organic phase
*	interfacial equilibrium condition
o	quantity at infinite dilution

Subscripts

A	carrier
C	solute
c	continuous phase
d	dispersed phase
E	extract phase
i	species i
L	large scale "industrial scale"
R	raffinate phase
S	small scale "pilot plant"
T	total quantity
1	refers to aqueous phase
2	refers to organic phase

Abbreviations Used in Table VII

bp	boiling point
C	carcinogen
F	flammable
HS	hazardous substance
HW	hazardous waste

ORM-A	an anesthetic, irritating, noxious, and toxic material
NF	not flammable
PB	poison B "less harmful"
PTP	priority toxic pollutant
V	volume basis
W	weight basis
i	insoluble
δ	slightly soluble

CHAPTER I

INTRODUCTION

In recent years, the concern about the eventual fuel shortage together with agricultural surpluses have renewed interests in commercial fermentation processes for the production of valuable chemicals such as organic alcohols, acids, and ketones. Alcohols are important chemical feedstocks and are used as additives to gasoline for upgrading octane rating and to extend the fuel supply.

The fermentation process utilizes five and six carbon sugars derived from renewable biomass resources to produce mixed solvents: butanol, acetone, and ethanol. The original organism, Clostridium acetobutylicum found by Weizmann (7) in 1914, was capable of fermenting corn starch to butanol, acetone, and ethanol. Fermentation processes have used corn, blackstrap molasses, or high test molasses as a substrate. However, other carbohydrate sources, such as waste products, are considered as potential feedstocks. These include industrial paper pulp wastes, wood wastes, corncobs and stover, whey, and municipal solid wastes. These feedstocks are abundant, inexpensive, and may be converted to products in relatively high yields with few processing steps.

The current technology to convert five and six carbon sugars to usable chemicals, fuels, and feedstocks via microbial fermentations has both cost and energy balance problems which include the need for an alternative purification process. The purification stage is the largest energy consumer, accounting for approximately 40 percent of total production cost. Seventy three percent of this cost is for steam distillation (11). Therefore, future research in fermentation processes should include reducing the costs and energy consumption of the purification stage.

Current research into the economical separation of butanol, acetone, and ethanol from fermentation broths, has led to the investigation of solvent extraction as an alternative to distillation. Solvent extraction techniques have the potential for tremendous energy savings in the recovery of fermentation products. These savings will have a direct impact on the economics for the entire fermentation scheme.

This dissertation presents research results on an alternative separation method which substantially reduces energy consumption during the separation stage of the fermentation process by substituting solvent extraction for conventional distillation at appropriate stages.

Several classes of solvents are evaluated for their ability to recover Clostridium fermentation products. A set of criteria for solvent selection, based on distribution coefficient, selectivity, toxicity, physical extractive properties and cost, are established. The potential solvents for the recovery of the Clostridium fermentation products are experimentally tested in a York Scheibel continuous extraction column. This information is used to design and develop an extraction purification process with substantially improved economics. Finally, an economic evaluation of the improved extraction process is compared with the distillation-fermentation process and the conventional petrochemical process.

CHAPTER II

LITERATURE SURVEY

As one of several mass transfer operations in chemical engineering, liquid-liquid extraction is based on the distribution of the substances among the solvent and solution phases. Solvent extraction, as a physical separation method, has demonstrated its unique abilities and usefulness where other competitive methods (i.e. distillation, crystallization, adsorption, etc.) are uneconomical or impossible. For example, close-boiling petroleum fractions have similar volatilities but are chemically different, hence, easily separated by extraction where ordinary distillation is impractical. Other applications of solvent extraction are in separating dilute mixtures, thermally degradable solutes, and components that form azeotropes.

General Principals in Liquid-Liquid Extraction

A simple extraction process consists of three essential components: the solute, the solvent, and the carrier. The basic concept in liquid-liquid extraction is the transfer of solute from the carrier phase to the solvent phase. Extraction processes require the intimate contacting of the two liquid phases (carrier and solvent) with an approach toward equilibrium. In the laboratory, this is performed by rigorously shaking phases in a separatory funnel, allowing the phases to settle, and then separating the phases for analysis. On the industrial scale, extraction utilizes mechanical agitation to assure efficient mixing of the phases. An exception may be found in packed and spray extractors where approach to equilibrium may not be achieved. The schematic of an extraction system, with the associated nomenclature, is shown in Figure 1. In extraction, the solvent can be the dispersed phase or the continuous phase depending on the physical properties of the carrier stream and the dynamics of the system. The dispersed phase is usually chosen as the basis for expressing the mass-transfer relations between the two terminal streams from an extractor: the extract (solvent-rich), and the raffinate (carrier-rich).

To relieve equilibrium limitations on the purity of the extracted material, the extractor is provided with a reflux stream that contains the extract product separated from the solvent. Figure 2 shows a typical extraction process equipped with a reflux and containing a stripper column for separation of solvent from solute. In many cases, the stripper may be replaced by one or more flash steps.

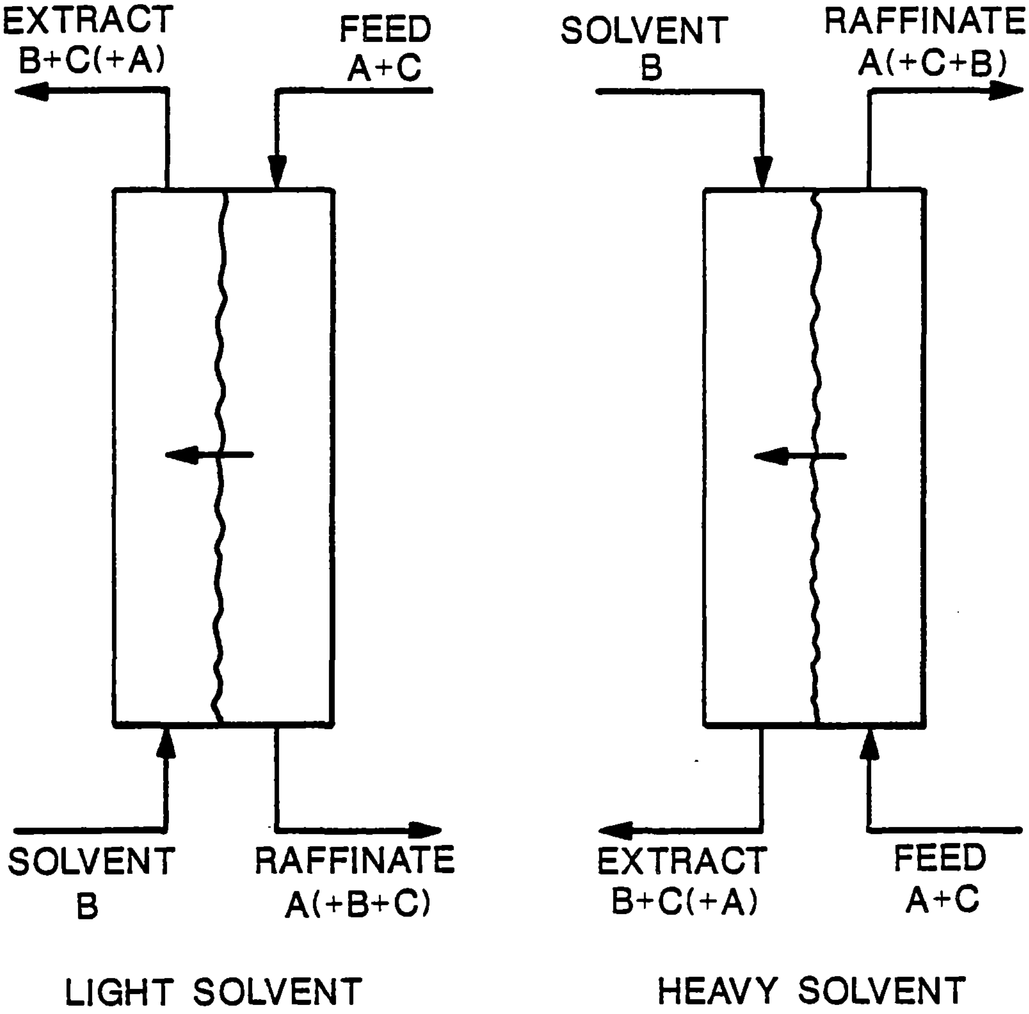
Phase Equilibrium

The equilibrium distribution of solute between the carrier and the solvent phases is represented by a quantity analogous to that for vapor-liquid systems, an equilibrium ratio (distribution coefficient), K_c:

$$K_c = \frac{\text{g mole solute/L in the extract phase}}{\text{g mole solute/L in the raffinate phase}} \tag{II-1}$$

Expressed in mole fractions:

$$K_c = \frac{(X_c)_E}{(X_c)_R} \tag{II-2}$$



A = CARRIER
B = SOLVENT
C = SOLUTE (DISTRIBUTED COMPONENT)

Figure 1. Schematic of a Liquid-Liquid Extraction System with the Associated Nomenclature (17)

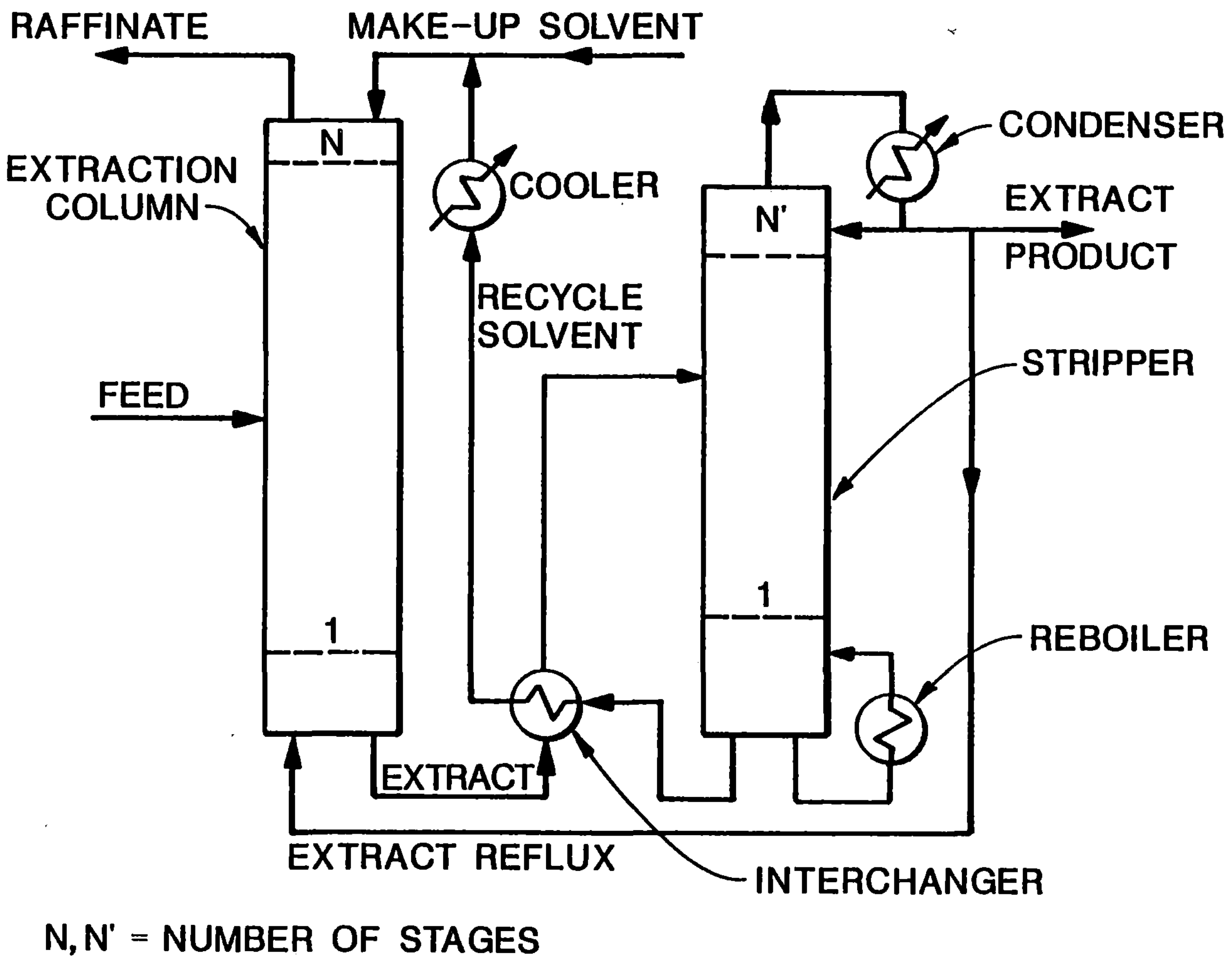


Figure 2. A Typical Extraction System with an Extraction Reflux and a Stripper (17)

where E and R denote components in the extract and raffinate, respectively. The equilibrium ratio, K_A, for the carrier is defined as:

$$K_A = \frac{(X_A)_E}{(X_A)_R} \tag{II-3}$$

A useful quantity in extraction calculations is the separation factor (selectivity coefficient). Equivalent to the relative volatility in distillation, the separation factor relates the equilibrium ratio of solvent and carrier (15):

$$\beta_{CA} = \frac{K_C}{K_A} = \frac{(X_C/X_A)_E}{(X_c/X_A)_R} \tag{II-4}$$

The separation factor can be expressed in terms of activity coefficients, γ, of the solute and the carrier in two liquid phases. In the laboratory where liquid-liquid equilibria are determined, the present vapor is in equilibrium with both liquid phases. Thermodynamically this can be expressed as:

$$\beta_{CA} = \left(\frac{\gamma_A}{\gamma_C}\right)_E \left(\frac{\gamma_C}{\gamma_A}\right)_R \tag{II-5}$$

A careful investigation of Equation II-5 reveals that vapor-liquid equilibria can be useful in predicting liquid-liquid equilibria. This allows for a vast bank of existing data on vapor-liquid equilibria to be utilized for determination of liquid-liquid equilibria. Equation II-5 also shows the required condition of nonideality for liquid-liquid separation. In ideal systems, there is no possibility that the liquids will separate into more than one liquid phase. It is evident from

Equation II-5 that the separation factor is greatly influenced by the composition of the solute in the extract and the raffinate phases, emphasizing the importance of composition dependency in liquid-liquid equilibria.

Thermodynamics of Liquid-Liquid Equilibria

The thermodynamics of multicomponent phase equilibria considers two phases in equilibrium when temperature, pressure, and the chemical potential of each component is the same in each phase. For practical purposes, the concept of chemical potential has been replaced by the fugacity which expresses the correction for nonideal behavior of gases.

For two liquid phases at the same temperature, the equilibrium relationship for each species i can be expressed as:

$$f_i' = f_i'' \qquad \text{(II-6)}$$

Where f denotes liquid phase fugacity and, ' and " designate different phases.

Relating the activity coefficient to the liquid phase fugacity and using the same standard-state fugacity in both phases, Equation II-6 can be expressed in terms of mole fractions of component i in each phase:

$$(\gamma_i X_i)' = (\gamma_i X_i)'' \qquad \text{(II-7)}$$

Some empirical liquid models correlate liquid-liquid equilibria by expressing equilibrium distribution ratios as a function of composition. Empirical models are only used for storage and interpolation (37). The other class of liquid models describe phase equilibria in relation with Gibbs energy, composition, and preferably temperature. These models express the activity coefficient as a function of equilibrium mole fractions for phase composition prediction.

The UNIQUAC (Universal Qusia Chemical) model proposed by Abrams and Prausnitz (1) has molecular and temperature dependency. This model requires two adjustable parameters per binary and is expressed based on the contribution of the combinational and residual molar excess Gibbs energy as shown in Table I. UNIQUAC has demonstrated its capabilities to predict vapor-liquid and liquid-liquid equilibria for binary and multicomponent systems reasonably well (37).

Computation of liquid-liquid equilibrium phase compositions can be performed either by minimizing the Gibbs energy expression or by the isoactivity method (37). The necessary and sufficient condition of equilibrium requires that the Gibbs energy of mixing must be a minimum. Mathematically, it can be expressed as:

$$n_T \, \Delta G = n' \, \Delta G' \, (n_1', n_2', \ldots) + n'' \, \Delta G'' \, (n_1'', n_2'', \ldots) \qquad \text{(II-8)}$$

where,

$$\Delta G' = RT \sum_i X_i' \ln X_i' + G^{E'} \qquad \text{(II-9)}$$

$$\Delta G'' = RT \sum_i x_i'' \ln x_i'' + G^{E''} \qquad \text{(II-10)}$$

$$G^E = RT \sum_i x_i \ln \gamma_i \qquad \text{(II-11)}$$

TABLE I

UNIQUAC MODEL FOR MULTICOMPONENT SYSTEMS

$$g^E = g^E \text{ (combinational)} + g^E \text{ (residual)}$$

$$\frac{g^E \text{ (residual)}}{RT} = -\sum_i q_i' \, x_i \, \ln\left(\sum_j \theta_j' \, \tau_{ji}\right)$$

$$\frac{g^E \text{ (combinational)}}{RT} = +\sum_i X_i \, \ln \frac{\phi_i}{X_i} + \frac{Z}{2} \sum_i q_i \, X_i \, \ln \frac{\Theta_i}{\phi_i}$$

$$\phi_i = \frac{r_i \, X_i}{\sum_i r_j \, X_j}$$

$$\Theta_i = \frac{q_i \, X_i}{\sum_j q_j \, X_j}$$

τ_{ji} and τ_{ij} are interaction binary parameters

$$\Theta_i' = \frac{q_i' \, X_i}{\sum_j q_j' \, X_j}$$

r, q, and q' are pure component parameters

Activity coefficient for any component i is given by:

$$\ln \gamma_i = \ln \frac{\phi_i}{X_i} + \frac{Z}{2} q_i \ln \frac{\Theta_i}{\phi_i} + l_i - \frac{\phi_i}{X_i} \sum_i X_j \, l_j$$

$$- q_i' \ln\left(\sum_j \Theta_j' \, \tau_{ji}\right) + q_i' - q_i' \sum_j \frac{\Theta_j' \, \tau_{ij}}{\sum_k \Theta'_K \, \tau_{KJ}}$$

$$l_J = \frac{Z}{2} (r_j - q_j) - (r_j - 1) \qquad Z = 10$$

$$RT \ln \gamma_i = \left(\frac{\partial n_T G^E}{\partial n_i}\right)_{T,P,n_j} \quad i = 1,2,\ldots N \text{ (components)} \qquad \text{(II-12)}$$

For a small change of composition at equilibrium the ΔG remains the same and therefore:

$$d(\Delta G)_{T,P} = 0 \qquad \text{(II-13)}$$

under the constraints:

$$n_i' + n_2'' = n_i \quad i = 1,2,\ldots N \text{ (components)} \qquad \text{(II-14)}$$

This procedure covers the necessary sufficient condition of equilibrium. However, the distinction between global and local minima must be made.

In the isoactivity approach, the following equations are solved for the unknown phase concentration:

$$(X_i \ \gamma_i)' = (X_i \ \gamma_i)'' \qquad \text{(II-15)}$$

The total number of moles is conserved:

$$n_i = n_i' + n_i'' \qquad \text{(II-16)}$$

The components mole fractions must add up to unity in each phase:

$$\sum_i x_i' = 1 \qquad \text{(II-17)}$$

and,

$$\sum_i X''_i = 1 \qquad \text{(II-18)}$$

where activity coefficients are expressed by one of the liquid equilibria models (i.e. UNIQUAC).

Sørensen et al. (37) suggested that the liquid phase composition computation should be based on minimization of the Gibbs energy expression, since this method covers the necessary and sufficient condition for equilibrium between two immiscible liquid phases. However, false solutions as a result of a local minimum or a saddle point can be obtained. Sørensen et al. (37) also concluded that the problems of isoactivity criterion can be drastic. The trivial solution of Equation II-15 could lead to the false conclusion that the system is in one phase. Failure of liquid equilibria models to predict activity coefficients at all conditions, inaccuracies in reported adjustable parameters and mathematical stiffness of the models could result in enormous errors in phase composition prediction. In any case, the results must be carefully examined against reliable experimental data and good engineering judgement.

Diffusion and Mass Transfer in Liquid-Liquid Extraction

The extraction process requires the transfer of solute from the bulk of the carrier phase to the interface and then into the solvent phase. This process can be treated as a mass transfer operation governed by molecular and eddy diffusion. Molecular diffusion is a slow transport process that arises from the random movement of the individual molecules due to a thermal gradient. Eddy diffusion or turbulent diffusion results from the bulk movement of the fluid as a result of some turbulence. These two transport mechanisms transfer solute from a region of high concentration to one of low concentration. Eddy diffusion is several orders of magnitude greater than molecular diffusion and dominates in the bulk phase and near the liquid-liquid interface (4). Molecular diffusion plays an important role in dispersing the solute near the solid surface, as eddies tend to dampen, and across the liquid-liquid interface. Both mechanisms must be considered when modeling liquid-liquid extraction processes.

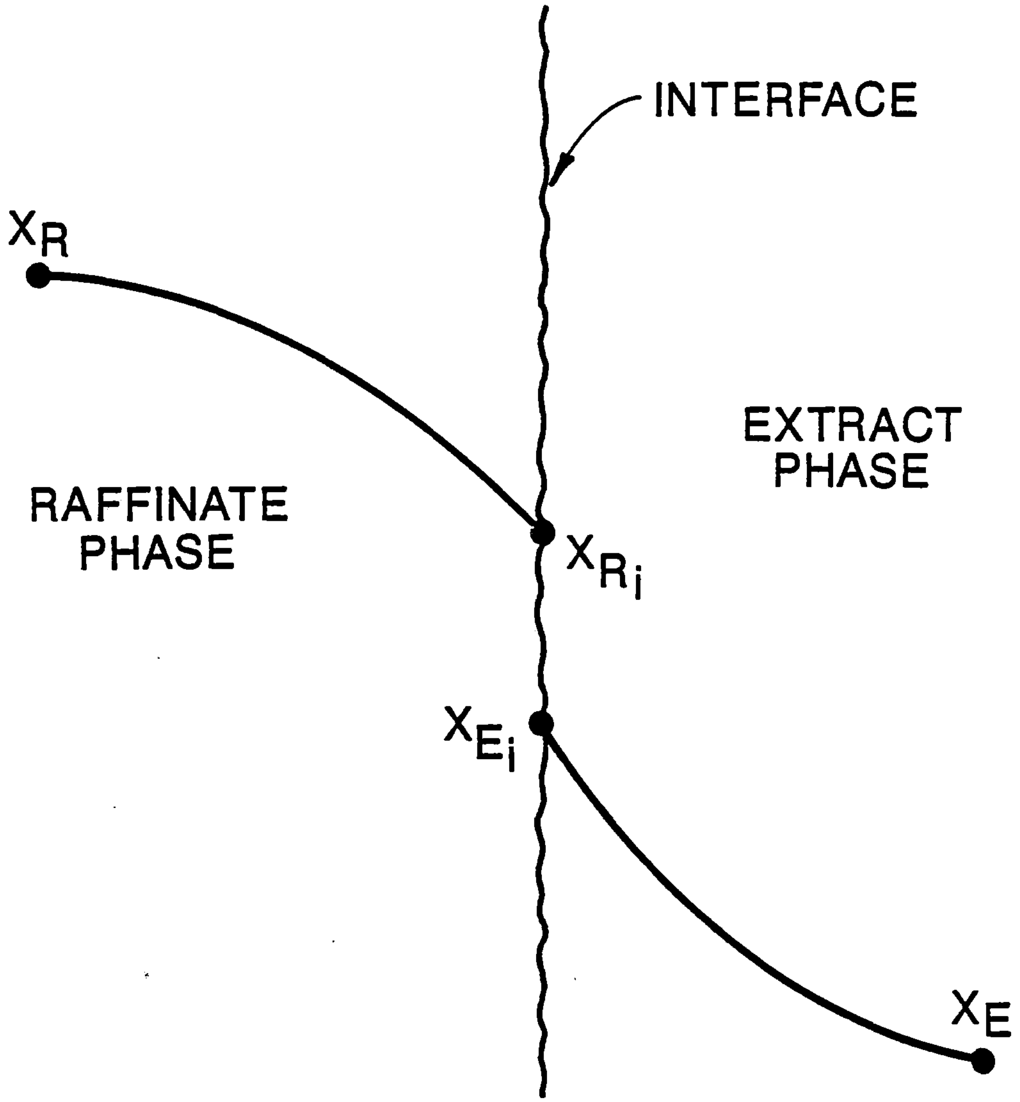
The rate of transfer of solute from the carrier to the solvent is proportional to the interfacial area and the deviation of the solute concentrations in the two phases from the equilibrium concentrations. Based on a two-film model, the rate of solute transfer from the carrier phase to the solvent phase is impeded by the two resistances in series (25). The interface is assumed to present no resistance to the transfer. Figure 3 shows the transfer process and the corresponding variables. The rate equations can be set forth:

$$J = k_R\,(X_R - X_{R_i}) = k_E\,(X_{E_i} - X_E) \tag{II-19}$$

To incorporate resistances of both phases:

$$J = K_R\,(X_R - X_R^*) = K_E\,(X_E^* - X_E) \tag{II-20}$$

Where J is the solute flux, k_E and k_R are the individual-phase transfer coefficients, and K_E and K_R are overall transfer coefficients. In



$K_R = X_E^*/X_R$ $\quad K_i = X_{E_i}/X_{R_i}$ $\quad K_E = X_E^*/X_R$

Concentrations refer to the transferring solute

Figure 3. Transfer Process Based on a Two-Film Model (17)

general, these mass transfer coefficients are influenced by the concentration of the transferring solutes.

Equations II-19 and II-20 can be combined to relate the individual mass transfer coefficients to the overall transfer coefficients, based on the extract phase:

$$\frac{1}{K_E} = \frac{1}{k_E} + \frac{M}{k_R} \qquad \text{(II-21)}$$

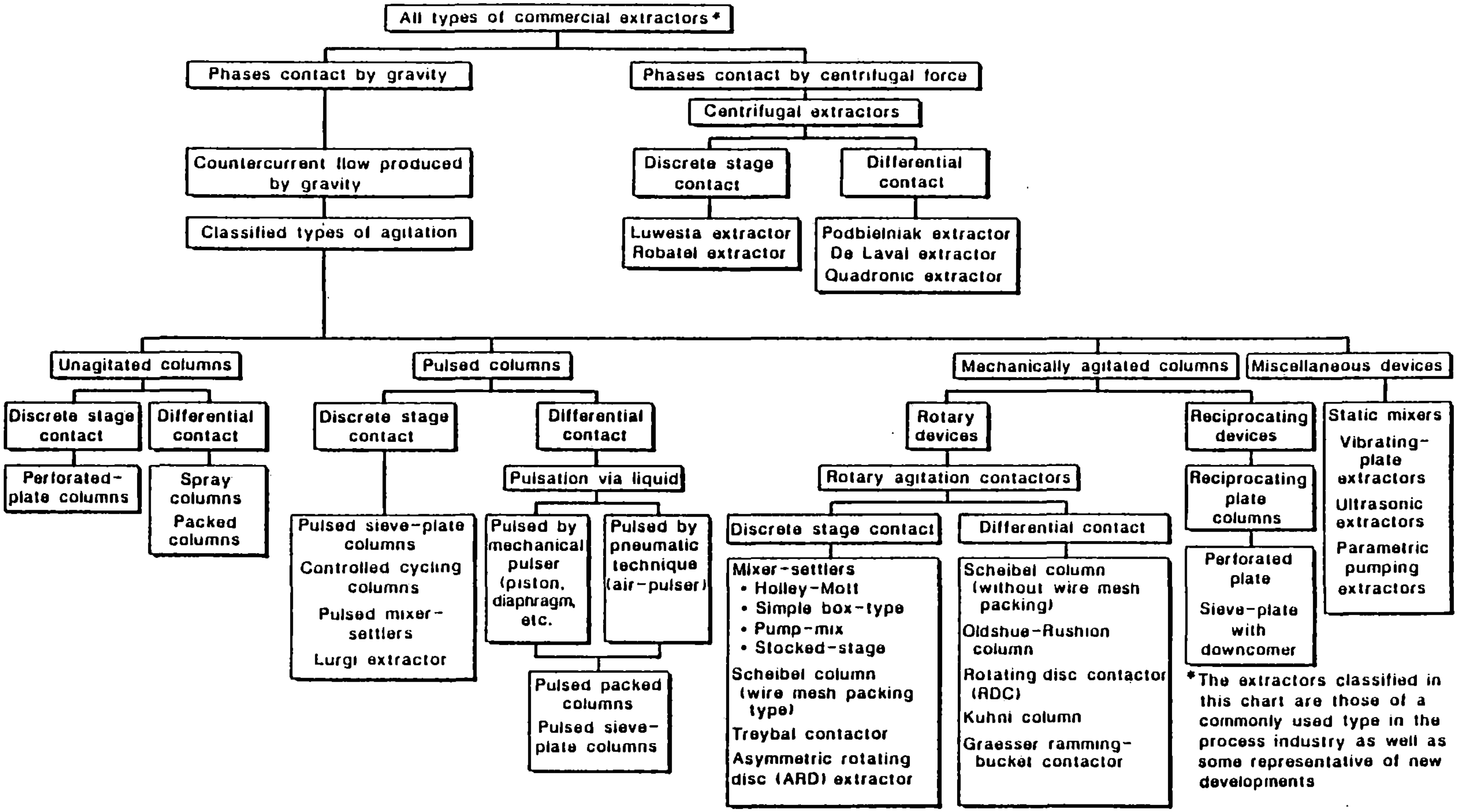
where M is the slope of the equilibrium curve. Over a concentration range where the equilibrium curve can be approximated by a straight line passing through the origin, then:

$$X_E^* = M\ X_R = K_E\ X_R \qquad \text{(II-22)}$$

The rate equation concept and the knowledge of the interphase mass transfer provides useful information on the design and the successful operation of extraction equipment. The use of the rate concept allows evaluation of the most important design parameters such as: height and diameter of the extractor, number of overall transfer units, height of individual phase transfer units, and stage and overall column efficiency.

Industrial Extraction Equipment

Solvent extraction equipment is designed and constructed to achieve intimate contacting of the solvent and carrier phases with approach to phase equilibrium. Lo (22) classifies the commercial contactors based on the methods employed for interdispersing phases and operational



*The extractors classified in this chart are those of a commonly used type in the process industry as well as some representative of new developments

Figure 4. Classification of Commercial Extractors (22)

characteristics. Figure 4 shows the classifications of commercial extractors. The main characteristics of major types of contactors are summarized in Table II. Humphrey et al. (17) classifies the extraction equipment into three general types of contacting-separating processes: mixer-settler systems, columns, and centrifugal extractors.

Mixer-Settlers

Mixer-settlers are among the most widely used extractors in the process industry due to their flexibility, reliability, established scale up procedures, and high capacity. Mixer-settlers consist of a mixing chamber for phase dispersion and a settling chamber for phase separation. Vertical or horizontal configurations are available. Particular use of mixer-settlers are in process operations requiring high capacity and few number of stages. Mining industries with capacity of up to 6000 gal/min have extensively employed mixer-settlers for the separation and purification of uranium and plutonium (42). The main disadvantages of mixer-settlers are high capital cost per stage for pumping and piping, large space requirements, and high inventory of solvent.

Column Extractors

Several types of column extractors have been developed for commercial applications. An extraction column is designed to operate at steady state. However, variation in the feed and the solvent flow rate upsets the operation by flooding the column and may damage product quality. As a result, the column extractor design should contain a sophisticated system of process control equipment (26). Figure 5 shows

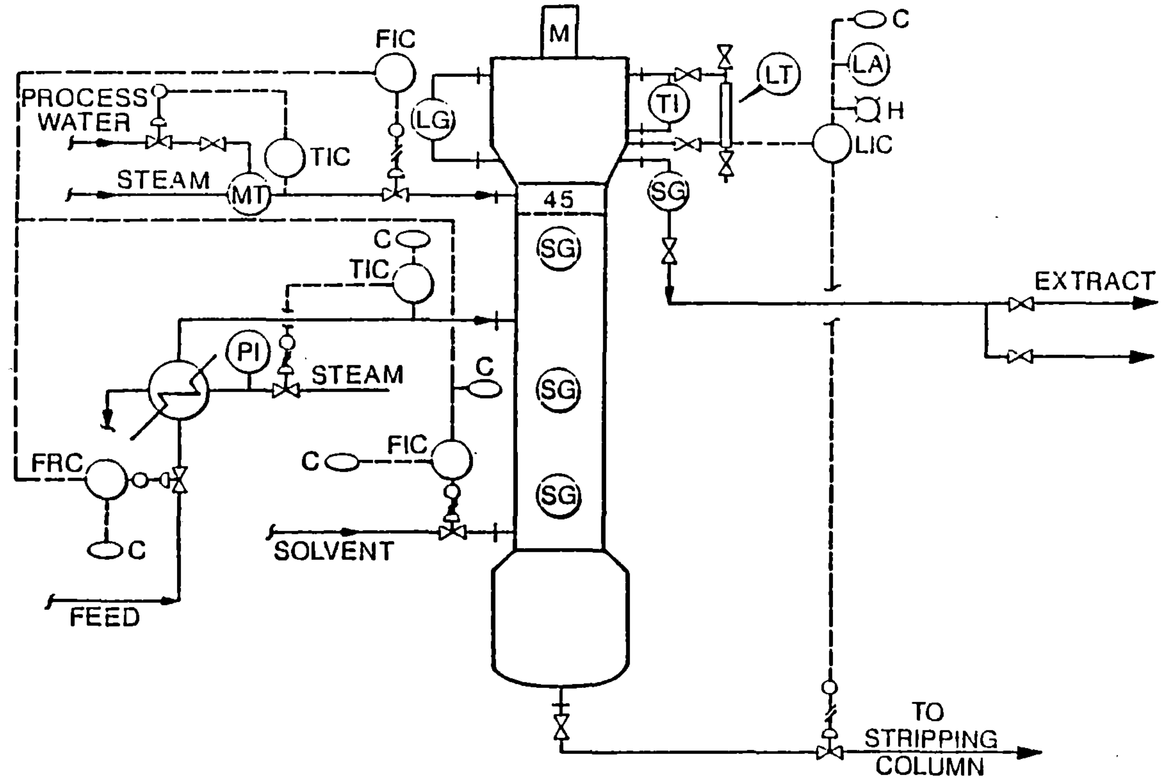
TABLE II

INDUSTRIAL APPLICATION OF COMMERCIAL EXTRACTORS (22)

Types of Extractor	General Features	Fields of Industrial Application
unagitated columns	low capital cost, low operating and maintenance cost, simplicity in construction, handles corrosive material	petrochemical, chemical
mixer-settlers	high-stage efficiency, handles wide solvent ratios, high capacity, good flexibility, reliable scale-up, handles liquids with high viscosity	petrochemical, nuclear, fertilizer, metallurgical
pulsed columns	low HETS, no internal moving parts, many stages possible	nuclear, petrochemical, metallurgical
rotary agitation columns	reasonable capacity, reasonable HETS, many stages possible, reasonable construction cost, low operating and maintenance cost	petrochemical, metallurgical pharmaceutical, fertilizer
reciprocating-plate columns	high throughput, low HETS, great versatility and flexibility, simplicity in construction, handles liquids containing suspended solids, handles mixtures with emulsifying tendencies	pharmaceutical, petrochemical metallurgical, chemical

TABLE II (CONTINUED)

Types of Extractor	General Features	Fields of Industrial Application
centrifugal extractors	short contacting time for unstable material, limited space required, handles easily-emulsified material, handles systems with little liquid density difference	pharmaceutical, nuclear, petrochemical



TIC = Temperature Indicating Controller
LIC = Level Indicating Controller
FIC = Flow Indicating Controller
FRC = Flow Recording Controller
TI = Temperature Indicator
SG = Sight Glass
H = Annunciator at Control Panel

LT = Level Transmitter
PI = Pressure Indicator
LA = Level Arm
MT = Mixing Tee
C = Computer
M = Motor

Figure 5. A Feed Forward Control Scheme for Industrial Extractors (22)

a flow diagram for an industrial extraction column equipped with a feed-forward control system.

Column extractors can be classified as either nonmechanical (no agitation) or mechanical agitation columns. Unagitated columns are simplest in construction and require minimum maintenance. However, these contactors have very low efficiency and high back mixing as a result of poor phase contacting. They provide one or two equilibrium stages and therefore are best used for processes that require a few theoretical stages, such as: washing, neutralization, and treating. The unagitated columns such as: spray, sieve tray, packed, perforated-plate, bubble-cap, and baffle-plate are still widely used in the process industry. This is primarily due to the relatively low capital cost, simple construction, and limited maintenance requirements.

Mechanically agitated columns create turbulence to increase mass-transfer efficiency by increasing the interfacial area per unit volume. This can be achieved by application of sinusoidal pulsation (pulsed column), rotating-disk agitation (rotary disk column), or rotating an impeller mounted on a central shaft (Scheibel column) to mix the contents of the column. Mechanically agitated columns are characterized by a high degree of mass-transfer, hence, high efficiency resulting in a significant reduction in HETS (height equivalent to theoretical stage). However, mechanical difficulties, frequent shutdowns for maintenance, and higher construction and operating costs of these contactors should be carefully evaluated. Due to the importance of the Scheibel column as part of this research study, its design and operating procedure will be described in detail.

Scheibel Columns

The important parameters in design of a multistage liquid extractor are simplicity and efficiency. Review of the performance characteristics of liquid extractors reveals that simple designs are easier to operate and maintain but less efficient. The design of Scheibel's (30) multistage extractor was based on a series of mixer-settler units. The phases are contacted in the mixing sections, with a flat bladed agitators, and the mixture is separated in calming zones of knitted wire-mesh packing. Figure 6 illustrates the first Scheibel column. The calming section was designed to prevent the loss of efficiency due to back mixing by isolating the agitator flow pattern in the mixing zones. Figure 7 shows the flow pattern in a mixing section and indicates the importance of the calming zone height to isolate the agitator flow pattern. In the absence of the packed calming sections, the agitation would cause severe back mixing resulting in only one theoretical stage throughout the column (21). The role of the packing in a four-stage Scheibel extractor has been studied by Honekamp and Burkhart (16). The simplicity in design and operation, has made the Scheibel column highly effective in pilot plant studies and laboratory scale processes where column diameter from 0.3 meters to 2.5 centimeters are constructed. The major disadvantage of this Scheibel column was the economic limitations in the scale up due to the large volume of expensive wire mesh packing. A more cost effective column extractor providing baffling in the mixing sections was designed by Scheibel (30) in 1956. Figure 8 illustrates the modifications of the first Scheibel design. The vertical flow in the mixing zone is by the horizontal baffles. The wire-mesh packing serves as a media to break up the

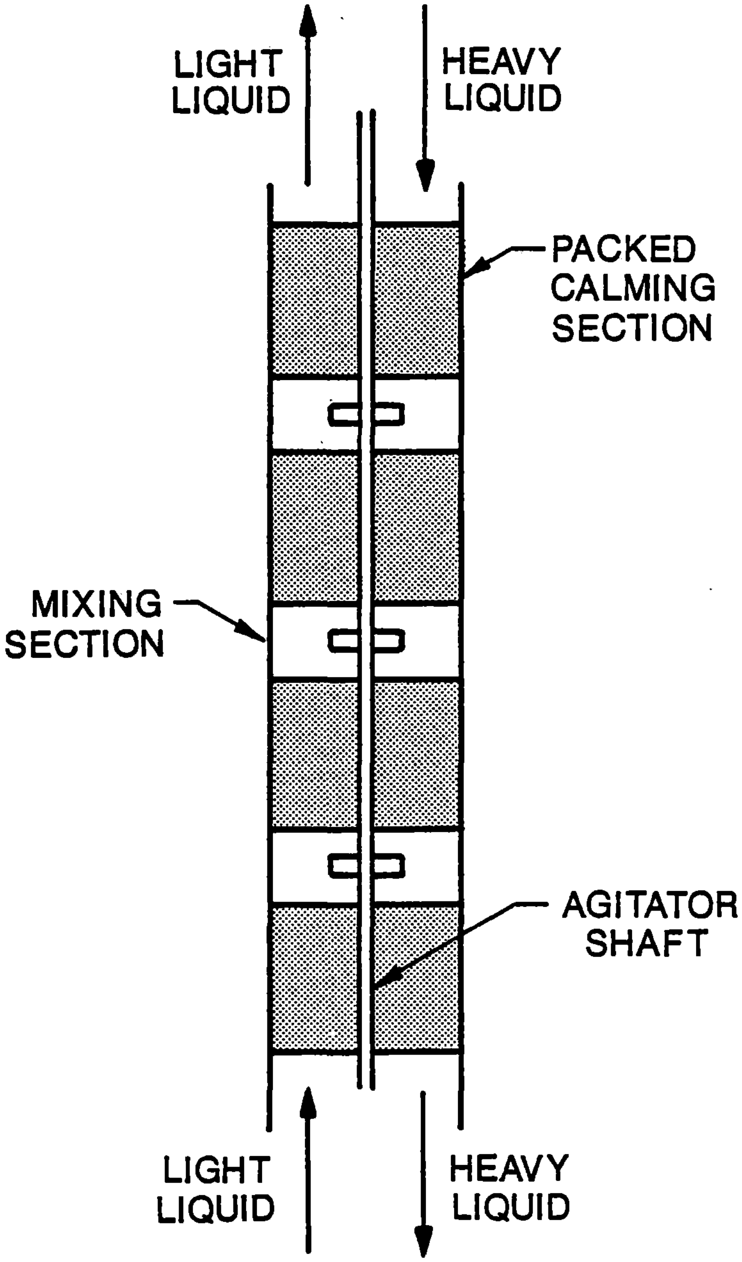


Figure 6. Schematic Diagram of the First Scheibel Column Design (21)

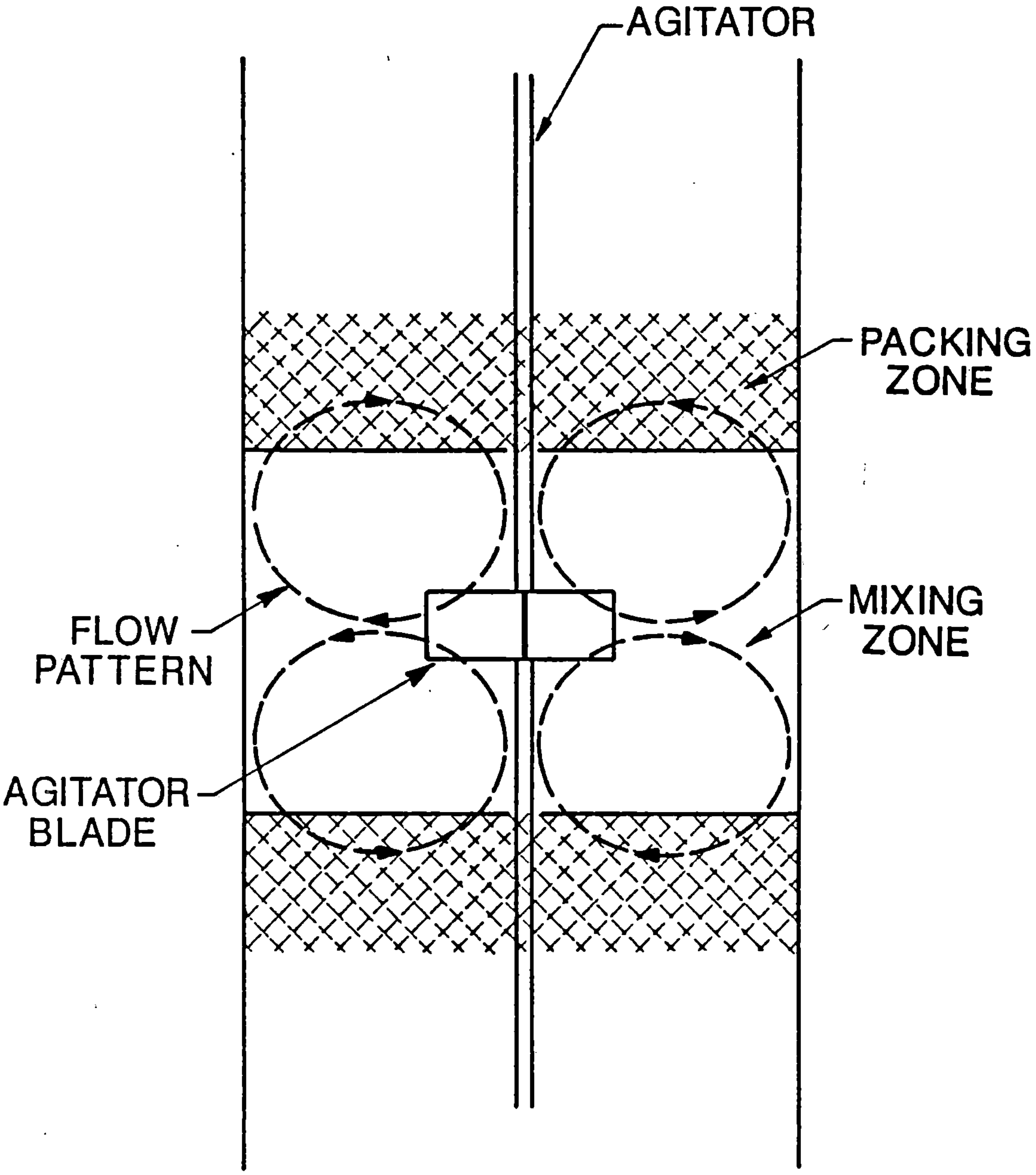


Figure 7. Flow Pattern in Mixing Stage of First Scheibel Column (21)

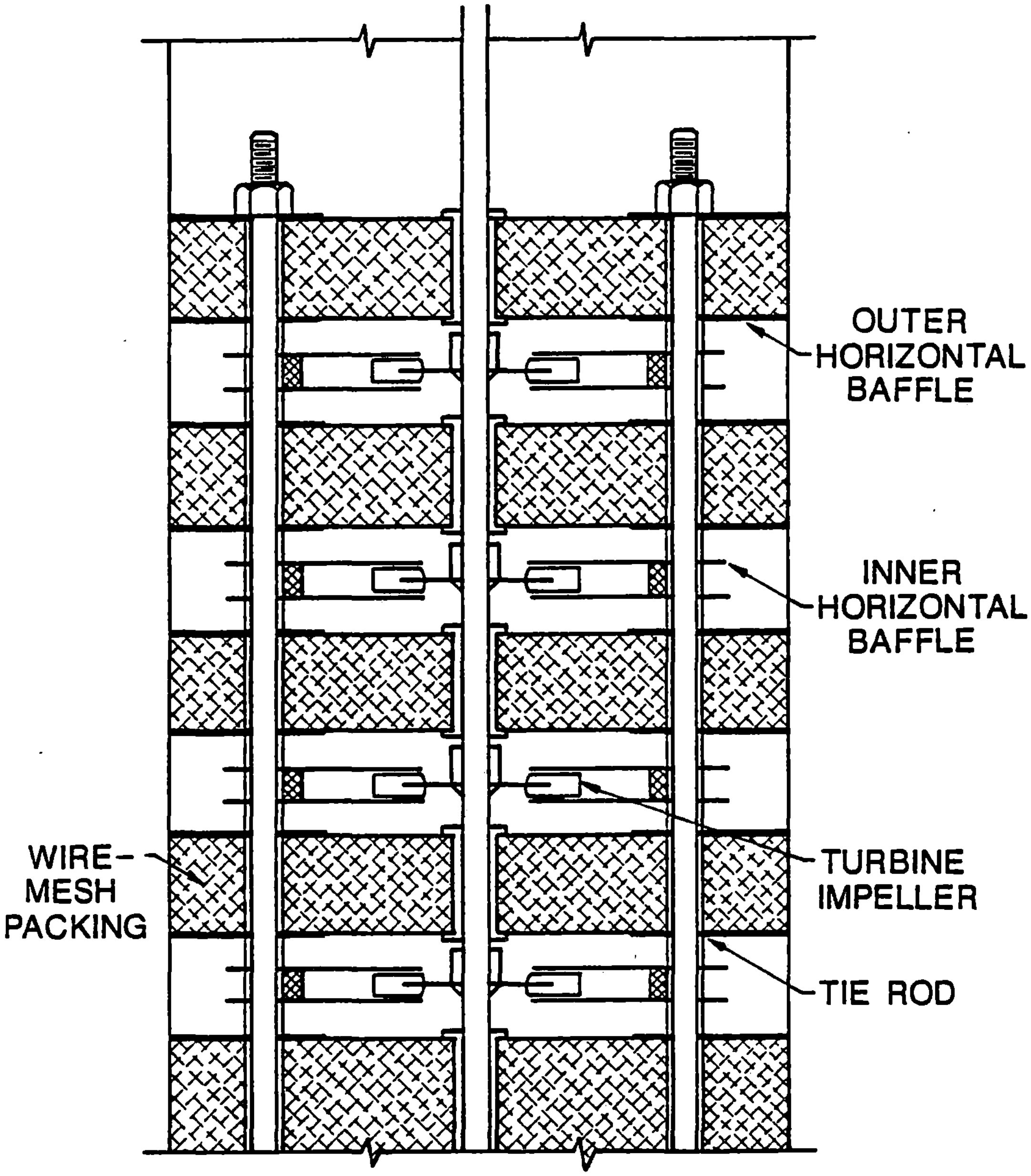


Figure 8. Second Scheibel Extractor with Baffled Mixing Stages and Intermediate Mesh Sections (21)

droplets and therefore increases the mass-transfer efficiency. The rotational motion in the mixing zone imparted by the impeller is also removed in the packing zone to avoid the back mixing. This design reduces the mesh packing volume and minimizes the height of the extractor with a specified number of theoretical stages. Column extractors of this type have been economically constructed and successfully operated for up to 1 meter in diameter (21).

The major disadvantage of Scheibel's second design was primarily due to a rigidly installed interval construction within the column. The mechanical limitations of baffled mixing stage prohibited the removal of the agitator shaft for regular inspection and accurate adjustment of the clearance between the impeller and the baffles. The latest design by Scheibel (33) consists of mixing sections assembled externally in cartridges as shown in Figure 9. These modifications provided the convenience of adjusting, inspecting, cleaning, and maintaining the internal moving parts of the extractor. This new design is especially suitable for extraction processes requiring multistage column extractors exceeding 1.5 meters in diameter.

Scheibel Column Efficiency

Karr and Scheibel (19) studied the efficiencies of mixing stages of the first Scheibel column. They concluded that the Murphree stage efficiency depends on the direction of mass transfer when the light phase was dispersed. A single correlation was developed when the heavy phase was dispersed. For solute mass-transfer into the droplets:

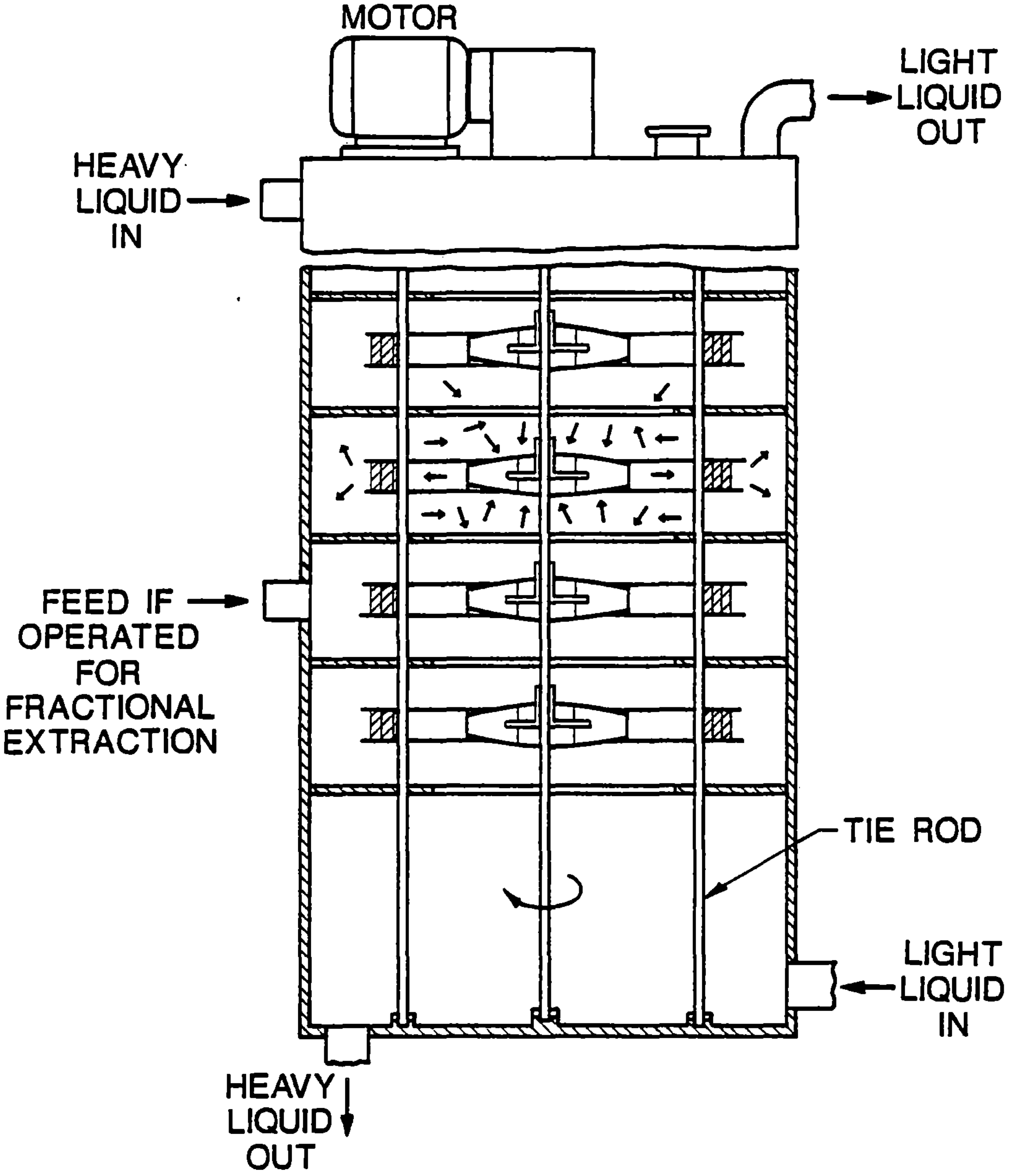


Figure 9. Construction Details of the Third Scheibel Column (21)

$$\frac{E_{md}}{1 - E_{md}} = 0.0091 \frac{H_c}{d_i} \frac{\partial (\gamma X)}{\partial C_d} (\frac{\Delta P}{\sigma})^{1.5} (N_{d_i})^4 \qquad \text{(II-23)}$$

Where E_{md} is the Murphree dispersed-phase stage efficiency. The term (γX) represents the product of the activity coefficient and the mole fraction of the solute in the dispersed phase. The quantity H_c is the height of mixing stage, C_d is the solute concentration, ΔP is the positive difference in density, d_i designates the impeller diameter, σ denotes the interfacial tension, and N is the agitator's speed in revolution per hour. All units are in metric system. For the reverse direction of diffusion:

$$\frac{E_{md}}{1 - E_{md}} = 0.092 \frac{H_c}{d_i V_d} \frac{\partial (\gamma X)}{\partial C_d} (\frac{\Delta P}{\sigma})^{1.5} (N_{d_i})^4 \qquad \text{(II-24)}$$

The quantity V_d stands for the superficial velocity of the dispersed phase. For the heavy phase dispersed, the mass transfer was found to be independent of the diffusion direction,

$$\frac{E_{md}}{1 - E_{md}} = 0.0028 \frac{H_c}{d_i^{0.3}} \frac{\partial (\gamma X)}{\partial C_d} (\frac{\Delta P}{\sigma})^{1.5} (N_{d_i})^3 \qquad \text{(II-25)}$$

These correlations have been developed based on the no radial flow through the packing of the first Scheibel column. The column efficiency is based on the simplifying concept that assumes a constant solute concentration over the mixing zone and a linear profile over the packing height.

Equilibrium - Stage Calculation

Multistage contactors are enhanced with countercurrent operation as illustrated in Figure 10. Feed entering stage one is contacted with the extract phase from the other stages. Fresh solvent contacts the raffinate stream leaving the last stage. This operation ensures the highest efficiency and, therefore, highest solute recovery for a given number of stages.

Industrial extraction processes involving ternary systems are described graphically using the triangular mass fraction diagram as shown in Figure 11. For a given feed, F, and solvent rate, S, values of the extract, E, and raffinate, R, can be determined by the equilibrium tie lines. The Δ operating point is located at the intersection of lines F_{E_1} and R_n E_{n+1}. In fact, Δ is a point common to all streams passing each other such as: R_1 E_2, R_2 E_3, R_3 E_4..., R_n E_{n+1}. Graphical construction of the other stages is accomplished from the feed at stage one to the raffinate at stage N using Δ and the tie lines. The required number of theoretical stages to reach a desired separation is obtained by first locating the operating point as described. Next a tie line through E_1 locates R_1. Then line $R_1\Delta$ is drawn and the point E_2 is located on the phase boundary. The tie line E_2 R_2 is drawn giving R_2. This procedure is repeated until the final raffinate composition, R_n, is reached. If a line to the point coincides with a tie line, the so-called pinch effect is reached. This corresponds to the minimum solvent to feed ratio requiring an infinite number of stages to reach the desired separation. The recommended optimum solvent-to-feed ratio is 1.5 to 2 times the minimum value.

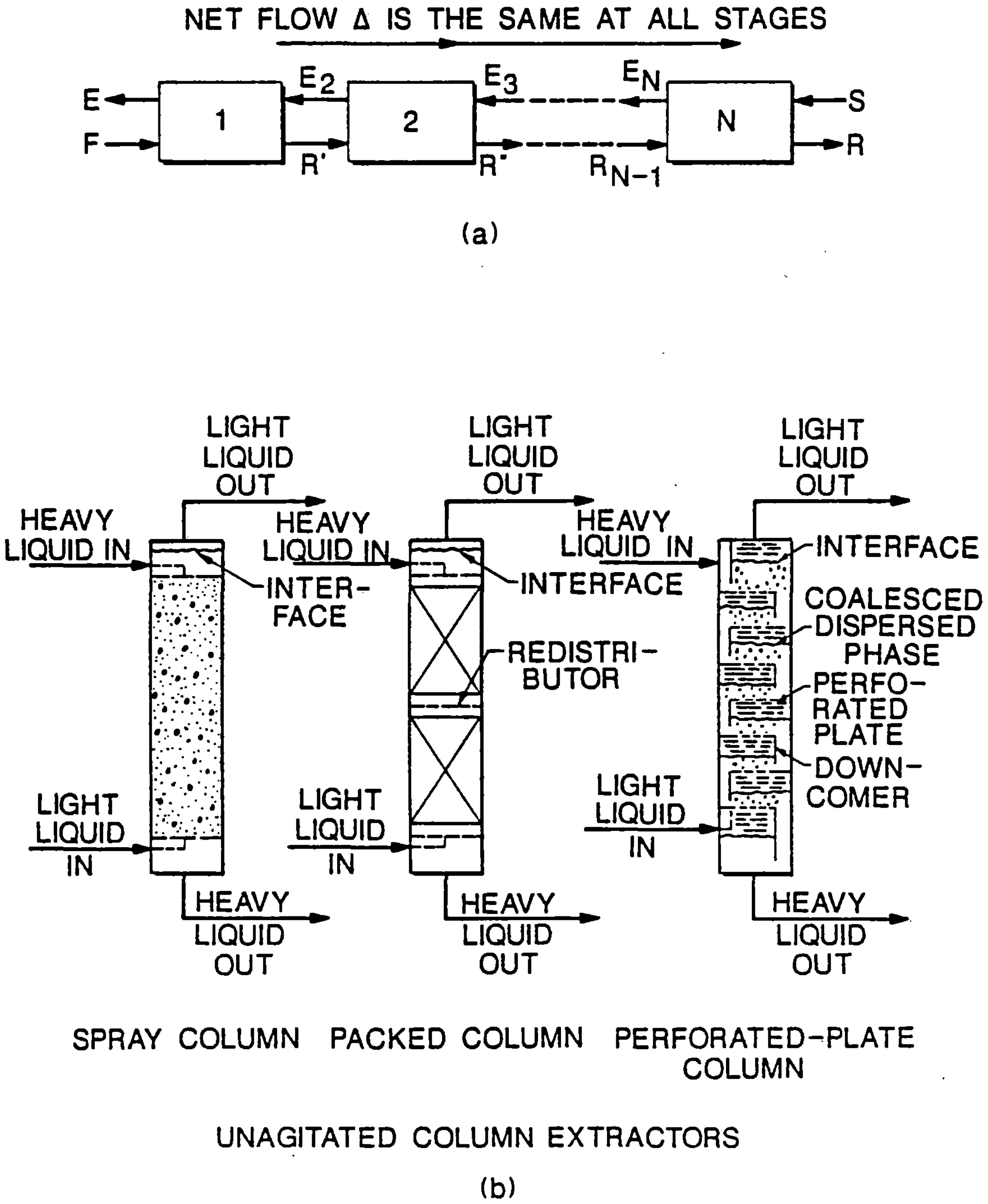


Figure 10. Countercurrent Stagewise Operation (22)
(a) Arrangement of Multistage Contactors
(b) Unagitated Multistage Column Extractors

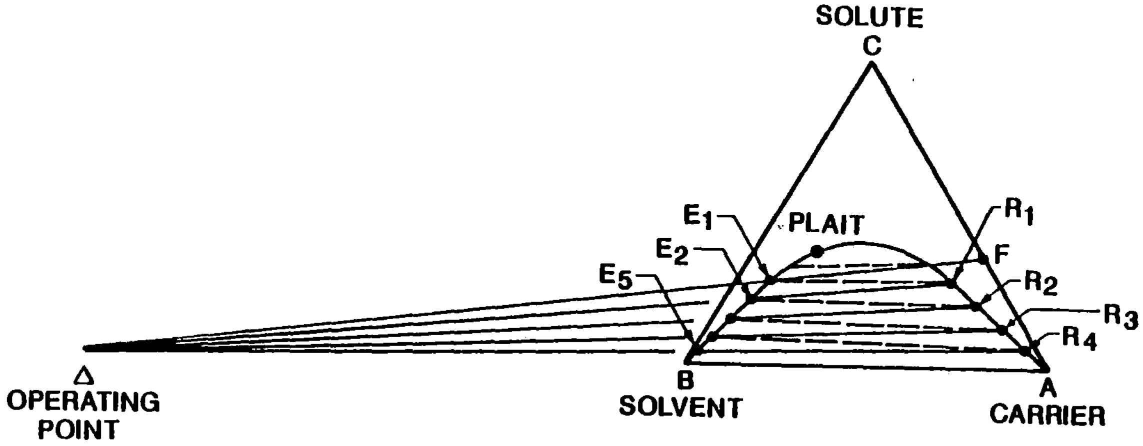


Figure 11. Graphical Construction for Ternary Extraction Systems

In most industrial extraction operations several compounds in the feed stream are extracted with a pure or mixed solvent. Multicomponent-multistage extraction has been investigated by Korchinsky (20), Scheibel (34), Henley and Seader (15), Jelinek and Hlavacek (18), Smith and Brinkley (39,40). No simple graphical method can be employed and more sophisticated data treatment is required. Stage-by-stage calculation is performed by assuming a composition and a rate profile for the solutes at each stage. The assumed phase profiles are modified by introducing an error term. This error is obtained by comparing the calculated values to the known feed and solvent compositions and flow rates. The iterative phase composition calculations converge when a set of composition and phase rate profiles satisfying the equilibrium and material balance requirements are obtained. In addition, the sum of the mole fractions in each stream throughout the column must add up to unity. The stage temperatures remain constant throughout the column corresponding to a specified operating condition. Hence, no enthalpy balance need be performed, instead, the solubilities govern the phase transfer rates.

The equilibrium stage approach provides useful information on the design and performance of the contactors with discrete stages, such as mixer-settlers and plate columns. However, in differential contactors where no discrete stage can be identified and approach toward equilibrium between phases is never established, the rate equation concept has been proven useful. Extraction processes carried out in packed columns or spray towers are best described by the transfer-unit concept. A shell balance on the differential extractor of Figure 12

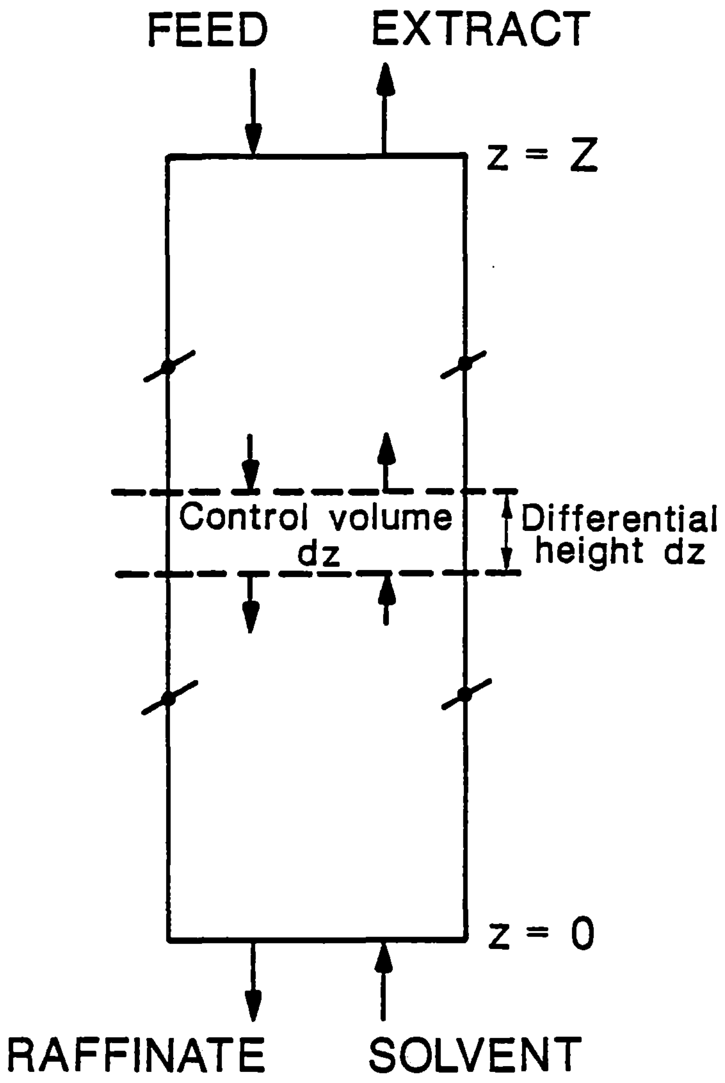


Figure 12. A Differential Countercurrent Contactor

over height ΔZ yields an expression for the number of overall transfer units, N_{oR}, based on the raffinate phase (17),

$$N_{oR} = \int_{X_{R2}}^{X_{R1}} \frac{dX_R}{X_R - X_R^*} + \frac{1}{2} \ln\left(\frac{1 - X_{R2}}{1 - X_{R1}}\right) \qquad \text{(II-26)}$$

The height of an overall transfer unit, H_{oR}, is given by:

$$H_{oR} = \frac{R_m}{K_R \; A \; (1 - X_R)_m} \qquad \text{(II-27)}$$

Where R_m is the molar flow rate of raffinate phase. Hence the total column height is:

$$Z = \int_o^z dZ = N_{oR} * H_{oR} \qquad \text{(II-28)}$$

The height of individual transfer units, based on the raffinate phase is,

$$H_R = \frac{R_m}{k_R \; A \; (1 - X_R)_m} \qquad \text{(II-29)}$$

and on the extract phase basis is:

$$H_E = \frac{E_m}{k_E \; A \; (1 - X_E)_m} \qquad \text{(II-30)}$$

where E_m denotes the molar flow rate of the extract phase. The quantities $(1-X_E)_m$ and $(1-X_R)_m$ are mean values of mole fraction of carrier in the extract phase and in the raffinate phase respectively.

Combining Equations II-29, II-30, and II-21 the height of the overall transfer unit (HTU) can be described as a function of individual HTUs:

$$H_{oR} = H_R + \left(\frac{R_m}{E_m M}\right) \left(\frac{(1 - X_E)_m}{(1 - X_R)_m}\right) H_E \qquad \text{(II-31)}$$

where M is the slope of the equilibrium curve relating the overall transfer coefficient, K_E, to individual transfer coefficients, k_E and k_R, as described by Equation II-21. The concept of stage efficiency can be formulated based on the continuous phase,

$$(E_m)_c = \frac{X_{c,n} - X_{c,n-1}}{X^*_{c,n} - X_{c,n-1}} \qquad \text{(II-32)}$$

or dispersed phase,

$$(E_m)_d = \frac{X_{d,n} - X_{d,n-1}}{X^*_{d,n} - X_{d,n-1}} \qquad \text{(II-33)}$$

where n designates a stage number and X^* is the equilibrium mole fraction of the solute.

Equations II-26 through II-33 are rigorous design equations limited to dilute and immiscible liquid phases. A detailed and more complicated treatment of differential contactors is provided by Treybal (41).

CHAPTER III

SOLVENT SELECTION CRITERIA

The key to any successful liquid-liquid extraction process is the choice of the appropriate solvent. In general the selection of the optimum solvent will be a compromise between solvent selectivity, capacity, and toxicity. A logical procedure is to obtain experimental equilibrium data for liquid-liquid extraction of solute with a variety of solvents. During the preliminary stage of the solvent selection process the potential solvents are screened based on the equilibrium distribution coefficients and separation factors while carefully studying the toxicological constraints. The selected solvents, normally from several classes of chemicals, are then evaluated based on the balance between capacity, recoverability, and cost.

The experimental solvent selection procedure provides a safe means for solvent evaluation, but it is prohibitively expensive and time consuming. The economics of solvent evaluation dictates the acquisition of minimum equilibrium data in combination with the thermodynamics of liquid-liquid or vapor-liquid phase equilibria.

Solvent Selection Variables

Several principles can be utilized to screen potential solvents. For conventional extraction processes the technical and economical preferences dictate the following solvent criteria:

Selectivity. This property of the solvent is defined as the ability to extract a component in the solution preferentially. High values of selectivity indicate fewer contactors, smaller plant equipment, and lower operational cost. Experimental values of selectivity coefficients can be obtained by phase composition analysis of solute(s), solvent, and carrier in the raffinate and the extract phases as indicated by equation II-4. The thermodynamics of phase equilibria introduces activity coefficients to determine the limiting values of selectivity coefficients. Equation II-5 is modified to an infinite-dilution expression and the term expressing the raffinate phase activity coefficients ratio of solute and carrier is assumed unity, hence:

$$\beta_{CA}^{0} = \frac{\gamma_{AB}^{0}}{\gamma_{CB}^{0}} \qquad \text{(III-1)}$$

Where β° and γ° are selectivity and activity coefficient at infinite dilution respectively. Equation III-1 provides a limiting value for the partitioning of a solute-solvent and carrier-solvent system.

Equilibrium Distribution Coefficient. This characteristic of the solvent determines the quantity of solvent to feed required to perform the extraction. Higher values of the equilibrium distribution coefficient demonstrate the ability of solvent to dissolve the solute in relatively large quantities. Thus, allowing for a lower feed to solvent ratio and ultimately reducing the total inventory of the solvent and the corresponding material and operating costs for process extraction. The optimum design and successful operation of liquid-liquid extraction processes is dependent on reliable acquisition of distribution data between solute(s), solvent, and carrier. Experimental liquid-liquid equilibrium data is obtained by careful phase analysis of single stage extraction. Theoretical developments for prediction of equilibrium distribution coefficient can be cost effective, time saving, and have a relatively good accuracy. The approach is based on activity coefficients for expressing liquid-liquid non-ideality. In general, the activity coefficient of the species of interest is expressed by one of the liquid models (i.e. UNIQUAC, Wilson, Van Larr, NRTL, Margules, etc.). The condition of thermodynamic equilibrium expressed in mathematical form by Equation II-7 is used to predict phase compositions, and hence to compute the distribution coefficients and selectivity values. The UNIQUAC model was developed by Maurer and Prausnitz (24) for prediction of liquid-liquid and vapor-liquid equilibria. this model uses molecular thermodynamics and incorporates the effect of temperature in liquid-liquid equilibria. UNIQUAC requires two interaction binary parameters for each binary pair. In addition, a set of three pure component data derived from the molecular structure of the participating species are required. Abrams and Prausnitz (1) and Sørensen and Arlt (38) provide information on UNIQUAC parameters for a selected number of solvents. The computer implementation of UNIQUAC model was originally developed by Anderson et al. (3). As part of this research study, the UNIQUAC program was modified at several fronts. For ease of use, the program was changed to an interactive-user-friendly mode. This allows the user to enter input data from a keyboard terminal and make changes for further use. To minimize program's input data requirements, numerous available data on components of interests: acetone, butanol, ethanol, and water system were stored within the program in a block data subroutine. Several useful comments and warning messages were incorporated where appropriate, to warn the user of possible errors. The user is allowed to save the output results in a retrievable file for future reference. An example of input dialog, input parameters, and output results of modified UNIQUAC program for prediction of phase composition and distribution coefficient is presented in Table III. The FORTRAN source code of the modified version of the UNIQUAC program is presented in Appendix A.

Recoverability. In all extraction processes the economics dictates that the solvent must be recovered from the extract phase for reuse. Some make-up solvent is usually required as in the case of partial immiscibility of solvent and solution. This mutual solubilities must be minimized and if possible avoided. The recoverability of a solvent greatly improves the cash flow of the entire project.

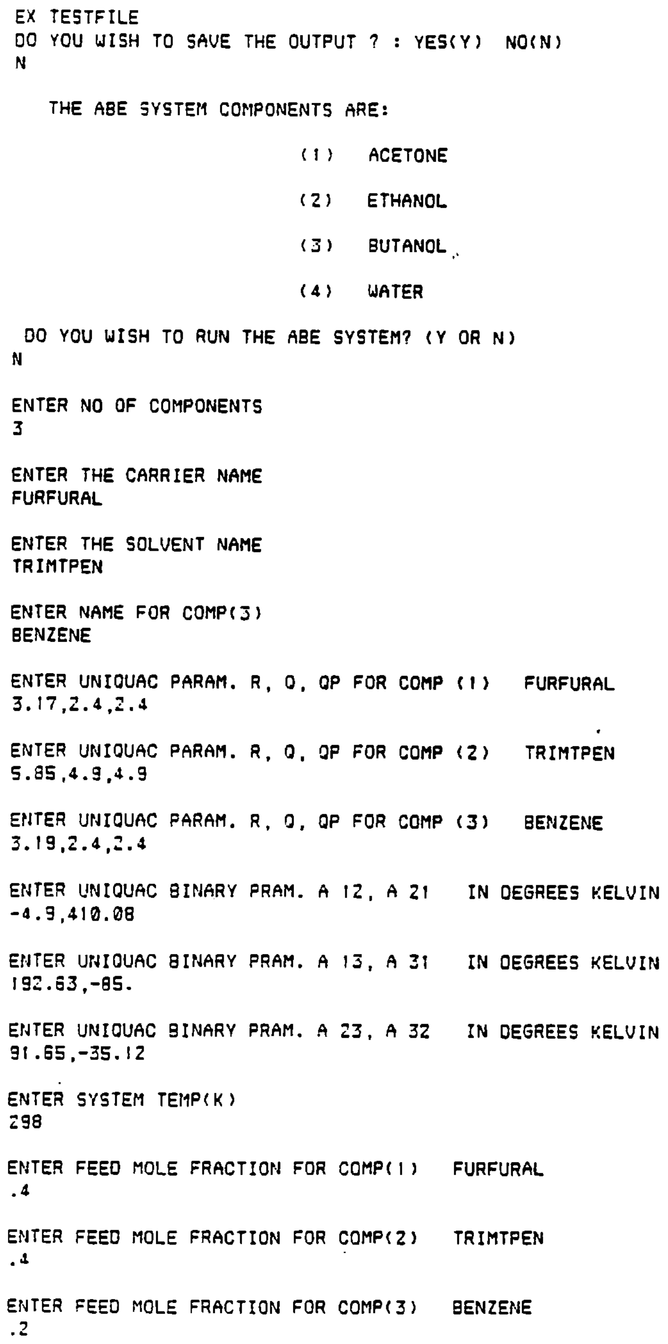
Density. A large density difference between the solvent and the solution is essential to ensure sharp and fast phase separation as well as enhancing the capacities in equipment, especially for gravity phase settlement.

Interfacial Tension. The effects of solvent interfacial tension is two fold. High values of interfacial tension leads to large energy requirements for phase dispersion but have a rapid rate of coalescence. Low interfacial tension aids the dispersion of phases but may lead to formation of stable emulsions. Higher values of interfacial tension are preferred.

Viscosity. Low power requirements for pumping and mixing and high rate of mass transfer require low viscosity by the solvent.

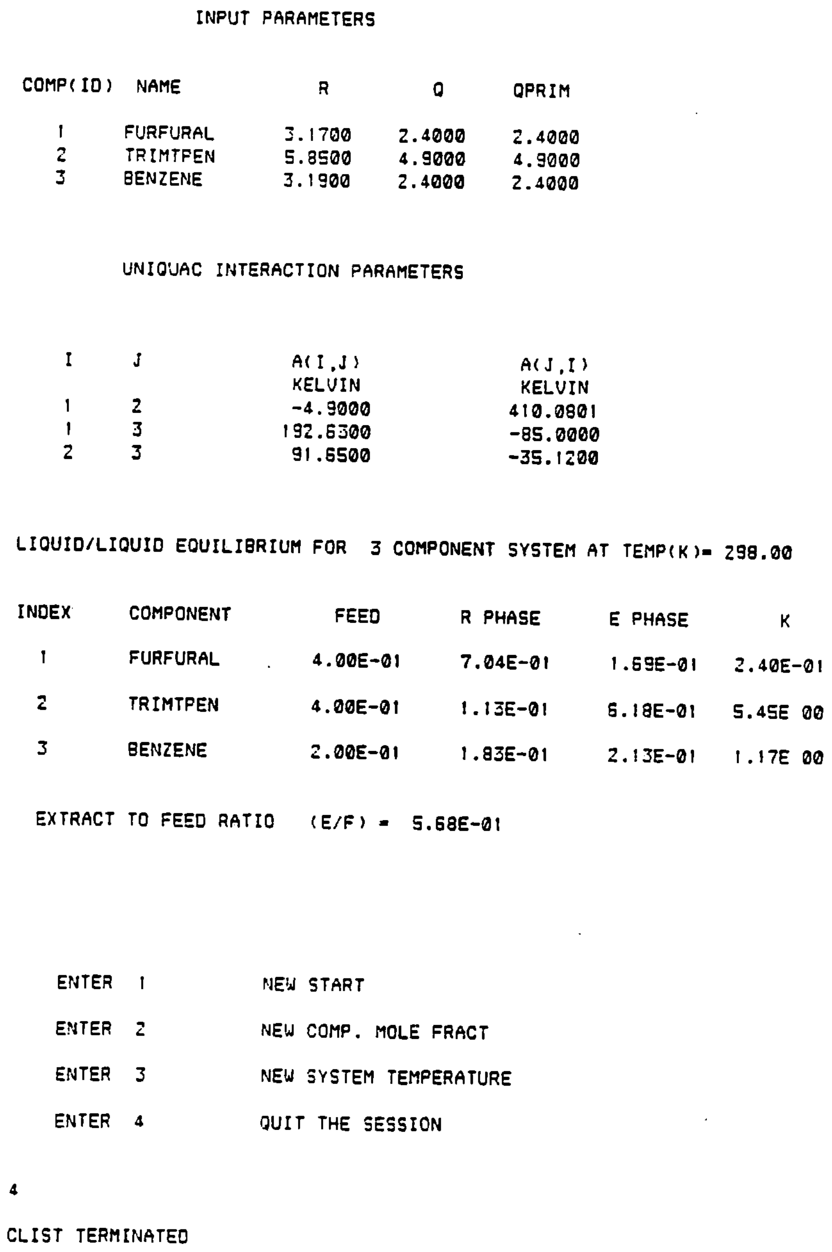
TABLE III

SAMPLE INPUT DIALOGUE AND OUTPUT RESULTS



```
EX TESTFILE
DO YOU WISH TO SAVE THE OUTPUT ? : YES(Y)  NO(N)
N

   THE ABE SYSTEM COMPONENTS ARE:

                       (1)   ACETONE

                       (2)   ETHANOL

                       (3)   BUTANOL

                       (4)   WATER

 DO YOU WISH TO RUN THE ABE SYSTEM? (Y OR N)
N

ENTER NO OF COMPONENTS
3

ENTER THE CARRIER NAME
FURFURAL

ENTER THE SOLVENT NAME
TRIMTPEN

ENTER NAME FOR COMP(3)
BENZENE

ENTER UNIQUAC PARAM. R, Q, QP FOR COMP (1)   FURFURAL
3.17,2.4,2.4

ENTER UNIQUAC PARAM. R, Q, QP FOR COMP (2)   TRIMTPEN
5.85,4.9,4.9

ENTER UNIQUAC PARAM. R, Q, QP FOR COMP (3)   BENZENE
3.19,2.4,2.4

ENTER UNIQUAC BINARY PRAM. A 12, A 21   IN DEGREES KELVIN
-4.9,410.08

ENTER UNIQUAC BINARY PRAM. A 13, A 31   IN DEGREES KELVIN
192.63,-85.

ENTER UNIQUAC BINARY PRAM. A 23, A 32   IN DEGREES KELVIN
91.65,-35.12

ENTER SYSTEM TEMP(K)
298

ENTER FEED MOLE FRACTION FOR COMP(1)   FURFURAL
.4

ENTER FEED MOLE FRACTION FOR COMP(2)   TRIMTPEN
.4

ENTER FEED MOLE FRACTION FOR COMP(3)   BENZENE
.2
```

TABLE III (CONTINUED)



```
                  INPUT PARAMETERS

COMP(ID)  NAME              R           Q         QPRIM

   1     FURFURAL        3.1700      2.4000      2.4000
   2     TRIMTPEN        5.8500      4.9000      4.9000
   3     BENZENE         3.1900      2.4000      2.4000


           UNIQUAC INTERACTION PARAMETERS


    I     J             A(I,J)             A(J,I)
                        KELVIN             KELVIN
    1     2            -4.9000            410.0801
    1     3           192.6300            -85.0000
    2     3            91.6500            -35.1200


LIQUID/LIQUID EQUILIBRIUM FOR  3 COMPONENT SYSTEM AT TEMP(K)= 298.00

INDEX    COMPONENT         FEED        R PHASE      E PHASE        K

  1      FURFURAL        4.00E-01     7.04E-01     1.69E-01    2.40E-01

  2      TRIMTPEN        4.00E-01     1.13E-01     6.18E-01    5.45E 00

  3      BENZENE         2.00E-01     1.83E-01     2.13E-01    1.17E 00

  EXTRACT TO FEED RATIO   (E/F) =  5.68E-01




    ENTER  1           NEW START

    ENTER  2           NEW COMP. MOLE FRACT

    ENTER  3           NEW SYSTEM TEMPERATURE

    ENTER  4           QUIT THE SESSION

4

CLIST TERMINATED
```

Immiscibility of Solvent. The solubilities of solvent and solution should be low. This will aid better solvent recovery and avoids a costly additional separation of solvent and the raffinate.

Toxicity. Toxicity of a solvent is an important factor to Occupational health, safety, and ease of handling. Toxic solvents require costly plant safety equipment and operation.

Cost and Availability. The desired solvent must satisfy the conditions of being reasonably cheap and readily available. Storage of expensive solvent requires large amounts of capital investment which directly affects the overall economic feasibility of the process.

Other Properties. Some of the desirable characteristics of a solvent are chemical stability, low vapor pressure, sufficiently low freezing and boiling points, low flammability, and low heat of vaporization.

All of the afore-mentioned properties of an optimum solvent for a liquid-liquid extraction process are technically essential. No single solvent has all the desirable properties and, therefore, some compromises should be made. The economic feasibility study of the process along with experience and careful engineering judgement should serve the best guide for screening and selecting the potential solvent for a separation by liquid-liquid extraction.

CHAPTER IV

EXPERIMENTAL EQUIPMENT AND ANALYTICAL PROCEDURE

The experimental work of this research program was carried out in two major studies. In the first, a series of single stage equilibrium extraction experiments were conducted to evaluate several classes of solvents for their ability to remove ethanol, butanol, and acetone from water. In the second study, the potential solvents from four different classes of chemical were continuously extracted in a modified York-Scheibel extraction column.

Study I: Batch Extraction

Forty-seven solvents were tested for their ability to remove ethanol, butanol, and acetone from water at concentrations similar to those found in fermentation broth. A feed mixture containing 2.0 percent butanol, 1.0 percent acetone, and 0.3 percent ethanol by volume in water was prepared. These percentages are in approximate ratios expected for butanol-acetone-ethanol fermentations (6:3:1) as reported by Bergstrom and Foutch (6). Ten milliliters of feed solution was placed in thirty milliliter vials, equipped with Teflon lined caps, containing ten milliliters of solvent. The mixture was then vigorously shaken for sixty seconds and allowed to stand and separate for four hours. The composition of each phase was determined by gas chromatography on a Hewlett-Packard Model 5880A Gas Chromatograph equipped with a Model 7671A automatic sampler. A 6.0 foot by 0.125 inch stainless steel column packed with Porapack Q (80-100 mesh) was used to elute the solvents: ethanol, butanol, acetone, and water. The injection and detection ports were set at 200 C. Oven temperature was maintained isothermally at 190 C. For those solvents with retention time near butanol's, the oven temperature was reduced to 170 C to produce sharp separation of peaks by the gas choromatograph. Helium at a flow rate of 45 milliliter per minute was used as a carrier gas through the thermal conductivity detector (TCD). The use of the thermal conductivity detector, versus the flame ionization detector (FID), allowed for the measurement of the amount of dissolved water in the solvent phase. Concentrations were determined by comparing 0.2 microliter injections with a calibration curve for each component.

Phase Composition Determination

Phase composition analysis was determined by the calibration curves for ethanol, butanol, and acetone. The calibration curves for these components were obtained by using a Hewlett-Packard 5880A series gas chromatograph. The column and all the heated zones were kept at the described conditions. Samples with known concentration of solute in water were prepared. A 0.2 microliter sample was injected into the gas chromatograph using the automatic sampler for greater accuracy. The calibration curves of ethanol, butanol, and acetone were constructed by plotting the peak area versus concentration, in moles per milliliter, for several repeated runs.

Study II: Continuous Extraction

For this study four potential solvents from different classes of chemicals were selected. These solvents were screened based on the evaluation of the results obtained from study I of this research. Table IV shows the selected solvents with the manufacture's specifications. The chemicals used in this investigation, were in excess of 99.95 percent pure, thus no purification was attempted.

Hood Design and Operation

To avoid the accumulation of any hazardous vapor associated with the use of toxic materials during the extraction process, a walk-in-hood was designed and constructed. A 4 by 4 by 8 ft hood was made of one half inch thick plywood. Two fans through the hood's ceiling were installed to transfer any fumes generated during the extractor operation to the building's main ventilation system. The hood was completely sealed from the inside except for a one half inch opening at the bottom of each side. This design feature forced the air to enter at the bottom of the hood and created turbulence that was carried out by the fans. The air velocity through hood was measured by means of a volumeter to ensure that the exit air velocity from the hood did not exceed the building's ventilation intake velocity. Temperature probes were installed at various locations inside the hood to monitor the temperature and to alarm the possible over heating of the pumps or any other equipment. Provisions were made for ease of access to product samples, flow rate control valves, interface control valve, temperature control powerstats, various switches for pumps, fans, mixer, and emergency shutdown circuit breaker.

TABLE IV

CHEMICAL SOURCE AND PURITY

Solvent	Manufacturer	Specification
Butyl acetate	Aldrich Chemical	99+% pure
Butanol	Fisher Chemical	99.8% pure
Acetone	Baker Chemical	99.9% pure
4-Methyl-2-pentanone	Aldrich Chemical	99.5% pure
1,1,1-Trichloroethane	Aldrich Chemical	99+% pure
Ethanol	U. S. Industrial Chemical Company	200% proof
2-Ethyl-1-hexanol	Aldrich Chemical	99% pure
Water	In House	distilled and deionized
Helium	Sooner Supplies	99.99% pure

Column Design and Operation

The schematic of the experimental setup for this study is shown in the Figure 13. The extraction column was a modified Scheibel continuous contactor which consisted of alternate packed calming and mixing zones. The detail design parameters of the experimental extraction column used in this research study is presented in Figure 14. A centrally located shaft with flat-bladed agitators ensured intimate contacting of the phases in the mixing sections of the column. The calming zones, filled with a woven wire mesh, were designed to separate the two liquid phases and to prevent back mixing by isolating the agitator flow patterns between adjacent mixing sections. The Scheibel column originally was designed for gravity flow of the feed and solvent from overhead reservoirs. This system was modified by installing two centrifugal pumps allowing a wide range of flow rates of feed and solvent through the column.

The heavier liquid was introduced at the top of the column and allowed to travel downward through the calming and the mixing zones where it was brought into intimate contact with the light liquid which was fed at the bottom of the column. The flow diagram with the corresponding experimental equipment is shown in Figure 15. The interface between the light liquid at the top and the heavy liquid at the bottom was controlled by a very fine needle valve. Column operations required continuous monitoring of the interface by adjusting the level-control valve for small perturbations in the feed or solvent flow rates.

A mixture of 2.0 percent butanol, 1.0 percent acetone, and 0.3 percent ethanol by volume in water was charged to the feed reservoir.

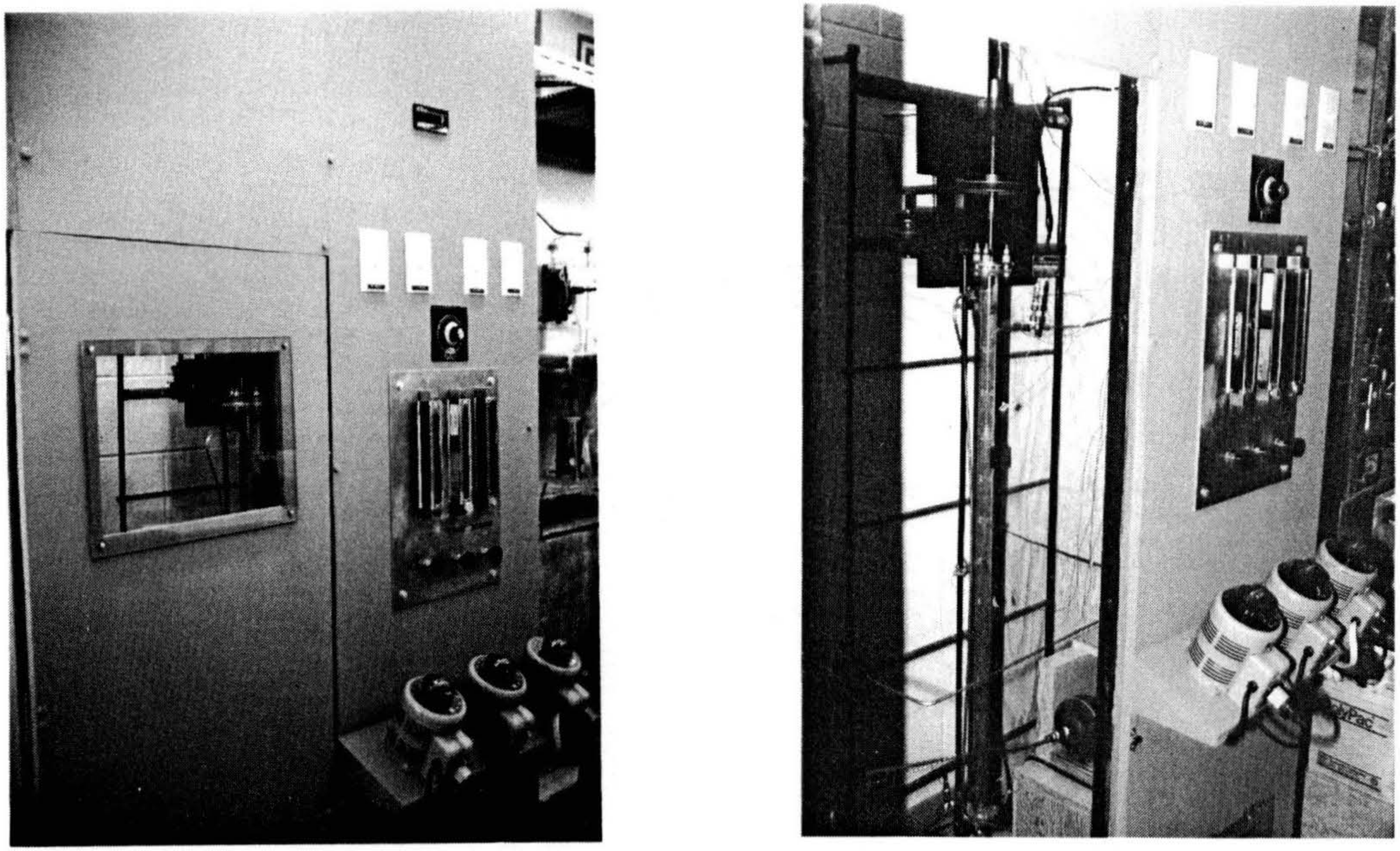


Figure 13. Experimental Setup of This Research Study

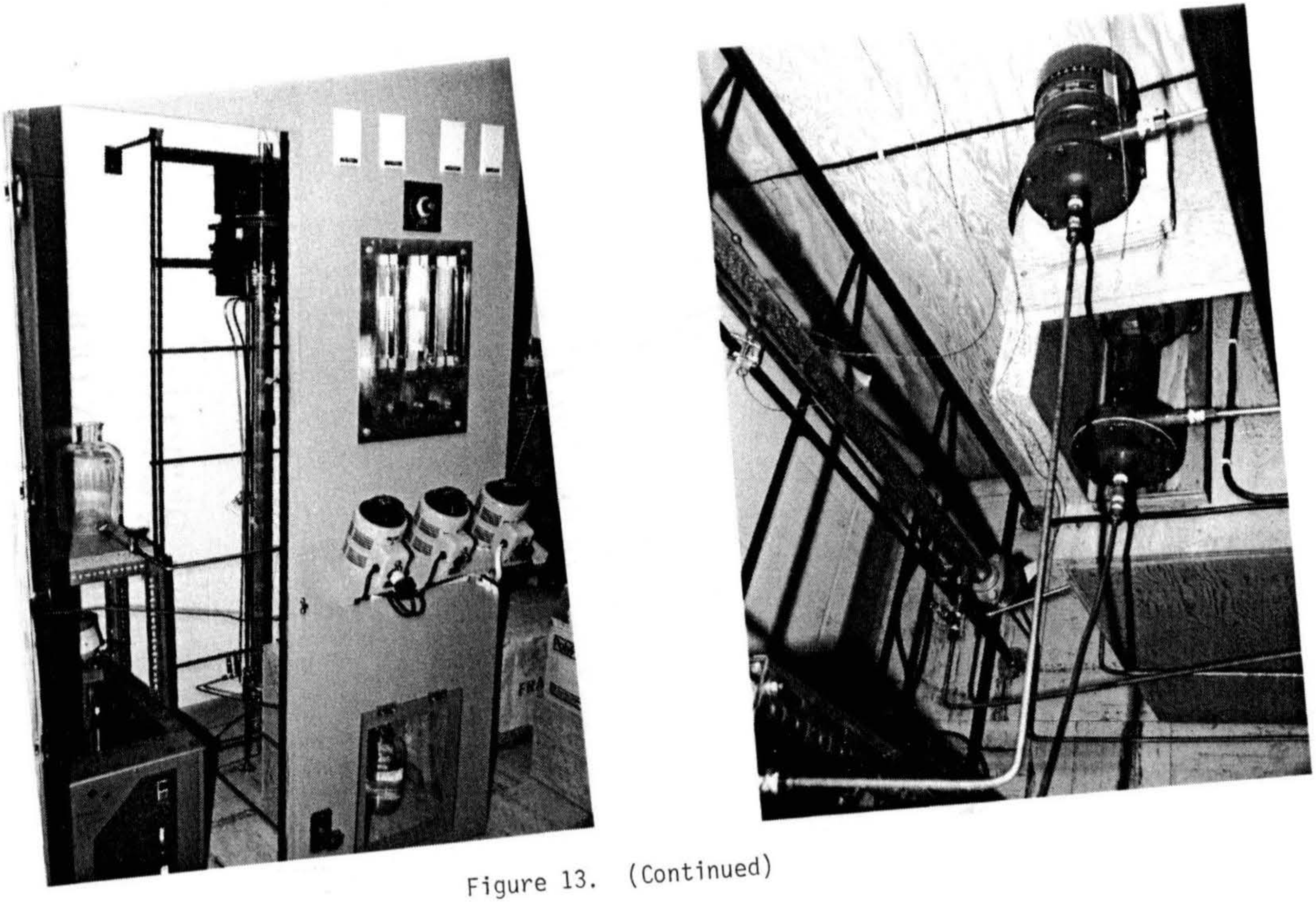


Figure 13. (Continued)

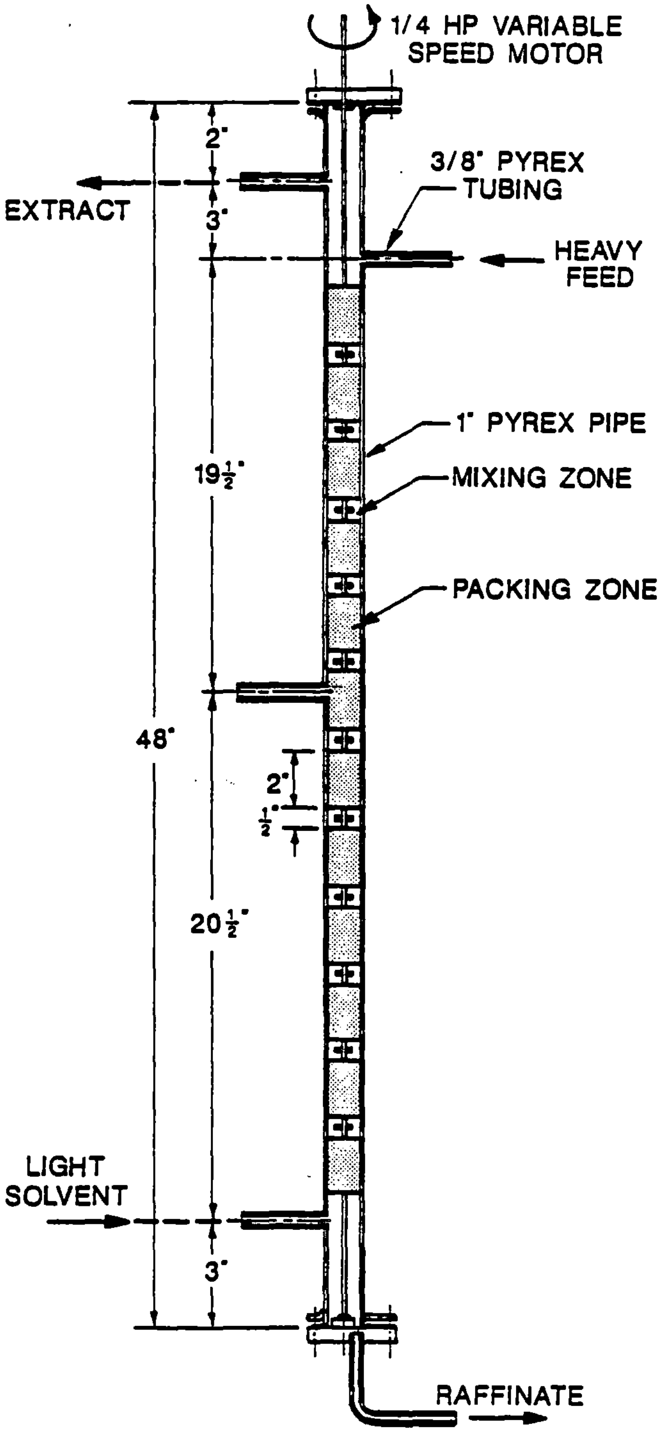
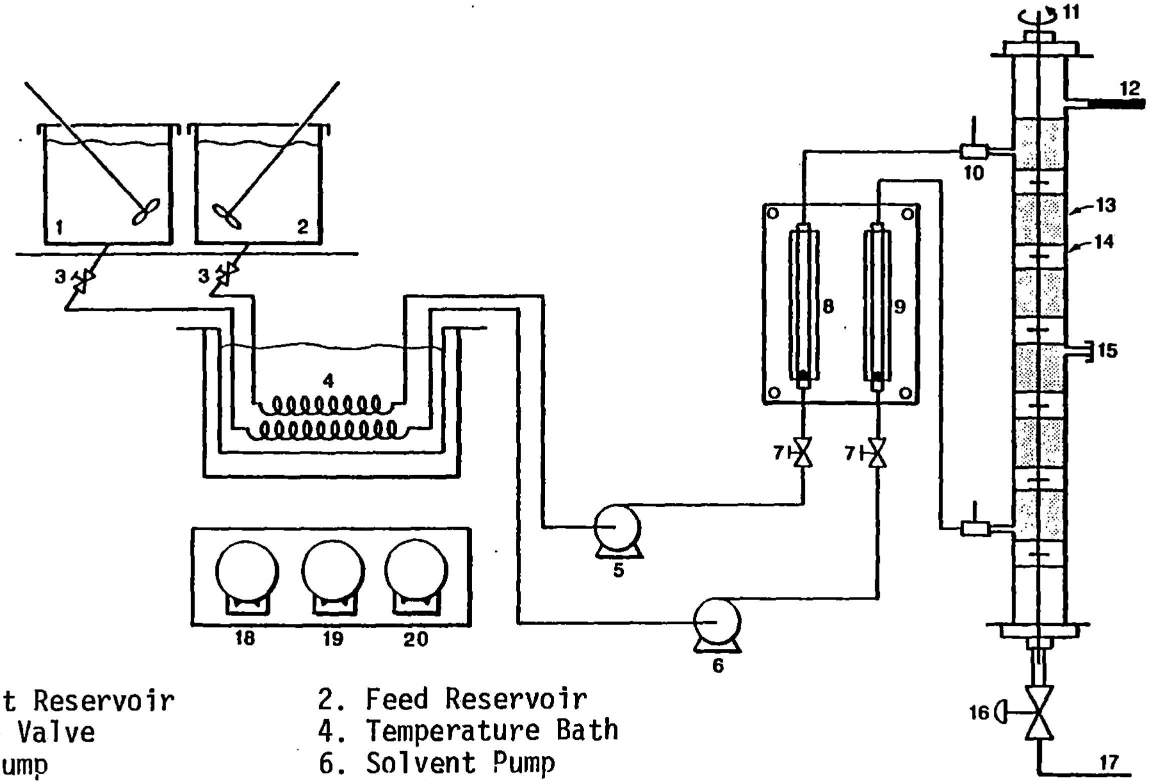


Figure 14. Mechanical Design Diagram of the Extractor Used in This Research Study



1. Solvent Reservoir
2. Feed Reservoir
3. Needle Valve
4. Temperature Bath
5. Feed Pump
6. Solvent Pump
7. Flow Valve
8. Feed Rotameter
9. Solvent Rotameter
10. Temperature Probe
11. Variable Motor
12. Extract Stream
13. Packing Section
14. Mixing Section
15. Sample Port
16. Interface Controller Valve
17. Raffinate Stream
18. Feed Pump Regulator
19. Solvent Pump Regulator
20. Column Temperature Regulator

Figure 15. Schematic Flow Diagram of This Research

The content of the solvent reservoir was filled with the desired solvent. The feed and the solvent flow rates were measured before each run by taking repeated measurements of the time elapse to fill a known volume. A needle valve was installed prior to each flowmeter to allow for a precise adjustment of the ball floats inside the rotameter. Higher flow rates were achieved by regulating the pump's rotational speed by a variable voltage transformer.

Feed, at a preset flowrate, was introduced at the top of the column (except for when trichloroethane was used as a solvent). The solvent was fed at the bottom of the column. The agitator was driven by a 1/4 horsepower Reliance Duty Master motor. The liquid-liquid interface in the column was controlled by adjusting the exit flow of the raffinate from the bottom of the column. The column was operated for 60 consecutive minutes and the products were sampled every five minutes. The extract and the raffinate volumes were collected and measured to ensure the constant operation of the column and to check the flow ratio. Several runs at 0.5, 1.0, 1.5, and 2.0 solvent to feed flow ratios for each solvent were made. The extract and the raffinate phase compositions were analyzed using the gas chromatograph method as described under study I.

CHAPTER V

EXPERIMENTAL RESULTS

Study I: Batch Extraction

In this study, the results of experimental investigation for the recovery of Clostridium fermentation products by liquid-liquid extraction will be presented. Forty-seven solvents from wide classes of chemicals were evaluated for their ability to remove butanol, ethanol, and acetone from fermentation broth. Equilibrium distribution coefficients for ethanol, butanol, and acetone were experimentally determined. Separation factors for removal of these products from water were calculated. The results are presented by Dadgar and Foutch (12).

The experimentally determined distribution coefficients and separation factors are presented in Table V. Solvents are segregated and classified by chemical type. Saturated aliphatic hydrocarbons as a class exhibit the lowest values for the distribution coefficients for all solutes. These values range from 0.56 to 0.11 for butanol, 0.31 to 0.07 for acetone, and 0.07 to 0.02 for ethanol.

Tables VI and VII present tabulated data compiled from the literature on the solvents of interest. As discussed previously, information about the physical extractive properties of solvents such as density, viscosity, boiling point, freezing point, surface tension, heat of vaporization, toxicity, flammability, and cost are essential in the solvent selection process. Cost is of particular note: some tabulated

TABLE V

EXPERIMENTAL LIQUID-LIQUID EXTRACTION PARAMETERS

Solvent	Distribution Coefficient			Equilibrium Ratio of Water	Separation Factor		
	Ethanol	Acetone	Butanol		Ethanol	Acetone	Butanol
I. <u>Saturated Aliphatic Hydrocarbons</u>							
Heptane	0.056	0.16	0.21	0.031	1.8	5.3	6.8
n-Dodecane	0.045	0.10	0.13	0.021	2.1	4.9	6.5
Decane	0.02	0.11	0.16	0.020	1.0	5.9	8.0
n-Tridecane	0.04	0.31	0.14	0.010	4.0	31	14
Tetradecane	0.10	0.07	0.12	0.035	29	22	34
Hexadecane	0.02	0.08	0.11	0.003	6.7	28	40
Hexane	0.07	0.17	0.02	0.023	3.2	7.4	0.87
Hexanes mix	0.05	0.15	0.14	0.023	2.2	6.7	6
Cyclohexane	0.066	0.18	0.27	0.057	1.2	3.3	4.8
Cyclooctane	0.02	0.15	0.56	0.017	1.2	33	33
Isopentane	0.20	0.14	0.13	0.20	1.0	0.7	0.66
2-Methylpentane	0.07	0.21	0.30	0.025	2.9	8.4	12
2,2,4-Trimethyl pentane	0.02	0.15	0.20	0.022	0.91	6.9	9.1
II. <u>Aromatic Hydrocarbons</u>							
Benzene	0.092	0.97	0.70	0.031	3.0	31	23
Cumene	0.18	1.40	1.70	0.035	5.3	40	49
Toluene	0.085	0.63	0.93	0.026	3.3	24	36
o-xylene	0.02	0.41	0.54	0.011	1.8	37	40

TABLE V (CONTINUED)

Solvent	Distribution Coefficient			Equilibrium Ratio of Water	Separation Factor		
	Ethanol	Acetone	Butanol		Ethanol	Acetone	Butanol
m-xylene	0.06	0.53	0.57	0.015	4.1	34	37
p-xylene	0.06	0.54	0.74	0.016	3.9	33	45
1,2,3,4-Tetrahydronaphthalene	0.05	0.34	0.51	0.0038	14	89	130
III. Unsaturated Hydrocarbons							
1-Heptene	0.04	0.21	0.40	0.014	3.4	15	29
IV. Aliphatic Alcohols							
1-Octanol	0.53	0.52	5.60	0.047	11	11	120
1-Heptanol	0.75	0.65	6.62	0.052	14	13	130
1-Pentanol	0.78	0.88	7.48	0.096	8.1	9.2	78
2-Ethyl-1-Hexanol	0.47	0.58	6.09	0.022	21	26	280
V. Phenols							
Phenol	2.15	8.45	24.00	0.29	7.3	29	81
VI. Ketones							
2-Butanone	0.93	1.37	3.50	0.16	5.7	8.5	22
4-Methyl-2-pentanone	0.34	1.08	4.02	0.032	11	34	130
3-Pentanone	0.34	1.32	4.50	0.065	5.2	20	69
3-Heptanone	0.23	0.84	3.22	0.026	8.8	32	120

TABLE V (CONTINUED)

Solvent	Distribution Coefficient			Equilibrium Ratio of Water	Separation Factor		
	Ethanol	Acetone	Butanol		Ethanol	Acetone	Butanol
VII. Acids							
Oleic acid	0.15	0.27	1.61	0.010	15	27	160
VIII. Esters							
Methyl acetate	0.91	1.35	3.37	0.13	6.7	10	25
Ethyl acetate	0.70	1.44	4.62	0.046	15	31	100
Vinyl acetate	0.21	1.36	2.40	0.042	5.0	32	57
Butyl acetate	0.26	0.97	3.58	0.018	14	54	200
n-Propyl acetate	0.30	1.16	4.34	0.023	13	50	190
Ethyl formate	0.23	1.37	1.75	0.045	5.1	30	39
Ethyl butyrate	0.39	0.83	2.86	0.024	16	35	120
Ethyl propionate	2.53	1.12	3.48	0.023	110	49	150
n-Butyl phthalate	0.10	0.57	1.36	0.018	6.1	32	76
IX. Halogenated Hydrocarbons							
Dichloromethane	0.28	4.91	2.14	0.035	8.0	140	61
Tetrachloromethane	0.038	0.45	0.40	0.041	0.92	11	9.9
1,2-Dichloroethane	0.12	2.05	1.07	0.051	2.4	40	21
1,1,1-Trichloroethane	0.09	1.04	0.61	0.0052	18	200	120
Monofluorotrichloromethane	0.21	0.38	0.23	0.010	21	38	23

TABLE V (CONTINUED)

Solvent	Distribution Coefficient			Equilibrium Ratio of Water	Separation Factor		
	Ethanol	Acetone	Butanol		Ethanol	Acetone	Butanol
X. <u>Aromatic Chlorinated Hydrocarbons</u>							
1,2,4-Trichlorobenzene	0.06	0.54	0.46	0.005	12	110	92
XI. <u>Nitro Compounds</u>							
Nitrobenzene	0.092	1.05	0.93	0.016	5.8	22	58

TABLE VI

SOLVENT PHYSICAL PROPERTIES (13,36,42,43)

Solvent	Density g/ml 20-30°C	Viscosity 20-30°C	Boiling Point °C, 760 mmHg	Freezing Point °C	Surface Tension dy/cm 20-30°C
I. Saturated Aliphatic Hydrocarbons					
Heptane	0.683	0.39	98.4	-90.6	19.27
n-Dodecane	0.748	0.38^{150}	216.3	-9.5	24.51
Decane	0.726	0.85	174.1	-29.6	22.91
n-Tridecane	0.756	0.38^{170}	235.4	-5.5	25.20
Tetradecane	0.762	0.37	253.7	5.8	25.70
Hexadecane	0.773	0.37^{225}	287.0	18.1	26.70
Hexane	0.659	0.29	68.7	-95.3	17.40
Hexanes mix					
Cyclohexane	0.778	0.89	80.7	6.5	23.82
Cyclooctane	0.834		148.5	14.3	
Isopentane	0.614	0.21	27.8	-159.8	15.00
2-Methylpentane	0.648	0.30	60.2	-153.6	17.30
2,2,4-Trimethyl pentane	0.686	0.50	99.2	-107.3	18.85
II. Aromatic Hydrocarbons					
Benzene	0.878	0.60	80.1	5.5	27.49
Cumene	0.861	0.73	152.3	-96.0	27.17
Toluene	0.862	0.55	110.6	-94.9	27.32
o-xylene	0.875	0.75	144.4	-25.1	28.93

TABLE VI (CONTINUED)

Solvent	Density g/ml 20-30°C	Viscosity 20-30°C	Boiling Point °C, 760 mmHg	Freezing Point °C	Surface Tension dy/cm 20-30°C
m-xylene	0.859	0.58	139.1	-47.8	27.54
p-xylene	0.856	0.60	138.3	27.2	10.128
1,2,3,4-Tetrahydronaphthalene	0.966	2.00	207.5	-35.8	32.44[33]
III. Unsaturated Hydrocarbons					
1-Heptene	0.697	0.24	93.6	-119.0	18.55
IV. Aliphatic Alcohols					
1-Octanol	0.827	6.12	194.4	-14.9	25.21
1-Heptanol	0.821		176.0	-34.1	
1-Pentanol	0.807	3.34	138.0	-78.8	24.72
2-Ethyl-1-Hexanol	0.832		185.0	<-76	
V. Phenols					
Phenol	1.057	4.07[45]	181.7	40.9	37.77[50]
VI. Ketones					
2-Butanone	0.799	0.36	79.5	-87.3	23.97
4-Methyl-2-pentanone	0.796		115.6	-83.5	23.64
3-Pentanone	0.809	0.47	101.7	-39.5	24.73
3-Heptanone	0.818		147.0		

TABLE VI (CONTINUED)

Solvent	Density g/ml 20-30°C	Viscosity 20-30°C	Boiling Point °C, 760 mmHg	Freezing Point °C	Surface Tension dy/cm 20-30°C
VII. Acids					
Oleic acid	0.887	27.64	286.0	16.30	
VIII. Esters					
Methyl acetate	0.923	0.36	56.3	-98.0	24.76
Ethyl acetate	0.894	0.42	77.1	-83.9	22.55
Vinyl acetate	0.931		72.2	-93.2	
Butyl acetate	0.876	0.68	126.1	-73.5	24.60
n-Propyl acetate	0.883	0.55	101.5	-95.0	24.28
Ethyl formate	0.928	0.35	54.1	-79.4	22.38
Ethyl butyrate	0.878		120.0	-93.3	
Ethyl propionate	0.879	0.47	99.1	-73.8	23.16
n-Butyl phthalate	1.042	16.47	340.0	-35.0	
IX. Halogenated Hydrocarbons					
Dichloromethane	1.307	0.39	39.9	-96.7	25.54
Tetrachloromethane	1.594	0.96	76.7	-22.9	26.15
1,2-Dichloroethane	1.235	0.73	83.4	-35.8	30.84
1,1,1-Trichloroethane	1.349	1.10	73.9	-30.4	24.76
Monofluorotrichloromethane	1.494		23.7	-110.0	

TABLE VI (CONTINUED)

Solvent	Density g/ml 20-30°C	Viscosity 20-30°C	Boiling Point °C, 760 mmHg	Freezing Point °C	Surface Tension dy/cm 20-30°C
X. Aromatic Chlorinated Hydrocarbons					
1,2,4-Trichlorobenzene	1.454		213.5		
XI. Nitro Compounds					
Nitrobenzene	1.203	1.63	210.8	5.76	42.17

Viscosity and surface tension at 20-30°C except as noted by superscript.

TABLE VII

ADDITIONAL SOLVENT CHARACTERISTICS (2,10,13,27,43,44)

Solvent	ΔH vap. Kcal/mol 25°C	Toxicity	Flammability	Solubility in Water	Cost $
I. Saturated Aliphatic Hydrocarbons					
Heptane	8.735		F	0.005% W	1.18/gal
n-Dodecane	14.65				36.10/lb*
Decane	12.276		NF		34.80/lb*
n-Tridecane	15.84			i	145.28/lb*
Tetradecane	17.00				51.96/lb*
Hexadecane	12.30^{bp}				29.83/lb*
Hexane	7.54		F	0.0111% V	1.12/gal
Hexanes mix					
Cyclohexane	7.895	HS, HW	F	0.01% W	0.98/gal
Cyclooctane				i	32.60/lb*
Isopentane	5.878			0.0097% W	6.98/lb*
2-Methylpentane	7.138				80.93/lb*
2,2,4-Trimethyl pentane	8.396			0.0055% W	24.85/gal*
II. Aromatic Hydrocarbons					
Benzene	8.09	C, HS, HW, PTP	F	0.18% W	0.85/gal
Cumene	10.789	HW	F		0.14/lb
Toluene	9.08	HS, HW, PTP	F	0.6279/ℓ sol.	1.70/gal

TABLE VII (CONTINUED)

Solvent	ΔH vap. Kcal/mol 25°C	Toxicity	Flammability	Solubility in Water	Cost $
o-xylene	10.381	HS, HW	F		0.125/lb
m-xylene	10.195	HS, HW	F	0.196 g/ℓ sol.	0.36/lb
p-xylene	10.128	HS, HW	F	0.19 g/ℓ sol.	0.195/lb
1,2,3,4-Tetrahydronaphthalene	10.48^{bp}				5.44/lb*
III. Unsaturated Hydrocarbons					
1-Heptene	8.62				638.8/gal*
IV. Aliphatic Alcohols					
1-Octanol	17.43			0.0538% W	0.70/lb
1-Heptanol				δ	16.82/lb*
1-Pentanol	13.60		F	2.19% W	4.31/lb*
2-Ethyl-1-Hexanol				i	0.35/lb
V. Phenols					
Phenol		HS, HW, PTP, PB	NF	8.66% W	0.25/lb
VI. Ketones					
2-Butanone	7.693^{bp}	HW	F	26.3% W	0.36/lb
4-Methyl-2-pentanone	8.710^{bp}	HW	F	1.7% W	0.50/lb
3-Pentanone			F		8.11/lb*
3-Heptanone			NF		28.56/lb*

TABLE VII (CONTINUED)

Solvent	ΔH vap. Kcal/mol 25°C	Toxicity	Flammability	Solubility in Water	Cost $
VII. Acids					
Oleic acid				i	0.46/lb
VIII. Esters					
Methyl acetate	7.268^{bp}		F		6.18/lb*
Ethyl acetate	7.713^{bp}	HW	F	8.08% W	0.415/lb
Vinyl acetate		HS	F	i	0.39/lb
Butyl acetate	8.58^{bp}	HS	F		0.52/lb
n-Propyl acetate	8.20^{bp}			1.89 g/100 cc	0.535/lb
Ethyl formate	7.201^{bp}		F	10.5% W	13.06/lb*
Ethyl butyrate					1.35/lb
Ethyl propionate	8.178		F	2% W	10.73/lb*
n-Butyl phthalate	18.93^{bp}			< 0.01% W	0.54/lb
IX. Halogenated Hydrocarbons					
Dichloromethane	6.688^{bp}	C, HW, PTP, ORM-A	NF	1.32% W	0.35/lb
Tetrachloromethane	7.161^{bp}	C, HS, HW, PTP, ORM-A	NF	0.077 g/100 cc	0.26/lb
1,2-Dichloroethane	7.654^{bp}	HW, PTP	F	0.81% W	0.26/lb
1,1,1-Trichloroethane	7.692^{bp}	HW, PTP, ORM-A	NF		0.405/lb
Monofluorotrichloromethane					83.27/gal*

TABLE VII (CONTINUED)

Solvent	ΔH vap. Kcal/mol 25°C	Toxicity	Flammability	Solubility in Water	Cost $
X. Aromatic Chlorinated Hydrocarbons					
1,2,4-Trichlorobenzene		PTP	NF		0.615/lb
XI. Nitro Compounds					
Nitrobenzene	9.744^{bp}	HS, HW, PB, PTP	NF	0.206% W	0.33/lb

Cost data from reference 10 except as noted, * reference 2.

values are obtained from bulk cost data, other values are reported from small quantity chemical suppliers due to the lack of available bulk cost data.

Study II: Continuous Extraction

Based on the investigation of the experimental results of study I, the classes of solvents which demonstrated desirable characteristics for extraction of ethanol, butanol, and acetone from water are aliphatic alcohols, ketones, esters and halogenated hydrocarbons. For further evaluation, 2-ethyl-1-hexnol from aliphatic alcohols, 4-methyl-2-pentanone from ketones, butyl acetate from esters, and 1,1,1-trichloroethane from halogenated hydrocarbons class were selected for continuous extraction in a multistage York Scheibel column. As an example, the column performance data for 4-methyl-2-pentane at 42.18 and 70.38 ml/min for feed flow rate of 44 ml/min are shown in Figures 16 and 17. The concentrations of ethanol, butanol, and acetone in the extract phase are plotted as a function of the sampling time. The first 30 minutes of column operation showed unsteady state behavior, primarily, due to perturbations in the solvent and feed flows as a result of interface-level fluctuations between the two liquid phases. The concentrations of ethanol, acetone, and butanol in the extract phase exhibit a growth with time and eventually reach a plateau during the steady-state operation. No significant change in the extract concentration of solutes after 30 minutes of column operation could be detected. Therefore, solutes concentrations averaged over the last 30 minutes of extraction operation was used to investigate the effects of feed to solvent flow ratio on the solute recovery.

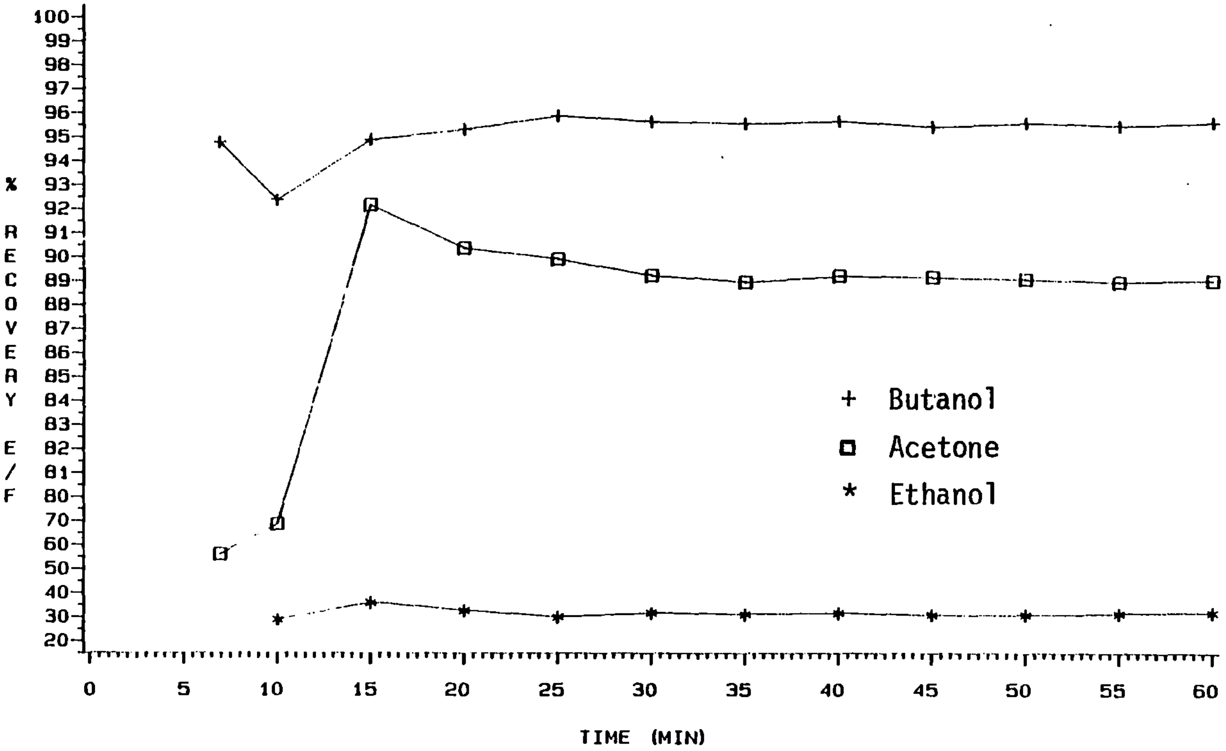


Figure 16. Experimental Column Performance of 4-methyl-2-pentanone for Feed to Solvent Ratio of 1

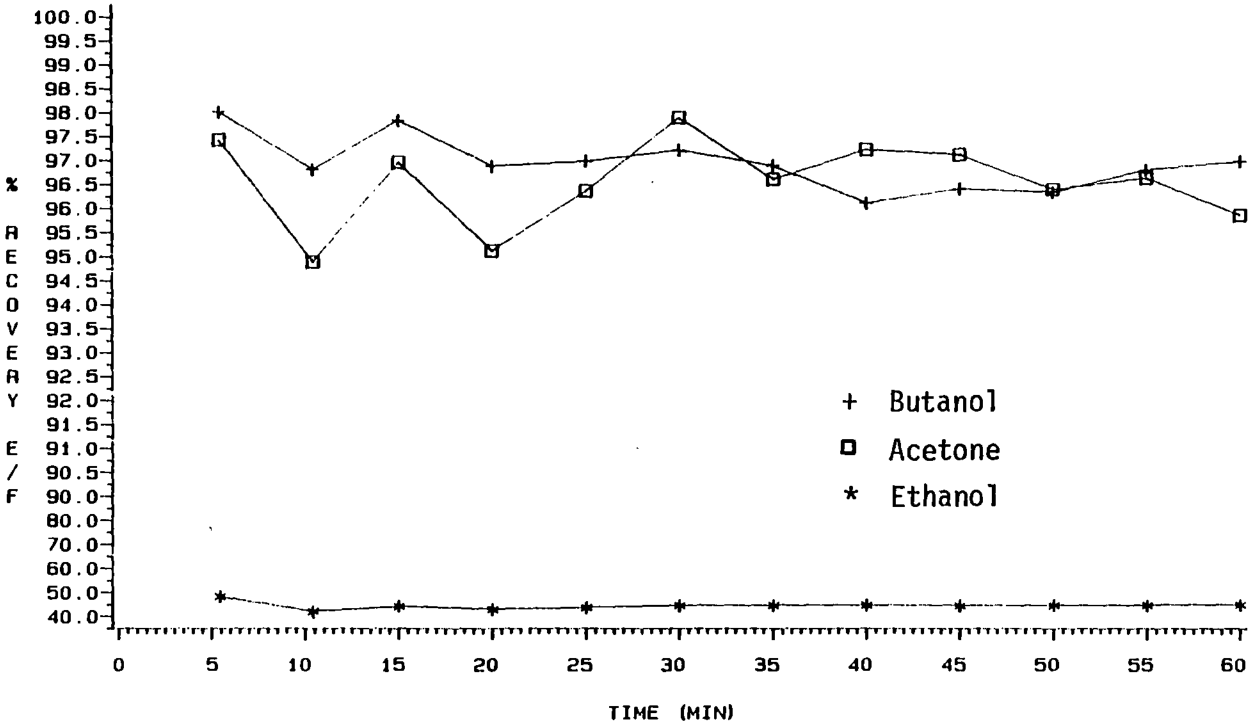


Figure 17. Experimental Column Performance of 4-methyl-2-pentanone for Feed to Solvent Ratio of 0.63

A study of the material balance around the column on ethanol, acetone, and butanol reveals the relationship between feed to solvent flow ratio and the amount of solute recovered in the extract phase. Feed, extract, and raffinate composition of solutes at different feed to solvent flow are presented in Tables VIII-XI. In general, lower values of feed to solvent flow ratio indicate a higher solute recovery in the extract phase. At low flow rates, the residence time in the extraction column increases, therefore, allowing more time for the intimate contacting of the two liquid phases. The column through-put in all these runs provided information about the flooding rates in the column. At near flooding, any slight change in the interface level caused the column to flood. On the basis of this data, the error in the column material balance varies from 0.5 to less than 5 percent. The major portion of this error is expected to have come from fluctuations in the feed and the solvent flow rates during the column operations as compared with the error involved in the analytical phase composition determination.

The experimental data for the recovery of ethanol, acetone, and butanol in the extract phase, as a function of feed to solvent ratio, are presented in Figures 18-20. The data are reported as the ratio of the concentration of the solute in the extract phase to the concentration of solute in the feed stream as a function of feed to solvent ratio. In all cases, the highest solute recovery is obtained at lowest feed to solvent ratio. The maximum ethanol recovery is obtained by 2-ethyl-1-hexanol with 66 percent, followed by 4-methyl-2-pentanone with 50 percent, butyl acetate with 44 percent, and least by trichloroethane with 10 percent for feed to solvent ratio of 0.5 (see

TABLE VIII

EXPERIMENTAL EXTRACTION PERFORMANCE OF 4-METHYL-2-PENTANONE AT 80°F

Solute	Solvent Flow, S ml/min	Feed Flow, F ml/min	F/S	% E/F	% R/F	% Loss
Ethanol	70.3	44.4	0.63	44.8	53.1	2.1
Acetone				96.8	2.8	0.4
Butanol				96.7	2.1	1.2
Ethanol	42.18	44.4	1.05	31.5	65.3	3.2
Acetone				89.1	8.9	2.0
Butanol				95.6	2.8	1.6
Ethanol	43.69	71.51	1.64	19.2	78.3	2.5
Acetone				70.4	26.9	2.7
Butanol				95.0	3.1	1.9
Ethanol	27.23	54.0	1.98	17.2	78.1	4.7
Acetone				61.1	36.7	2.2
Butanol				94.2	4.1	1.7

TABLE IX

EXPERIMENTAL EXTRACTION PERFORMANCE OF BUTYL ACETATE AT 80°F

Solute	Solvent Flow, S ml/min	Feed Flow, F ml/min	F/S	% E/F	% R/F	% Loss
Ethanol	75.4	40.4	0.54	43.0	54.7	2.3
Acetone				4.1	4.0	1.9
Butanol				93.5	4.1	2.4
Ethanol	40.2	10.4	1.01	22.8	74.5	2.7
Acetone				78.2	18.9	2.9
Butanol				92.1	7.2	0.7
Ethanol	44.9	7.5	1.57	16.2	80.9	2.9
Acetone				63.0	32.7	4.3
Butanol				90.0	8.7	1.3
Ethanol	28.2	57.8	2.05	9.1	86.1	4.8
Acetone				57.2	41.9	0.9
Butanol				85.3	12.9	1.8

TABLE X

EXPERIMENTAL EXTRACTION PERFORMANCE OF 2-ETHYL-1-HEXANOL AT 80°F

Solute	Solvent Flow, S ml/min	Feed Flow, F ml/min	F/S	% E/F	% R/F	% Loss
Ethanol	30.0	44.6	0.67	59.3	39.8	0.9
Acetone				81.8	17.6	0.6
Butanol				98.6	0.9	0.5
Ethanol	47.0	43.8	0.93	47.6	51.1	1.3
Acetone				63.6	33.4	3.0
Butanol				97.0	1.7	1.3
Ethanol	43.1	64.6	1.50	35.3	60.9	3.8
Acetone				51.3	45.5	3.2
Butanol				96.3	2.6	1.1
Ethanol	25.3	66.4	2.63	18.1	77.4	4.5
Acetone				45.4	53.0	1.6
Butanol				95.9	1.3	2.8

TABLE XI

EXPERIMENTAL EXTRACTION PERFORMANCE OF 1,1,1-TRICHLOROETHANE AT 80°F

Solute	Solvent Flow, S ml/min	Feed Flow, F ml/min	F/S	% E/F	% R/F	% Loss
Ethanol	59.0	33.4	0.57	9.6	85.7	4.7
Acetone				91.2	7.4	1.4
Butanol				96.1	2.3	1.6
Ethanol	43.6	41.0	0.94	8.1	87.6	4.3
Acetone				71.3	25.8	2.9
Butanol				85.0	12.7	2.3
Ethanol	41.0	64.6	1.57	6.0	89.2	4.8
Acetone				60.3	36.9	2.8
Butanol				81.7	15.8	2.5
Ethanol	40.3	83.3	2.07	4.5	90.5	5.0
Acetone				54.7	41.9	3.4
Butanol				78.8	17.2	4.0

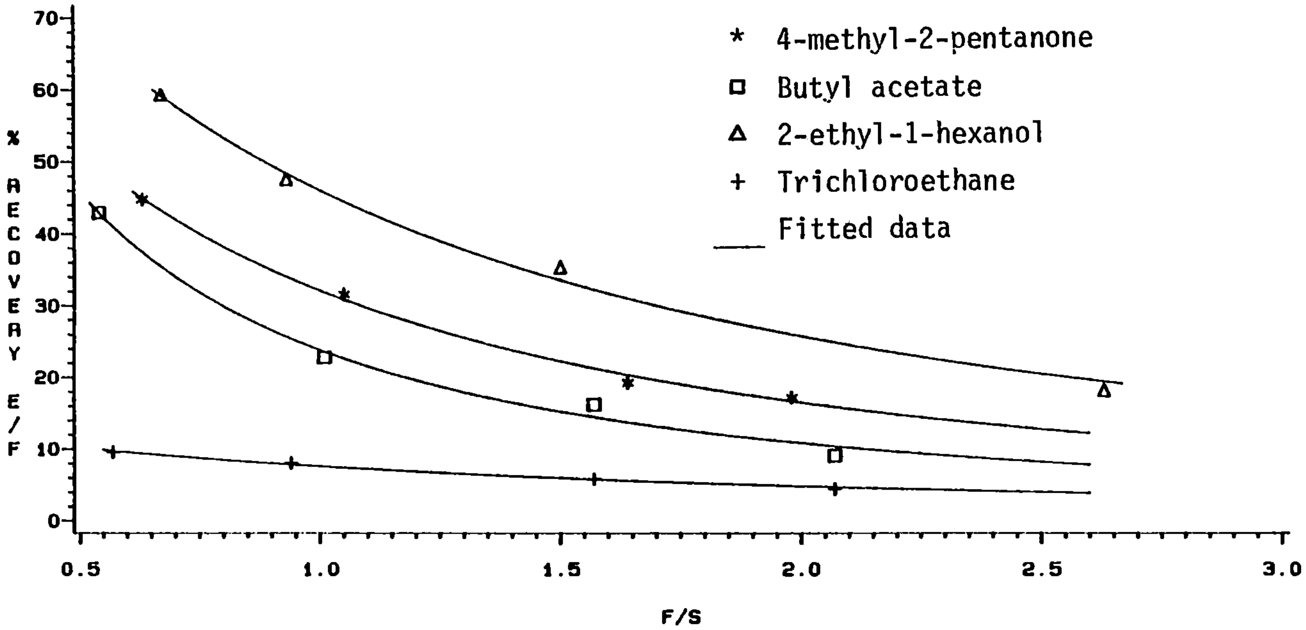


Figure 18. Experimental Investigation of the Effect of Feed to Solvent Ratio on Ethanol Recovery

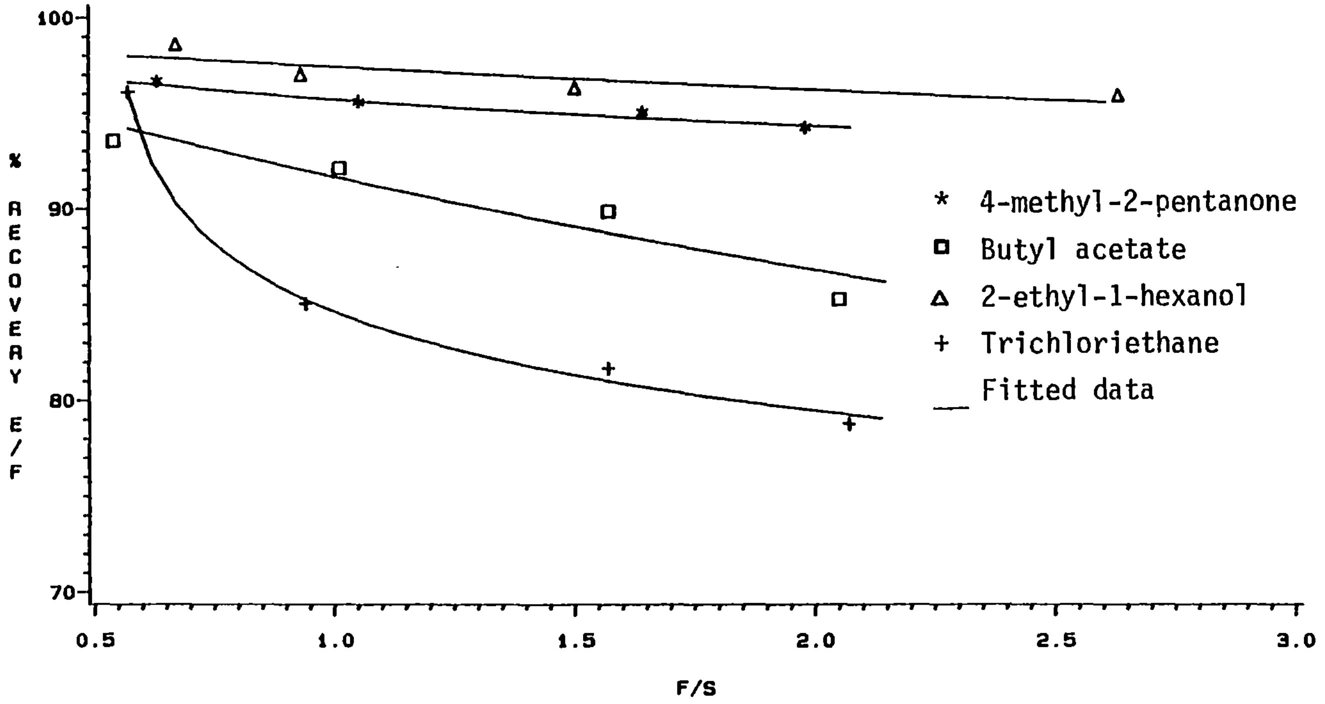


Figure 19. Experimental Investigation of the Effect of Feed to Solvent Ratio on Acetone Recovery

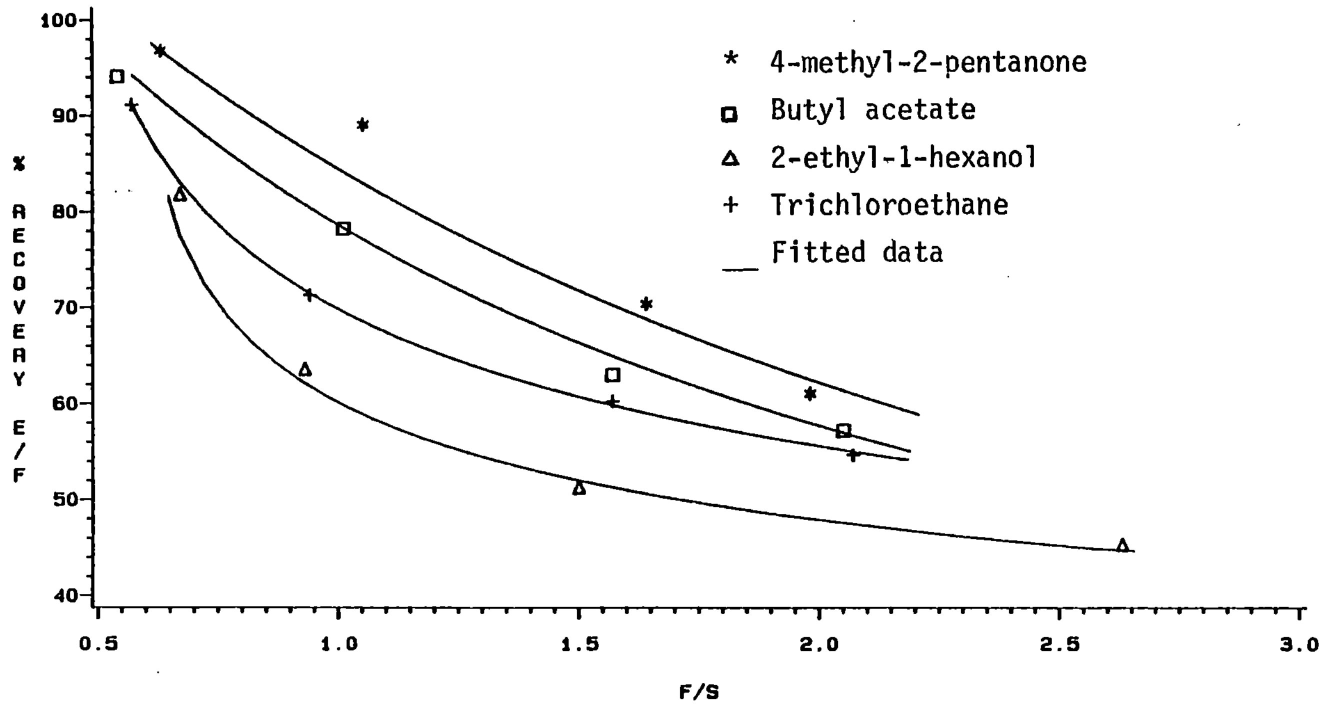


Figure 20. Experimental Investigation of the Effect of Feed to Solvent Ratio on Butanol Recovery

Figure 18). Trichloroethane shows a linear profile whereas the other three solvents exhibit a non-linear exponential decay. The solvent with the highest tendency for acetone is 4-methyl-2-pentanone with a linear relation as a function of feed to solvent ratio (see Figure 19). In general, since both acetone and 4-methyl-2-pentanone are from the ketone class of chemicals, it is expected that acetone would demonstrate a higher tendency to be extracted by 4-methyl-2-pentanone than any other of the three solvents. 2-ethyl-1-hexanol from the aliphatic alcohol class by far shows the least tendency toward acetone recovery. Butanol recovery, owing to the higher concentration of butanol in the feed, ranges from 93 percent for butyl acetate to 98 percent for 2-ethyl-1-hexanol (see Figure 20). Isomethyl butyl-ketone and 2-ethyl-1-hexanol show a linear relation, however, the behavior of butyl acetate and trichloroethane are highly non-linear decay as a function of feed to solvent ratio.

It is highly desirable to correlate the experimental extraction data of acetone, butanol, and ethanol to facilitate the design computations and to study the effect of variables change. The general behavior of Figures 18-20 exhibit a decay of solute recovery as a function of feed to solvent ratio described by a power law function of the form:

$$\left(\frac{E}{F}\right) = \Theta\left(\alpha + \left(\frac{F}{S}\right)\right)^{\gamma}$$

where,

$\frac{E}{F}$ = % solute recovery in the extract phase

$\frac{F}{S}$ = feed-to-solvent flow ratio

Exponential decay functions were also considered but the physical behavior of the data could not be properly described at the origin where the ordinate approaches a value of infinity. Second order Polynomials exhibit a decay followed by a rise leading to false conclusions and enormous computational error. A nonlinear least square curve fitting routine (MARQ) developed by Chandler and Jackson (8) for in-house use at Oklahoma State University was utilized to obtain the best fit to the data. Tables XII-XIV present the extraction correlation results for acetone, ethanol, and butanol respectively.

TABLE XII

ETHANOL RECOVERY CORRELATION COEFFICIENTS

Solvent	Θ	α	γ
1,1,1-trichloroethane	98.66	0.986	-1.638
2-ethyl-1-hexanol	37.13	0.364	-1.434
butyl acetate	166.53	1.25	-1.587
4-methyl-2-pentanone	33.73	1.764	-1.468

TABLE XIII

ACETONE RECOVERY CORRELATION COEFFICIENTS

Solvent	Θ	α	γ
1,1,1-trichloroethane	356.48	2.326	-1.181
2-ethyl-1-hexanol	139.18	1.104	-0.784
butyl acetate	51.51	-0.577	-0.194
4-methyl-2-pentanone	62.76	-0.353	-0.243

TABLE XIV

BUTANOL RECOVERY CORRELATION COEFFICIENTS

Solvent	θ	α	γ
1,1,1-trichloroethane	96.43	0.290	-0.0262
2-ethyl-1-hexanol	130.88	3.164	-0.251
butyl acetate	109.09	4.09	-0.0697
4-methyl-2-pentanone	81.21	-0.520	-0.0558

CHAPTER VI

DISCUSSION

The research and development effort of this study was primarily concentrated toward the development of an improved separation technique for economic recovery of acetone, butanol, and ethanol (ABE) from Clostridium fermentation broth. The economics of the current distillation technology for the ABE fermentation process indicates that the separation stage is overwhelmingly the largest consumer of energy. Although the current technology to convert a vast variety of hydrocarbon sources to ABE products via microbial fermentation is well developed and long established, it is not economically competitive with the conventional petrochemical routes from propylene. In view of the preceding comment, present and future research and development in ABE fermentation should be aimed in alternative separation schemes which reduce energy consumption during the separation stage.

The steam cost for distillation is the single largest utilities cost during the ABE purification process. This high steam requirement is due to the low concentration of ABE solutes in the fermentation broth. Another important design consideration of the ABE process is the limitation set by the extent of the fermentation productivity. The product yield and the fermentation efficiency is controlled by the microorganism's tolerance to solvents. Butanol toxicity disrupts the cell membrane, and therefore, stops metabolic activity. Present and future research in genetic engineering should focus on the development of an improved bacterial strain that can satisfactorily ferment five and six carbon sugars to ABE products while surviving a higher butanol concentration.

To develop an improved separation technique with substantial savings in the process energy requirements, the relative concentration of ABE in the product stream should be greatly increased. Alternatively, the most energy consuming species in the product stream may be replaced by a solvent with desirable characteristics for distillation separation. This suggests the application of a liquid-liquid extraction scheme, at appropriate stages of the product separation, for removal of water from the fermentation broth.

The successful design and operation of a liquid-liquid extraction process is governed by the selection of the most optimum solvent. The final evaluation of desirable solvents is the balance between solvent selectivity, capacity, and toxicity. The most appropriate solvent for a liquid-liquid separation process must satisfy the criteria outlined in Chapter III. Although data acquisition on liquid-liquid equilibria is an essential step for any extraction design, utilization of this experimental procedure alone for solvent evaluation can be prohibitively expensive, technically difficult, and time consuming. The application of the thermodynamics of liquid-liquid phase equilibria facilitates phase composition prediction and offers a means of highlighting possible solvent groups. However, the disadvantages of thermodynamic techniques stem from model considerations with several adjustable binary interaction parameters. The only reliable source for these parameters is accurate experimental measurements of activity coefficients. As a result, a reliable means for solvent classification with minimum experimental data is desirable.

For the classes of chemicals evaluated in this laboratory, the order of extractivity of solvents toward ethanol, acetone, and primarily butanol was aliphatic alcohols > ketones > esters > halogenated hydrocarbons > aromatic hydrocarbons > saturated aliphatic hydrocarbons. Saturated hydrocarbons, as a class, exhibit the least tendency for ABE extraction. Due to the poor solvent properties, aliphatic hydrocarbons tend to give the lowest values for separation factor and distribution coefficient. In general, as the number of carbon atoms in a straight chain increases the extraction tendency for ABE recovery decreases. Aromatic hydrocarbons show a marginal improvement over straight chain hydrocarbons. Ketones and esters have substantially higher values of distribution coefficients than aliphatic hydrocarbons but lower than aliphatic alcohols. Substitution of halogen groups on the straight chain hydrocarbons greatly improves the distribution coefficients for butanol, acetone, and ethanol. Of the 47 solvents tested only 15 have separation factors greater than 10 for all three solutes. Most of these come from the aliphatic alcohols, ketones, esters, and chlorinated hydrocarbons classifications. Of these 15, five have butanol separation factors greater than 150. This is particularly important since butanol is present in the highest concentration and has the highest value of any solute.

An examination of the physical extractive properties of the solvents of interest reveals several important features. The aliphatic alcohols are characterized by high boiling points, high viscosity, and substantially higher heats of vaporization than esters and ketones.

However, both esters and ketones have higher solubility in water than aliphatic alcohols. In addition, esters have the added disadvantage of less chemical stability and a smaller density difference with respect to water than aliphatic alcohols and ketones. The chlorinated hydrocarbons, owing to their good polar characteristics, exhibit a high affinity for ethanol, butanol, and acetone. This class of solvents have a relatively low heat of vaporization and solubility characteristics, but are much more toxic.

The classes of solvent which demonstrated desirable characteristics were aliphatic alcohols, ketones, esters, and halogenated hydrocarbon. Those solvents which deserved further evaluation were 2-ethyl-1-hexanol, butyl acetate, 4-methyl-2-pentanone, and 1,1,1-trichloroethane. Screening tests of these organic solvents, based on the results of study II of this research, showed that 2-ethyl-1-hexanol and 4-methyl-2-pentanone are the best candidates for the extraction of ABE products.

Further evaluation of these two solvents indicate that 2-ethyl-1-hexanol has a higher selectivity and distribution coefficient, hence, indicating a higher degree of recoverability from water and a better potential for extracting ABE products. The cost considerations between the price of 2-ethyl-1-hexanol and 4-methyl-2-pentanone is a significant factor affecting the overall process economics. The sales price for 4-methyl-2-pentanone is about 32 percent higher than the cost of 2-ethyl-1-hexanol in mid-1986 dollars. The second consideration factor in evaluation of these two solvents was their relative solubility in water. Experimental solubility determination indicates that 4-methyl-2-pentanone is 1.7 weight percent soluble in water compared with 2-ethyl-1-hexanol which has negligible solubility in water.

As a result, the optimum solvent with the most desirable extractive properties for extraction of ABE products was 2-ethyl-1-hexanol from the aliphatic alcohol class. An improved ABE separation process based on the 2-ethyl-1-hexanol is designed. Details of design, development, and economic evaluation of the improved ABE separation process are presented in the following chapter.

CHAPTER VII

PROCESS DESIGN AND DEVELOPMENT

Production of acetone, butanol, and ethanol (ABE) from carbohydrates sources via microbial fermentation is accomplished in four major steps: pretreatment, enzyme hydrolysis, fermentation, and purification. Feasible feedstocks for ABE fermentation include corn, blackstrap molasses, wood, wood waste, agricultural wastes, whey, and municipal solid wastes. The most appropriate substrates must be technically and economically viable; with low cost, readily available, and high potential for conversion to products.

In recent years, advances in enzyme technology, specifically production of improved bacterial strain via genetic manipulation, have improved enzyme hydrolysis as a viable route. The ABE fermentation process for wood cellulose to fermentable sugars includes acid prehydrolysis - pretreatment, enzyme hydrolysis, enzyme production, fermentation, and purification facilities. A brief description of these processing steps follows.

Prehydrolysis

During this stage green wood chips are ground to a desired particle size by a hammer mill and sent to a prehydrolysis plug flow reactor. Sulfuric acid at 0.5 weight percent is added. The reactor temperature is brought to 374 F by addition of heat while a pressure of 180 Psia is maintained to avoid any boiling. At these operating conditions all the hemicellulose and amorphous cellulose are converted to xylose and glucose. The contents of the reactor are then quenched to 212 F in a flash tank before the centrifugation step. About 99 percent of the solids are removed and sent to an enzyme hydrolysis facility. A portion of this solid stream is saved for enzyme growth. Virtually all the impurities, especially furfural and hydroxymethyl furfural are removed by subjecting the sugar stream to a series of carbon beds. The final sugar stream with a concentration of 5.2 weight percent is recovered for fermentation (11).

Enzyme Hydrolysis

The solid cellulose from the pretreatment step is mixed with the enzyme hydrolyzers and cellulase to 8 weight percent. The temperature is maintained constant at 122 F with a pH of 4.8 (11). Approximately, 95 mole percent of cellulose is converted to glucose during a 24 hour period. The solution is filtered and the unconverted cellulose is recovered. A small portion of this cellulose is used as a substrate for further enzyme growth while the rest is concentrated and burned as fuel. The glucose remaining in filtrate with a concentration of 5.4 weight percent is sent to fermentation.

The enzymes for the hydrolysis of cellulose are produced in a two stage continuous fermentation reactor. The temperature for enzyme production is kept at 86 F with pH at 4.8. An enzyme mixture of endoglucanase and -glucosidase is produced from a mutation of T. Reesei. The necessary nutrients, carbon and nitrogen sources, are provided by Ligna-cellulose and corn steep liquor, respectively. Oxygen requirements are provided by sparging air into the fermenters. Provisions must be made for the ventilation of carbon dioxide and nitrogen gases produced during the process. The content of the enzyme fermentation is centrifuged. A portion of the solids from the centrifuge step is recycled to the enzyme fermenters as an enzyme seed while the rest is recovered as a single cell protein by-product. The filtrate from the centrifuge is pumped to the enzyme hydrolyzers.

Fermentation

During this stage of the ABE production, the sugars from prehydrolysis are neutralized with calcium hydroxide and filtered to remove the calcium sulfate salt and other residual solids. This sugar stream is combined with the enzyme hydrolysis sugar and sent to batch fermenters for ABE production. The fermenter reactors are inoculated with *Clostridium acetobutylicum*. The media, ammonium sulfate, superphosphate, and calcium carbonate are feed to the fermenters while maintaining a temperature of 33 C by removing excess heat from the fermentation vessels. The pressure inside the fermenters is kept between 10 to 15 Psig. Carbon dioxide gas is produced during the ABE fermentation as a by-product of cell respiration in considerably large volumes. The evolved carbon dioxide is recovered, purified, and further processed to liquid carbon dioxide at 300 psig for sale or use in other sections of the plant.

Three major classes of chemicals are produced during the fermentation. These include:

a) Organic alcohols-acetone, butanol, and ethanol.

b) Organic acids-acetic, lactic, and butyric.

c) Gases- carbon dioxide and hydrogen.

In the early stages of the fermentation process organic acids and gases are the primary products. After a while, the organic acids, especially butyric acid, are consumed by the organisms and alcohol production starts, following a marked reduction in hydrogen production. The final fermentation products, ethanol, butanol, and acetone, are collected in a beer well prior to purification.

The conventional scheme for the purification of ABE products has been based on the application of distillation technology. Due to the low concentration of ABE products in the fermentation broth, high energy requirements for purification of these products has made the ABE process prohibitively expensive, hence, economically unattractive. The experimental research and development effort of this study has been devoted to the design of an improved purification technique with the aim of substantial savings energy requirements. A description of process design, plant layout, energy and material requirements, and economic evaluation of the improved process follows.

Purification

Improved Process Description.

The improved ABE process purification flow diagram is presented in Figure 21. In contrast to conventional methods, the stream from the fermentation broth is sent to an extraction column prior to distillation. The advantage of utilizing extraction in combination with distillation is to remove the water content of the fermentation broth, and therefore, improve the economics by reducing the size, steam cost, and overall process energy requirements.

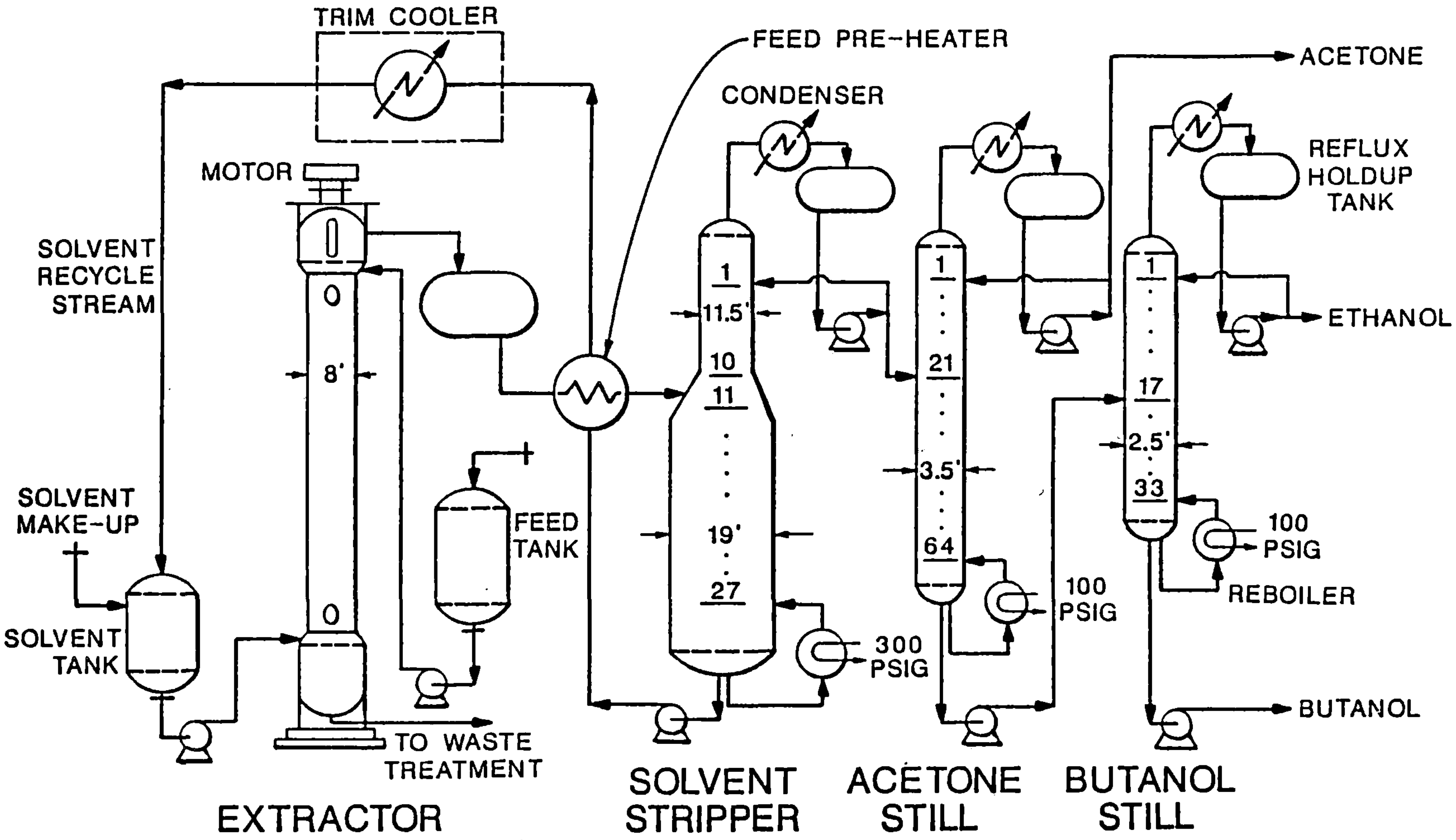


Figure 21. Schematic Process Flow Diagram of the Separation Stage of the Improved ABE Process

Fermentation broth containing 0.79 weight percent acetone, 0.23 weight percent ethanol, 1.63 weight percent butanol, and 97.35 weight percent water is pumped to a continuous Scheibel extraction column. The most desirable solvent was screened and selected based on the criteria presented in Chapter III. The potential solvent for ABE extraction was 2-ethyl-1-hexanol, an aliphatic alcohol, with excellent characteristics for removal of ethanol, butanol, and acetone from water. The solvent enters the column from the bottom section and moves up through the column where it is brought into intimate contact with the feed (fermentation broth) in a series of mixing and calming sections. The raffinate phase from the extraction unit contains 99.5 percent water and is sent to the waste treatment facility before discharging to a river. The extract phase, containing 98 percent solvent, is sent to a solvent stripper after being reheated to 360 F in a feed pre-heater by the stream leaving the bottom of the solvent stripper column. The solvent stream from the bottom of this still, with a 99.95 percent purity, is recycled to a solvent make-up reservoir for reuse. The overhead from the solvent stripper is cooled to 188 F in a water-cooled heat exchanger and is then fed to a distillation column where acetone with 99 percent purity is collected in the distillate. The bottom stream from this unit containing 93 percent butanol enters a butanol still. Operating temperature and pressure of 300 F and 20 Psig are maintained in the butanol distillation unit. The overhead from this still contains 99.8 percent ethanol and the bottom contains 99.6 percent butanol. The ABE product separation and solvent recovery for this process were designed and optimized by a proprietary simulation package to minimize the energy costs.

Process Design Variables. Preliminary design of distillation units for this process were based on the 10 degree approach procedure. Final changes in the design and operation of these stills were made using the Process Simulation Package. Column design parameters were set as follows: Cooling water supply at 85 F enters the water-cooled heat exchangers for a gain of 20 F in temperature. Using the 10 degree approach, a bubble point calculation at 95 F on distillate composition gives the condenser pressure. At this pressure, a dew point calculation on distillate composition yields the top tray temperature. For most distillation columns a 10 psi pressure drop through the column is reasonably acceptable. To obtain the bottom tray temperature, a bubble point calculation at the bottom tray pressure is performed. These parameters together with reflux ratio, feed plate location, and reboiler duty must be optimized to minimize the process equipment size and operation costs.

The solvent stripper column was optimized for 27 plates with feed entering at plate 11. The total height of this column was 72 ft allowing for a 4 ft open section at the top and a 10 ft open section at the bottom. Due to mechanical and stability considerations, the solvent stripper was optimized for 11.5 ft at the top and 19 ft at the bottom in diameter. The operating conditions were 240 F and 20 psig at the top section and 440 F at the bottom section of this unit. Valve trays in all distillation column were designed based on a 70 percent efficiency. Column trays spacing were set at 2 ft. The energy requirements for the solvent stripper column were provided by a 300 Psig steam reboiler. The acetone still was optimized for a 3.5 ft diameter column, 140 ft tall, and 64 plates. The feed to this unit entered plate

21 with design temperature and pressure optimized at 290 F and 20 Psig, respectively. The butanol still required 33 plates. This unit was 2.5 ft in diameter, and 78 ft tall with feed plate location of 17. Temperature and pressure were optimized for 300 F and 20 psig respectively. Energy for both acetone and butanol still units were provided by 100 Psig steam reboilers. The feed pre-heater was configured as a shell and tube heat exchanger with 7 shells in series based on the graphical method described by Bell (5). For this preliminary design, the major unit operation equipment is only designed and cost estimated. Hence, pumps and storage tanks are not included. The selected material of construction for all major equipment was carbon steel, except for extractors where the only available cost data was based on the stainless steel construction. Detailed material and energy balance computations are presented in Appendix B.

The extraction column was designed and scaled up based on the experimental data of this research study obtained on a 1 in continuous Scheibel column. Four Scheibel extractors were required with a design height of 24 ft and a diameter of 8 ft. The feed to solvent flow ratio was optimized at 0.93 for extraction of 97 percent of butanol in the feed. Detailed numerical computations for extraction design, scale up, analysis of pilot plant data, HETS calculations, internal parameters sizing, computation of number of theoretical stages, column diameter, and column agitation power requirements are presented in Appendix C.

Economic Evaluation of The Improved Purification Process. The economic evaluation of the ABE purification process was based on the production of 200 million lb/year n-butanol at a plant located on the U.S. Gulf Coast in mid-1986. Capital costs of major unit operations including heat exchangers, cooling towers, boilers, and distillation columns are based on Guthrie's method (14). The extractors cost was obtained by the method outlined by Wood (45). Manufacturing costs for solvent and coproducts are obtained from the chemical marketing reporter (10). Details of captial investment for the ABE purification plant are presented in Table XV. The total capital investment in mid-1986 is $8.94 million.

The annual operating cost is listed in Table XVI. The utilities investment includes cooling water cost, steam cost, waste treatment, electricity, and solvent make-up cost. The total annual operating cost in mid-1986 is $6.6 million. Steam cost for distillation deserves careful considerations. The key contributing item in the list of operating expenses, is the steam cost which accounts for more than 60 percent of the total annual utility cost and will have a definite affect on the economic and technical feasibility of the final process design evaluation. The waste treatment facility was designed for processing the raffinate stream from the extractors using air stripping towers flowing into a holding pond. A residence time of 48 hours was considered for complete biochemical oxidation of the all volatile components in the waste stream. As a result, the holding pond requirements were computed as a 1000 ft long, 420 ft wide, and 3 ft deep pool.

The revenue from the sales of butanol, ethanol, and acetone are shown in Table XVII. These prices are taken from Chemical Marketing reporter (10) based on the mid-1986 sales price. The major co-product credit contributor is butanol followed by acetone and finally ethanol. The total annual product sales in mid-1986 is about $89 million. The

TABLE XV

CAPITAL INVESTMENT FOR THE IMPROVED ABE PROCESS
(Basis: 200 MMlb BuOH/yr, 325 days/yr)

	Process Equipment	$
I.	Extractors	1,074,500
II.	Interchanger	1,468,000
III.	Cooling Towers	671,500
IV.	Boilers	2,956,000
V.	Column (distillation)	
	solvent stripper	1,460,000
	acetone product	1,029,000
	butanol product	281,000
	TOTAL (Mid-1986)	8,940,000

TABLE XVI

UTILITY COSTS FOR THE IMPROVED ABE PROCESS
(Basis: 200 MMlb BuOH/yr, 325 days/yr)

	Process Equipment	Cost $/yr
I.	Cooling water (8¢/1000 gal)	5,300
II.	100 psig steam ($2.5/1000 lb)	260,000
III.	300 psig steam ($3.5/1000 lb)	3,820,000
IV.	Waste treatment	1,200,000
V.	Electricity (5¢/kw-hr)	66,000
VI.	Solvent make-up (35¢/lb)	197,000
	TOTAL (mid-1986)	6,548,300

TABLE XVII

ANNUAL PRODUCT CREDITS FOR IMPROVED ABE PROCESS

	Chemical	$ MM
I.	Butanol (3¢/lb)	6.79
II.	Ethanol (26.3¢/lb)	3.37
III.	Acetone (27¢/lb)	1.77
	TOTAL REVENUE (Mid-1986)	88.97

comparative economics of the ABE extraction process, conventional ABE distillation technology, and petrochemical process follows.

Comparative Economics

Petrochemical Process

The conventional technology for n-butanol production, in the petrochemical industries, is based on the hydroformylation of propylene with hydrogen and carbon monoxide in the presence of a soluble rhodium catalyst. The carbonylation reactor is optimized for operation at 100 C and 20 ATM. The intermediate product of this reactor is a mixture of normal and iso-butyraldehyde which can be further hydrogenated to alcohols. The final products are separated by distillation and n-butanol is recovered with a purity of 99.9 weight percent (11). The extent of the hydrogenation process, in the carbonylation reactor, depends on the catalyst type and reactor operating conditions. The most commercially used catalysts for hydroformylation of propylene to n-butanol are cobalt carbonyl or rhodium carbonyl based-catalysts. These metal based-catalysts permit for a lower operating pressure while maintaining a relatively high yield of propylene conversion to n-butanol. The economic evaluation of a 200 million pound per year n-butanol plant based on the rhodium catalyst oxo process is presented by Marlatt and Datta (23). The capital investment costs are updated for mid-1986. The result is shown in Table XVIII. For propylene cost of 19 ¢/lb, the rational price of n-butanol is 27.50 ¢/lb.

TABLE XVIII

CAPITAL AND MANUFACTURING COSTS FOR RHODIUM CATALYST PROCESS (23)

(Basis: 200 MM lb BuOH/yr, 325 days/yr)

Installed Capital	$MM	
Inside battery limits	35.4	
Outside battery limits	23.9	
Start-up	0.2	
Working capital	9.1	
Total Capital Investment	68.6	
Raw Materials	Price	¢/lb BuOH
Propylene	17.25¢/lb	11.9
Synthesis Gas	0.3¢/SCF	3.7
Hydrogen	50¢/lb	1.5
Catalyst	$4.36/lb	0.3
Co-Products		
Isobutanol	25¢/lb	(2.0)
Fuel Gas	$4/MM Btu	(0.9)
Fuel	$4/MM Btu	(0.3)
Utilities		
150 psig Steam	$2.50/1000 lb	0.4
Electricity	5¢/kw-hr	0.5
Cooling Water	8¢/1000 gal	0.1
Total Variable Costs		15.20
Fixed Costs		
Operating Labor	22 operators at $40,000/yr	0.4
Maintenance	3% of OSBL, 2% of ISBL	0.7
Plant Overhead	0.6% of ISBL + OSBL	0.2
Taxes and Insurance	1.5% of ISBL + OSBL	0.5
Fixed Utilities	88¢/1000 lb of steam	0.2
Total Fixed Costs		2.0
Total Cash Costs	(Fixed + Variable)	17.20
Capital Charges	(30% of Total Capital)	10.30
Rational Price	(Cash Costs + Capital Charges)	27.50

Distillation Fermentation Process

The Schematic process flow diagram of the ABE process designed by Marlatt and Datta (23) is illustrated in Figure 22. The major plant sections are feed preparation, fermentation, cell and protein recovery, and control room units. The process was optimized based on the utilization of corn as a hydrocarbon source in multistage continuous fermentors. The fermentation broth with a concentration of 1.5 percent butanol, 0.6 percent acetone, and 0.2 percent ethanol by weight was subjected to a series of distillation columns where a split was made between acetone, ethanol, and butanol. Ethanol was recovered at the azeotropic concentration of 95 weight percent in water. Butanol and acetone were produced with purity of 99.6 and 99 weight percent respectively. Capital cost estimates and manufacturing costs for a 200 million pound per year n-butanol production plant using this process are shown in Tables XIX and XX. These cost estimates are adjusted to mid 1986 basis using the Chemical Engineering Plant Cost Index (9). Based on a corn price of $3 per bushel, co-product credits at current sales price, and for 18% discounted cash flow return on investment the price for n-butanol is 30.2 ¢/lb.

Economic Evaluation of the Improved ABE Process

The economic evaluation of the improved ABE process is provided in Table XXI. For comparisons, a similar approach with the same design specifications as Marlatt and Datta's (23) work was chosen. The total capital investment in mid-1986 is $93.7 million which indicates a 21 percent reduction compared with the distillation technology. The co-product and the utility costs are different from Datta's design. The

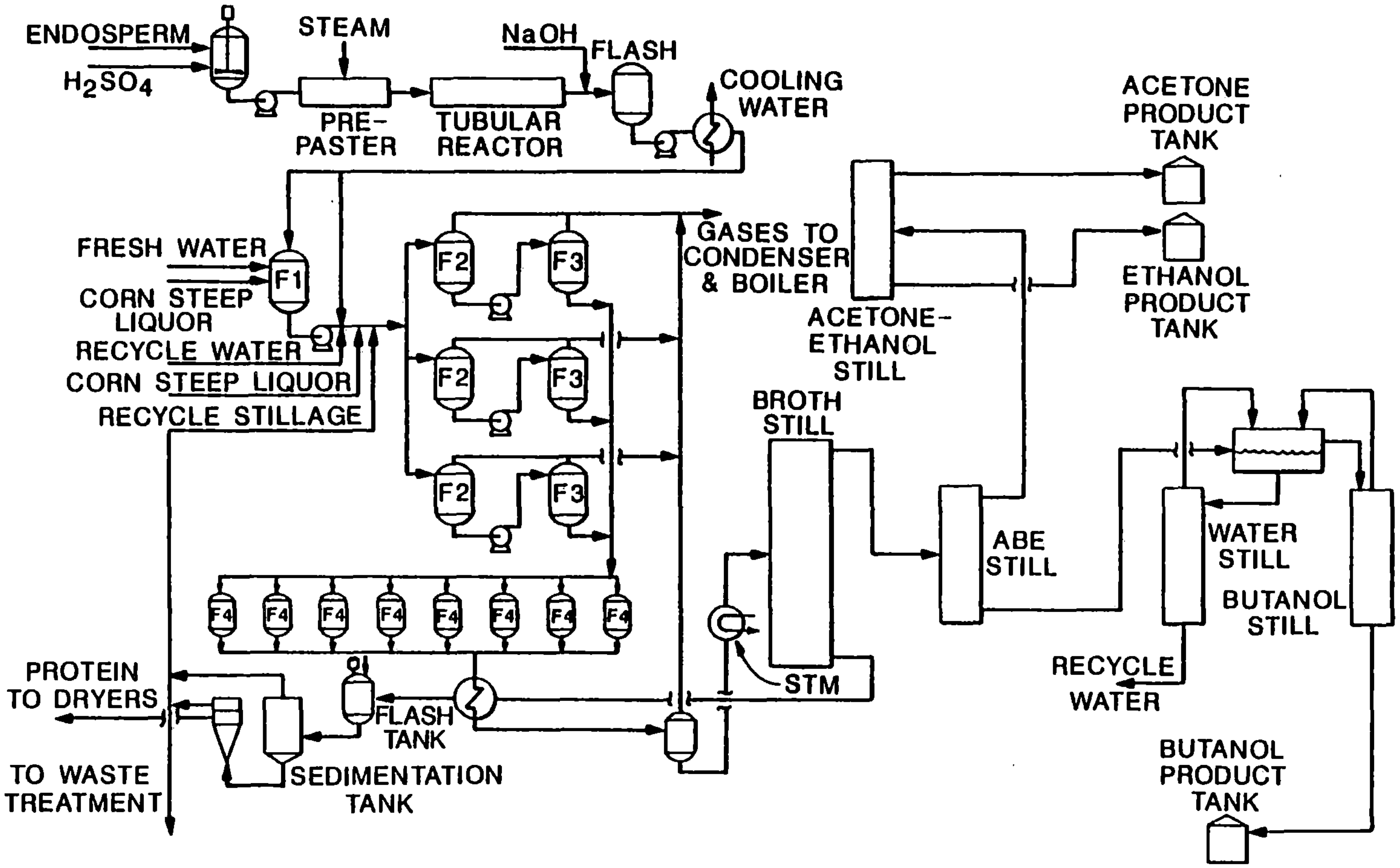


Figure 22. Schematic of the ABE Distillation-Fermentation Process (23)

TABLE XIX

CAPITAL INVESTMENT FOR ABE DISTILLATION PROCESS (23)
(Basis: 200 MM lb BuOH/yr, 325 days/yr)

I.	Inside Battery Limits	$ MM
	Feed preparation section	14.79
	Fermentaion Section	8.80
	Protein and Cell Recovery	9.36
	Distillation and Solvent Recovery	23.37
	Control Room	2.94
		59.26
II.	Outside Battery Limits	
	Land and site work	4.9
	Product storage tanks and warehouse	2.1
	Office and laboratory	1.5
	Cooling tower	0.3
	Railroad and locomotive	2.8
	Coal boiler	10.32
	Turbines	1.69
	Engineering and contractors fee	22.67
		46.28
III.	Start-up expense	2.52
IV.	Working capital	$ MM
	Corn and starch	1.68
	Finished fermentation and feed products	1.47
	Accounts receivable	5.55
	Cash	0.68
	Spare parts	1.26
		10.64
TOTAL INVESTMENT (Mid-1986)		118.70

TABLE XX

MANUFACTURING COSTS FOR ABE DISTILLATION PROCESS (23)
(Basis: 200 MM lb BuOH/yr, 325 days/yr)

Raw Materials	Basis	¢/lb BuOH
Corn	$3/bu	34.5
Cornsteep liquor	2.5¢/lb	2.6
Supplies		0.8
Co-Products		
Corn feed	3.4¢/lb	(2.0)
High protein meal	11¢/lb	(15.4)
Corn gem	7.9¢/lb	(5.8)
Acetone	23¢/lb	(9.2)
Ethanol	26.3/lb	(2.4)
Utilities		
150 psig Steam	$0.49/1000 lb	0.4
Electricity	5¢/kw-hr	1.7
Cooling Water	8¢/1000 gal	0.3
Process Water	$1.5/1000 gal	0.3
Waste Treatment	$98.4/1000 lb BOD	2.4
Total Variable Costs		8.2
Fixed Costs		
Labor	32 operators at $40,000/yr	0.6
Control Lab	7 scientists at $80,000/yr	0.3
Maintenance	3% of OSBL, 2% ISBL	1.3
Fixed Utilities	88¢/1000 lb of steam	0.5
Plant Overhead	18 people at $80,000/yr	0.7
Taxes and Insurance	1.5% of ISBL + OSBL	0.8
Total Fixed Costs		4.2
Total Cash Costs	(Fixed + Variable)	12.4
Capital Charges	(30% of Total Capital)	17.8
Rational Price	(Cash Costs + Capital Charges)	30.20

TABLE XXI

CAPITAL AND MANUFACTURING COSTS FOR THE IMPROVED ABE PROCESS
(Basis: 200 MM lb BuOH/yr, 325 days/yr)

		$ MM	
Inside Battery Limits		35.89	
Extraction-distillation products separation		8.94	
Outside Battery Limits		35.66	
Start up		2.52	
Working capital		10.64	
Total Capital Investment (Mid-1986)		93.65	
Raw Material	Basis		¢/lb Butanol
Corn	$3/bu		34.5
Cornsteep liquor	2.5¢/lb		2.6
Supplies			0.8
Co-Products			
Corn feed	3.4¢/lb		(2.0)
High protein meal	11¢/lb		(15.4)
Corn gem	7.9¢/lb		(5.8)
Acetone	(27¢/lb)		(8.85)
Ethanol	26.3¢/lb)		(1.69)
Utilities			
Steam (100 psig, $2.5/1000 lb; 300 psig $3.5/1000 lb)			2.04
Waste Treatment			0.6
Electricity (5¢/kw-hr)			1.7
Solvent make up (35¢/lb)			0.1
Process water ($1.5/1000 gal); cooling water			0.3
Total variable costs			8.90
Total fixed costs			3.70
Total cash costs			12.60
Capital charges (30% of total capital)			14.05
Rational Price			26.65

steam cost accounts for 43 percent of the total utility expenses and 8 percent of the n-butanol production cost. The rational price of n-butanol based on corn fermentation for 18 percent discounted cash flow return on investment is 26.7 ¢/lb. The cash costs and capital charges constitute for 47 percent and 53 percent of the total n-butanol production cost, respectively.

Comparison of the Three ABE Processes

The comparative economics of the ABE distillation, petrochemical, and the improved extraction process can be evaluated based on the relative significance of cash costs (fixed + variable), capital charges, and allocation of raw material cost. In the overall analysis, the ABE fermentation process has a lower cash cost but a higher capital charge compared with the advanced petrochemical process. This is primarily due to the significantly higher capital investment required by the fermentation scheme. The total capital investment of the ABE rhodium catalyst process is 42 percent lower than the ABE distillation-fermentation and 24 percent lower than the improved extraction-fermentation process.

The economic sensitivity of the ABE fermentation process to the allocation of raw material cost is of important note. Presently, propylene at 17.25 ¢/lb has a tremendous price advantage over the cost of corn at $3 per bushel. However, the ABE fermentation process is capable of utilizing considerably cheaper feedstocks such as: industrial paper pulp wastes, wood wastes, corncobs, and municipal solid wastes that could make the process economics more attractive. For utilization of these alternative feedstocks, the fermentation productivity, reactor stability, and product toxicity implications should be carefully investigated. Based on the process design and optimization results of this study, further technical improvements to significantly reduce the energy requirements of the ABE fermentation process is not foreseen.

The improved ABE process designed, developed, and evaluated in this study looks promising and certainly worth the investment. This scheme appears to be competitive with the petrochemical process and offers a considerable improvement over the ABE distillation process. Comparing the cost of production of n-butanol as an overall economic indicator, the improved process shows a 12 percent reduction over the distillation process. This cost reduction is essential to make the fermentation scheme economically competitive with the conventional petrochemical process. For completeness, the implementation of improved ABE fermentation technology should consider additional research to accurately evaluate the marketing potential of ABE products based on the current and future demands.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

In light of the experimental results and development efforts of this research study, the following conclusions can be drawn:

1. Saturated aliphatic hydrocarbons are poor extractants for acetone, butanol, and ethanol (ABE). This is primarily due to their non-polar characteristics. In general, as the number of carbon atoms in a straight chain increases the extraction tendency for ABE recovery decreases.

2. Aromatic hydrocarbons show a marginal improvement for ABE extraction compared with straight chain hydrocarbons.

3. Substitution of halogen groups on the straight chain hydrocarbon greatly improves the distribution coefficient for removal of ABE products.

4. Among the solvents tested in this study aliphatic alcohols demonstrated the best potential for extracting the ABE products. The order of extractivity was found to be aliphatic alcohols > ketones > esters > halogenated hydrocarbons > aromatic hydrocarbons > saturated aliphatic hydrocarbons.

5. The optimum solvent for extraction of ABE products was 2-ethyl-1-hexanol from the aliphatic alcohol class.

6. The solvent selection procedure for a liquid-liquid extraction system, as dictated by the technical and economical preferences, are based on solvent's characteristics such as: selectivity, distribution

coefficient, recoverability, density, interfacial tension, viscosity, immiscibility, toxicity, cost, and availability.

7. The separation stage of the current distillation technology of the ABE fermentation process is overwhelmingly the largest consumer of energy. A substantial reduction in energy consumption can be expected by substituting a solvent extraction scheme at appropriate stages of the product purification.

8. The economic evaluation of the improved ABE extractive fermentation process looks promising. This process is competitive with the petrochemical-rhodium catalyst process.

9. The steam cost of the improved ABE extractive fermentation accounts for 43 percent of the total utility expenses and 8 percent of the n-butanol production cost.

10. The improved ABE extractive-fermentation process indicates considerable improvement over the ABE distillation-fermentation where a 12 percent reduction in the total n-butanol production cost can be expected.

The following recommendations are made for future studies:

1. Utilization of lower cost raw material such as wood wastes, municipal solid wastes, and paper pulp wastes should be considered. The fermentation operation, stability, and productivity of these feedstocks should be carefully evaluated.

2. The application and utilization of alternative separation techniques such as adsorption, reverse osmosis, and membrane filtration may prove useful in reducing the energy requirements of the purification stage of the ABE fermentation process.

3. An algorithm to implement the UNIQUAC binary interaction parameters for use with the modified liquid-liquid equilibria program could facilitate the use and increase the utility and potential of this program. The UNIFAC, a group-contribution method, offers a means of estimating these parameters by predicting the liquid phase activity coefficient.

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APPENDIX A

FORTRAN SOURCE LISTING FOR THE MODIFIED LIQUID-LIQUID EQUILIBRIA PROGRAM

```
$JOB           ,NOLIST
C     ************************************************************
C     *                                                          *
C     *             LIQUID-LIQUID EQUILIBRIUM                    *
C     *                                                          *
C     *  PURPOSE:                                                *
C     *     THIS PROGRAM CALCULATES MULTICOMPONENT LIQUID-LIQUID *
C     *     EQUILIBRIA USING UNIQUAC MODEL.                      *
C     *                                                          *
C     *  REFERENCE:                                              *
C     *     PRAUSNITZ J., ECKERT C., O'CONNELL J.,               *
C     *     ANDERSON T., GRENS E., HSIEH R., " COMPUTER          *
C     *     CALCULATIONS FOR MULTICOMPONENT VAPOR-LIQUID AND     *
C     *     LIQUID-LIQUID EQUILIBRIA", PRENTICE-HALL, INC.,      *
C     *     ENGLEWOOD CLIFFS, NEW JERSEY (1980).                 *
C     *                                                          *
C     *  MODIFIED BY ALI MEMARAN DADGAR                          *
C     *                                                          *
C     *  OKLAHOMA STATE UNIVERSITY                               *
C     *  SCHOOL OF CHEMICAL ENGINEERING                          *
C     *                                                          *
C     *                 VERSION 3.0                              *
C     *                    1986                                  *
C     ************************************************************
C
      CHARACTER*10 NM
      CHARACTER*1 IANS,IY,INO
      REAL Z(20),X(20),Y(20),K(20)
      INTEGER ID(20),ER
      COMMON/PURE/NM(20),RU(20),QU(20),QP(20)
      COMMON/BINARY/U(20,20)
      DATA IY,INO/'Y','N'/
      LP=6
      IN=9
      SAO=0.0
 101  WRITE(LP,10)
 10   FORMAT(1H1,2X,' THE ABE SYSTEM COMPONENTS ARE:'//26X
     > ,'(1)   ACETONE'//26X
     > ,'(2)   ETHANOL'//26X
     > ,'(3)   BUTANOL'//26X
     > ,'(4)   WATER ' //)
      WRITE(LP,20)
 20   FORMAT(2X,'DO YOU WISH TO RUN THE ABE SYSTEM? (Y OR N)')
      READ(IN,30) IANS
 30   FORMAT(A1)
      IF(IANS.EQ.IY) THEN
        IR=4
        IE=5
      CALL PARIN(M)
      ELSE
C
C       SET IR TO IDENTIFY I FOR THE CARRIER COMPONENT
C
        IR=1
C
C       SET IE TO IDENTIFY I FOR THE SOLVENT COMPONENT
C
        IE=2
        CALL INPUT(M)
      ENDIF
 159  CONTINUE
 102  WRITE(LP,3)
 3    FORMAT(/1X,'ENTER SYSTEM TEMP(K)')
      READ(IN,*) T
      IF(SAO.EQ.3) GO TO 103
      DO 7 I=1,M
      ID(I)=I
 7    CONTINUE
      KEY=1
 200  DO 35 I=1,M
      WRITE(LP,40) I,NM(I)
 40   FORMAT(/1X,'ENTER FEED MOLE FRACTION FOR COMP(',I1,')',
```

```
     1 3X,A10)
      READ(IN,50) Z(I)
50    FORMAT(F6.4)
35    CONTINUE
      SZ=0.0
      DO 212 I=1,M
212   SZ=SZ+Z(I)
      IF(SZ.LT.0.999.OR.SZ.GT.1.000) GO TO 540
103   WRITE(LP,21)
      WRITE(10,21)
21    FORMAT(16X,'INPUT PARAMETERS'//)
      WRITE(LP,22)
      WRITE(10,22)
22    FORMAT(1X,'COMP(ID)',2X,'NAME',12X,'R',9X,'Q',6X,'QPRIM'/)
      DO 36 I=1,M
      WRITE(LP,25) I,NM(I),RU(I),QU(I),QP(I)
      WRITE(10,25) I,NM(I),RU(I),QU(I),QP(I)
25    FORMAT(4X,I1,5X,A10,3F10.4)
36    CONTINUE
      WRITE(LP,23)
      WRITE(10,23)
23    FORMAT(//)
      WRITE(LP,24)
      WRITE(10,24)
24    FORMAT(10X,'UNIQUAC INTERACTION PARAMETERS'///)
      WRITE(LP,29)
      WRITE(10,29)
29    FORMAT(5X,'I',5X,'J',13X,'A(I,J)',14X,'A(J,I)'/25X,'KELVIN',
     > 14X,'KELVIN')
      MM=M-1
      DO 27 I=1,MM
      II=I+1
      DO 27 J=II,M
      WRITE(LP,28) I,J,U(I,J),U(J,I)
      WRITE(10,28) I,J,U(I,J),U(J,I)
28    FORMAT(5X,I1,5X,I1,10X,F10.4,10X,F10.4)
27    CONTINUE
      WRITE(LP,11) M,T
      WRITE(10,11) M,T
11    FORMAT(///30H LIQUID/LIQUID EQUILIBRIUM FOR,I3,
     > 29H COMPONENT SYSTEM AT TEMP(K)=,F7.2/)
      WRITE(LP,12)
      WRITE(10,12)
12    FORMAT(/1X,'INDEX',5X,'COMPONENT',9X,'FEED',7X,'R PHASE',
     > 6X,'E PHASE',8X,'K')
      N=M
      CALL ELIPS(N,ID,KEY,IR,IE,Z,T,V,X,Y,K,IER)
      IF(IER.EQ.1) THEN
      WRITE(LP,*)'COMPONENT COMBINATION LACKING DATA'
      WRITE(10,*)'COMPONENT COMBINATION LACKING DATA'
      GO TO 550
      ENDIF
      IF(IER.EQ.2) THEN
      WRITE(LP,*)'NO CONVERGENCE ACHIEVED'
      WRITE(10,*)'NO CONVERGENCE ACHIEVED'
      GO TO 550
      ENDIF
      IF(IER.EQ.7) THEN
      WRITE(LP,*)'FEED IS TOO NEAR THE PLAIT POINT'
      WRITE(10,*)'FEED IS TOO NEAR THE PLAIT POINT'
      GO TO 550
      ENDIF
220   DO 229 I=1,M
      II=ID(I)
      WRITE(LP,14) II,NM(II),Z(I),X(I),Y(I),K(I)
      WRITE(10,14) II,NM(II),Z(I),X(I),Y(I),K(I)
14    FORMAT(/1X,I3,7X,A10,4X,1PE10.2,3X,1PE10.2,3X,1PE10.2,1X,1PE10.2)
229   CONTINUE
      WRITE(LP,15) V
      WRITE(10,15) V
15    FORMAT(//3X,'EXTRACT TO FEED RATIO   (E/F) = ',1PE9.2///)
      GO TO 550
```

```
 540  WRITE(LP,16)
 16   FORMAT(1X,'** SUM OF MOLE FRACTIONS IS NOT 1 **'/)
      GO TO 200
 550  WRITE(LP,551)
 551  FORMAT(///5X,'ENTER  1',10X,'NEW START'
     > //5X,'ENTER  2',10X,'NEW COMP. MOLE FRACT'
     > //5X,'ENTER  3',10X,'NEW SYSTEM TEMPERATURE'
     > //5X,'ENTER  4',10X,'QUIT THE SESSION'//)
      READ(IN,*) SAO
      IF(SAO.EQ.1.0) GO TO 101
      IF(SAO.EQ.2.0) GO TO 200
      IF(SAO.EQ.3) GO TO 102
 560  STOP
      END
C
      SUBROUTINE PARIN(M)
C
C READS PURE COMPONENT AND BINARY PARAMETERS INTO COMMON STORAGE
C BLOCKS /PURE/ AND /BINARY/ FOR A LIBRARY OF M(LE.20) COMP.
C
      INTEGER ID(20)
      CHARACTER*10 NM
      COMMON/PURE/NM(20),RU(20),QU(20),QP(20)
      COMMON/BINARY/U(20,20)
      LP=6
      IN=9
       WRITE(LP,*) 'RUNNING ABE SYSTEM EXTRACTION'
      WRITE(LP,*)'ENTER NUMBER OF COMPONENT  FOR M.LE.5 '
      READ(IN,*) M
C
C READ IN PURE COMP. PARAM.
C
      WRITE(LP,20)
 20   FORMAT(/1X,'ENTER SOLVENT NAME (MAX 10 CHARACTER)')
      READ(IN,21) NM(M)
 21   FORMAT(A10)
      WRITE(LP,5)
 5    FORMAT(1X,'ENTER UNIQUAC PRAM. R , Q , QPRIM  FOR SOLVENT'/)
      READ(IN,*) RU(M),QU(M),QP(M)
C
C INITIALLY ZERO UNIQUAC BINARY INTERACTION PARA.
C
 120  DO 121 I=1,M
      DO 121 J=1,M
 121  U(I,J)=0.0
C
C SET UNIQUAC BINARY PRAM. FOR COMPS.
C
      U(1,2)=404.49
      U(2,1)=-131.25
      U(1,3)=-123.83
      U(3,1)=445.88
      U(1,4)=336.17
      U(4,1)=-74.348
      U(2,3)=-302.23
      U(3,2)=-40.847
      U(2,4)=-185.30
      U(4,2)=-167.38
      U(4,3)=267.1
      U(3,4)=-9.1794
C
C READ IN UNIQUAC BINARY PARA.
C
      DO 125 I=1,M
      IF(I.EQ.M) GO TO 125
      WRITE(LP,15) I,M,M,I
 15   FORMAT(1X,'ENTER UNIQUAC BINARY PRAM. A ',I1,I1, ', A ',I1,I1,
     > 3X,'IN DEGREES KELVIN'/)
      READ(IN,*) U(I,M),U(M,I)
 125  CONTINUE
      RETURN
      END
```

```
C
      SUBROUTINE LILIK(N,ID,KEY,XR,XE,T,K,GAR,GAE,ERR)
C
      REAL XR(N),XE(N),K(N),GAR(N),GAE(N),X(20),Y(20),GX(20),GY(20)
      INTEGER ID(N),IDF(20),ERR,ERG
 100  ERR=0.0
C
C COVERT COMP. VECTORS TO DIMENSION 20 TO MATCH LOWER
C LEVEL SUB.
C
 101  DO 102 I=1,N
      X(I)=XR(I)
      Y(I)=XE(I)
 102  IDF(I)=ID(I)
C
C GET R AND E PHASE ACTIVITY COEFF.
C
      CALL GAMMA(N,IDF,KEY,X,T,GX,ERG)
      CALL GAMMA(N,IDF,3,Y,T,GY,ERG)
C
C CONVERT ACTIVITY COEFF. VECTORS TO DIM. N
C
 110  DO 119 I=1,N
      GAR(I)=GX(I)
      GAE(I)=GY(I)
      K(I)=GAR(I)/GAE(I)
      IF(K(I).LE.0.0.OR.K(I).GT.1.E+19) GO TO 900
 119  CONTINUE
      ERR=ERG
      RETURN
C
C FOR K VALUE OUT OF RANGE SET ERR TO 2
C
 900  ERR=2
      DO 905 I=1,N
 905  K(I)=0.0
      RETURN
      END
C
      SUBROUTINE GAMMA(N,ID,KEY,X,T,GAM,ERG)
C
C GAMMA CALC. LIQUID PHASE ACTIVITY COEFF. USING UNIQUAC.
C
      CHARACTER*10 NM
      REAL X(20),GAM(20),PT(20),PTS(20)
      INTEGER ID(20),ERG
      COMMON/PURE/NM(20),RU(20),QU(20),QP(20)
      COMMON/BINARY/U(20,20)
      COMMON/GS/IER,RL(20),TH(20),TP(20),GCL(20),TAU(20,20)
      DATA Z/10.0/
C
C SKIP SYSTEM INITILIZATION ON SUBSEQUENT CALC.
C
 100  GO TO (110,120,120,130,130,120,130,120,110,120),KEY
 110  ERG=0.0
C
C CALC. COMPOSITION INDEPENDENT TERMS
C
 111  DO 119 I=1,N
      II=ID(I)
 119  RL(I)=Z*(RU(II)-QU(II))/2.-RU(II)+1.0
C
C CALC. SEGMENT AND AREA FRACTIONS FOR COMPONENTS IN MIXTURE
C
 120  SP=1.E-30
      ST=1.E-30
      STP=1.E-30
      SS=0.0
      SL=0.0
 121  DO 125 I=1,N
      II=ID(I)
      TH(I)=X(I)*QU(II)
```

```
      TP(I)=X(I)*QP(II)
      SP=SP+X(I)*RU(II)
      ST=ST+TH(I)
      STP=STP+TP(I)
C
C SKIP FOR NONCONDENSABLE COMPONENTS
C
      IF(U(II,II).GT.1.E+19) GO TO 125
      SS=SS+X(I)
      SL=SL+X(I)*RL(I)
 125  CONTINUE
 126  DO 129 I=1,N
      II=ID(I)
      TH(I)=TH(I)/ST
      TP(I)=TP(I)/STP
      IF(U(II,II).GT.1.E+19) GO TO 128
C
C CALC. COMBINATINAL COMPUTATION TO EXCESS FREE ENERGY
C
 127  GCL(I)=RL(I)-RU(II)*SL/SP+ALOG(RU(II)*SS/SP)+Z*QU(II)*
     > ALOG(QU(II)*SP/(RU(II)*ST))/2.0
      GO TO 129
 128  GCL(I)=0.0
 129  CONTINUE
      IF(KEY.EQ.3) GO TO 140
C
C GET UNIQUAC BINARY INTERACTION PARA.
C
 130  CALL TAUS(N,ID,T,TAU,IER)
C
C CALC. RESIDUAL COTRIBUTION TO EXCESS FREE ENERGY
C
 140  DO 141 I=1,N
 141  PTS(I)=0.0
 142  DO 149 I=1,N
      PT(I)=1.E-30
      DO 143 J=1,N
 143  PT(I)=PT(I)+TP(J)*TAU(J,I)
      DO 145 J=1,N
 145  PTS(J)=PTS(J)+TP(I)*TAU(J,I)/PT(I)
 149  CONTINUE
 150  DO 159 I=1,N
      II=ID(I)
      IF(U(II,II).GT.1.E+19) GO TO 155
C
C RESIDUAL FREE ENERGY FOR CONDENSABLE COMPONENTS
C
      GRL=QP(II)*(1.0-ALOG(PT(I))-PTS(I))
      GO TO 158
 155  GRL=0.0
      DO 156 J=1,N
      JJ=ID(J)
C
C RESIDUAL FREE ENERGY FOR NONCONDENSABLE COMPONENTS
C
 156  GRL=GRL+TH(J)*(U(II,JJ)+U(JJ,II)/T)
C
C CALC. ACTIVITY COEFF.
C
 158  GAM(I)=EXP(GCL(I)+GRL)
 159  CONTINUE
      IF(IABS(IER).EQ.1) EGR=1
      RETURN
      END
C
      SUBROUTINE TAUS(N,ID,T,TAU,IER)
C
C TAUS CALC. TEMP. DEPENENT INTERACTION COEFF. TAU FOR
C USE IN SUB. GAMMA.
C
      REAL TAU(20,20)
      INTEGER ID(20)
```

```
      COMMON/BINARY/U(20,20)
 100  IER=0
 110  DO 119 I=1,N
      II=ID(I)
C
C CHECK IF ANY COMP. IS NONCONDENSABLE AND FLAG IER
C
      IF(U(II,II).GT.1.E+19) IER=ISIGN(IER**2-2,-1)
      DO 119 J=1,N
      IF(J.EQ.I) GO TO 115
      JJ=ID(J)
C
C CHECK IF BINARY PAIR ARE BOTH NONCONDENSABLES
C
      IF(U(II,II).GT.1.E+19.AND.U(JJ,JJ).GT.1.E+19) GO TO 115
C
C CHECK IF BINARY DATA ARE MISSING
C
      IF(ABS(U(II,JJ)).LT.1.E-19) GO TO 112
C
C CHECK IF EITHER COMPONENT IN BINARY PAIR IS A NONCONDENSABLE
      IF((U(II,II)+U(JJ,JJ)).GT.1.E+19) GO TO 115
C
C CALC. INTERACTION TERM
C
      TAU(I,J)=EXP(-U(II,JJ)/T)
      GO TO 119
 112  IER=ISIGN(1,IER)
C
C SET INTERACTION TERM EQUAL TO UNITY FOR PAIR WITH MISSING DATA
C
 115  TAU(I,J)=1.0
 119  CONTINUE
      RETURN
      END
C
      SUBROUTINE ELIPS(N,ID,KEY,IR,IE,Z,T,A,XR,XE,K,ERR)
C
C ELIPS CALC. XR AND XE
C
      REAL Z(N),XR(N),XE(N),K(N),GAR(20),GAE(20),K1(20),
     > KS,KP,K2,RX(20),EX(20)
      INTEGER ID(N),ERR,ERL
 100  ERR=0
      SS=0.0
      LP=6
      KEE=KEY
      IF(IR.EQ.0.OR.IE.EQ.0) GO TO 101
      GO TO (101,130,130,130,130,130,130,130,101,130),KEY
C
C FOR NEW SYSTEMS WITHOUT IR,IE SPECIFIED, FIND IR,IE AS LEAST
C SOLUBLE PAIR
C
 101  KS=1.0
      KP=1.0
 110  DO 115 I=1,N
      XR(I)=0.0
 115  XE(I)=0.0
      J1=1
      IF(IR.NE.0) GO TO 120
      IF(IE.NE.0) GO TO 121
 116  DO 119 J=2,N
      XR(J1)=0.0
      XE(J1)=0.0
      J1=J-1
      XR(J)=0.98
      XE(J)=0.02
      XR(J-1)=0.0
      XE(J-1)=0.0
      IF(Z(J).LT.0.10) GO TO 119
      DO 118 I=1,J1
      XE(I)=0.98
```

```
      XR(I)=0.02
      IF(I.GT.1) XE(I-1)=0.0
      IF(I.GT.1) XR(I-1)=0.0
      IF(Z(I).LT.0.10) GO TO 118
      CALL LILIK(N,ID,KEE,XR,XE,T,K,GAR,GAE,ERL)
      IF(ERL.GT.1) GO TO 900
      KEE=3
      IF(K(I).LE.KS) GO TO 117
      KS=K(I)
      IS=I
 117  IF(1.0/K(J).LE.KS) GO TO 118
      KS=1.0/K(J)
      IS=J
 118  CONTINUE
 119  CONTINUE
      XR(N)=0.0
      XE(N)=0.0
      XR(J1)=0.0
      XE(J1)=0.0
      GO TO 125
 120  IF(IE.NE.0) GO TO 130
      IS=IR
      GO TO 125
 121  IS=IE
 125  XE(IS)=0.98
      XR(IS)=0.02
 126  DO 129 J=1,N
      IF(J.EQ.IS) GO TO 129
      XR(J)=0.98
      XE(J)=0.02
      IF(J.EQ.(IS+1)) GO TO 128
      IF(J.GT.1) XR(J-1)=0.0
      IF(J.GT.1) XE(J-1)=0.0
 127  IF(Z(J).LT.0.10) GO TO 129
      CALL LILIK(N,ID,KEE,XR,XE,T,K,GAR,GAE,ERL)
      IF(ERL.GT.1) GO TO 900
      KEE=3
      IF(K(J).GE.KP) GO TO 129
      KP=K(J)
      IP=J
      GO TO 129
 128  IF(J.GT.2) XR(J-2)=0.0
      IF(J.GT.2) XE(J-2)=0.0
      GO TO 127
 129  CONTINUE
      IE=IP
      IF(IR.NE.IS) IE=IS
      IF(IR.NE.IS) IR=IP
C
C INITILIZE R AND E PHASE COMPOSITIONS
C
 130  DO 131 I=1,N
      XR(I)=0.0
 131  XE(I)=0.0
      XR(IR)=0.98
      XE(IR)=0.02
      XR(IE)=0.02
      XE(IE)=0.98
C
C GET INITIAL ESTIMATES FOR K VALUES
C
 135  CALL LILIK(N,ID,KEE,XR,XE,T,K,GAR,GAE,ERL)
      IF(ERL.GT.1) GO TO 900
      SZ=0.0
 136  DO 137 I=1,N
      SZ=SZ+Z(I)
 137  K1(I)=K(I)-1.0
      IF(ABS(SZ-1.0).GT.0.01) GO TO 903
C
C GET INITIAL ESTIMATE FOR A
C
      A=Z(IE)/(Z(IE)+Z(IR))
```

```
      A=-A/K1(IR)+(A-1.0)/K1(IE)
      IF(A.LT.0.0) A=0.0
      IF(A.GT.1.0) A=1.0
      A0=A
      IT=0
      KAC=0
C
C CONDUCT ITERATION OVER PHASE COMP.
C
 200  IT=IT+1
      IF(IT.GT.50) GO TO 900
      AA=A0
      A0=A
C
C CONDUCT NEWTON-RAPHSON ITERATION FOR A AT FIXED K VALUES
C
 300  DO 319 M=1,10
      F=0.0
      DF=0.0
 301  DO 309 I=1,N
      K2=A*K1(I)+1.0
      F=F+Z(I)*K1(I)/K2
 309  DF=DF-Z(I)*(K1(I)/K2)**2
      IF(ABS(F).LT.1.E-5) GO TO 210
      DA=F/DF
 310  AN=A-DA
C
C LIMIT A TO RANGE 0-1 IF IT FALLS OUTSIDE POLES OF F
C
      IF(AN.LT.-1./K1(IR)) GO TO 312
      AN=A+(1.0/K1(IR)+A)/2.0
      GO TO 319
 312  IF(AN.GT.-1.0/K1(IE)) GO TO 319
      AN=A+(1.0/K1(IE)+A)/2.0
 319  A=AN
      GO TO 900
 210  A=AN
      SR=0.0
      SE=0.0
C
C FIND NEW R AND E PHASE COMPOSITIONS
C
 211  DO 215 I=1,N
      XR(I)=Z(I)/(A*K1(I)+1.0)
      XE(I)=K(I)*XR(I)
      SR=SR+XR(I)
 215  SE=SE+XE(I)
 220  DO 225 I=1,N
      XR(I)=XR(I)/SR
 225  XE(I)=XE(I)/SE
C
C AT ALTERNATE ITERATIONS AFTER 3 ACCELERATE PHASE COMPOSITIONS BY
C WEGSTEIN METHOD BASED ON SUM OF DEVIATIONS OF COMPONENT FUGACITIES
C
 230  IF(IT.LT.3) GO TO 250
      IF(IT.LE.5.AND.(A.LT.0.0.OR.A.GT.1.0)) GO TO 250
      IF(KAC.GE.1) GO TO 239
      IF(SS.GT.SL) GO TO 250
      IF(SS.GT.0.2) GO TO 250
      KAC=1
      WG=SS/(SL-SS)
      WK=1.0+WG
      SR=0.0
      SE=0.0
      DO 235 I=1,N
      XR(I)=WK*XR(I)-WG*RX(I)
C
C ALLOW NO NEGATIVE MOL FRACTION
C
      IF(XR(I).LT.0.0) XR(I)=0.0
      XE(I)=WK*XE(I)-WG*EX(I)
      IF(XE(I).LT.0.0) XE(I)=0.0
```

```
      SR=SR+XR(I)
  235 SE=SE+XE(I)
C
C NORMALIZE ACCELERATED COMP. TO ALLOW FOR XR(I) OR XE(I)
C SET TO ZERO
C
  236 DO 237 I=1,N
      XR(I)=XR(I)/SR
  237 XE(I)=XE(I)/SE
      GO TO 250
  239 KAC=0
C
C GET NEW K AND GAMMA VALLUES
C
  250 CALL LILIK(N,ID,3,XR,XE,T,K,GAR,GAE,ERL)
      IF(ERL.GT.1) GO TO 900
      ESS=1.E-03
      IF(IT.LE.5) GO TO 252
C
C CHECK FOR VICINITY OF A PLAIT POINT
C
      PPI=K(IR)/K(IE)+K(IE)/K(IR)
      IF(PPI.GT.10.0.OR.SS.GT.0.05) GO TO 251
C
C EXIT IF TOO NEAR PLAIT POINT
C
      IF(IT.GE.20) GO TO 290
      IF(PPI.GT.7.0) GO TO 251
C
C CHECK IF CALC. NEAR PLAIT POINT IS PROBABLY IN SINGLE
C PHASE REGION--IF SO CONTINUE
C
      DE=AO
      IF(DE.GT.0.5) DE=AO-1.0
      DI=(AA-A)/DE
      IF(DI.LT.0.1) GO TO 290
  251 IF(PPI.LT.20) ESS=2.E-4
  252 SL=SS
      SS=0.0
  253 DO 255 I=1,N
      K1(I)=K(I)-1.0
C
C CALC. OBJECTIVE FUNCTION
C
  255 SS=SS+ABS(GAE(I)*XE(I)-GAR(I)*XR(I))
C
C CHECK CONVERGENCE
C
      IF(SS.LE.ESS) GO TO 190
      IF(A.GT.0.0.AND.A.LE.1.0) GO TO 260
      IF(IT.LE.3.OR.SS.GT.0.20) GO TO 260
      IF(IT.LE.5.AND.SS.GT.0.05) GO TO 260
C
C CHECK IF A MOVING AWAY FROM 0-1 REGION
C
      IF((ABS(A)-ABS(AO)).GT.0.0) GO TO 195
C
C SAVE LAST PHASE COMPOSITIONS FOR USE IN ACCELERATION
C
  260 DO 265 I=1,N
      RX(I)=XR(I)
  265 EX(I)=XE(I)
      GO TO 200
C
C FEED IN VICINITY OF PLAIT POINT--CHECK IF IN TWO PHASE REGION
C
  290 IF(A.GE.0.0.AND.A.LE.1.0) GO TO 905
      GO TO 195
C
C DO NOT ALLOW CONVERGENCE ON ACCELERATED ITERATION
C
  190 IF(KAC.EQ.1) GO TO 260
```

```
C
C CONVERGED SOLUTION--CHECK IF IN TWO PHASE REGION
C
 191  IF(A.LT.0.0.OR.A.GT.1.0) GO TO 195
      ERR=ERL
      RETURN
C
C FEED OUTSIDE TWO PHASE REGION
C
 195  DO 196 I=1,N
      XR(I)=Z(I)
 196  XE(I)=Z(I)
      IF(A.LT.0.0) A=0.0
      IF(A.GT.1.0) A=1.0
      ERR=ERL
      RETURN
C
C ON FAILURE TO CONVERGE SET A TO -1 AND ERR TO 2
C
 900  ERR=2
      GO TO 910
C
C FOR BAD INPUT DATA SET A TO -1 AND ERR TO 5
C
 903  ERR=5
      GO TO 910
C
C FOR FEED TOO NEAR PLAIT POINT SET A TO -1 AND ERR TO 7
C
 905  ERR=7
 910  DO 911 I=1,N
      XR(I)=Z(I)
 911  XE(I)=Z(I)
      A=-1.0
      RETURN
      END
C
C BLOCK DATA SUBROUTINE
C
      BLOCK DATA
      CHARACTER*10 NM
      COMMON/PURE/NM(20).RU(20).QU(20),QP(20)
      COMMON/BINARY/U(20,20)
      DATA NM/'ACETONE','ETHANOL','BUTANOL'.'WATER'.16*' '/
      DATA RU/2.5735.2.1055,3.4543.0.92,16*0.0/
      DATA QU/2.336.1.972,3.052.1.4.16*0.0/
      DATA QP/2.34,0.92,0.88,1.00.16*0.0/
      END
C
      SUBROUTINE INPUT(M)
C
C READS PURE COMPONENT AND BINARY PARAMETERS INTO COMMON STORAGE
C BLOCKS /PURE/ AND /BINARY/ FOR A LIBRARY OF M(LE.20) COMP.
C
      INTEGER ID(20)
      CHARACTER*10 NM
      COMMON/PURE/NM(20),RU(20).QU(20).QP(20)
      COMMON/BINARY/U(20,20)
      LP=6
      IN=9
      WRITE(LP,*) ' '
      WRITE(LP,*) 'ENTER NO OF COMPONENTS (MAX 20)'
      READ(IN,*) M
C
      DO 5 I=1,M
      IF(I.EQ.1) THEN
      WRITE(LP,*) ' '
         WRITE(LP,*) 'ENTER THE CARRIER NAME (MAX 10 CHARACTER)'
      GOTO 5
      ENDIF
      IF(I.EQ.2) THEN
      WRITE(LP,*) ' '
```

```
         WRITE(LP,*) 'ENTER THE SOLVENT NAME '
      GOTO 5
      ENDIF
      WRITE(LP,7) I
 7    FORMAT(/1X,'ENTER NAME FOR COMP(',I1,')')
 5    READ(IN,6) NM(I)
 6    FORMAT(A10)
C
      DO 10 I=1,M
      WRITE(LP,20) I,NM(I)
 20   FORMAT(/1X,'ENTER UNIQUAC PARAM. R, Q, QP FOR COMP (',I1,
     1 ')   ',A10)
      READ(IN,*) RU(I),QU(I),QP(I)
 10   CONTINUE
C
C INITIALLY ZERO UNIQUAC BINARY INTERACTION PARA.
C
 120  DO 121 I=1,M
      DO 121 J=1,M
 121  U(I,J)=0.0
C
C READ IN UNIQUAC BINARY PARA.
C
      DO 125 I=1,M
      K=I+1
      IF(K.GT.M) GO TO 126
      DO 125 J=K,M
      WRITE(LP,15) I,J,J,I
 15   FORMAT(/1X,'ENTER UNIQUAC BINARY PRAM. A ',I1,I1, ', A ',I1,
     > I1,3X,'IN DEGREES KELVIN')
      READ(IN,*) U(I,J),U(J,I)
 125  CONTINUE
 126  CONTINUE
      RETURN
      END
$ENTRY
$IBSYS
//
```

APPENDIX B

ENERGY AND MATERIAL BALANCES FOR THE IMPROVED ABE PROCESS

The schematic of the improved purification process is presented in Figure 23. The process flow streams are numbered for identification and use with Table XXII. The process material balance and the corresponding stream temperature and pressure are shown in Table XXII. The process energy requirements including the reboiler and condenser heat duties, the column temperature, pressure, liquid, and vapor tray profiles are presented in Tables XXIII-XXV for the solvent stripper column, acetone still, and butanol still, respectively.

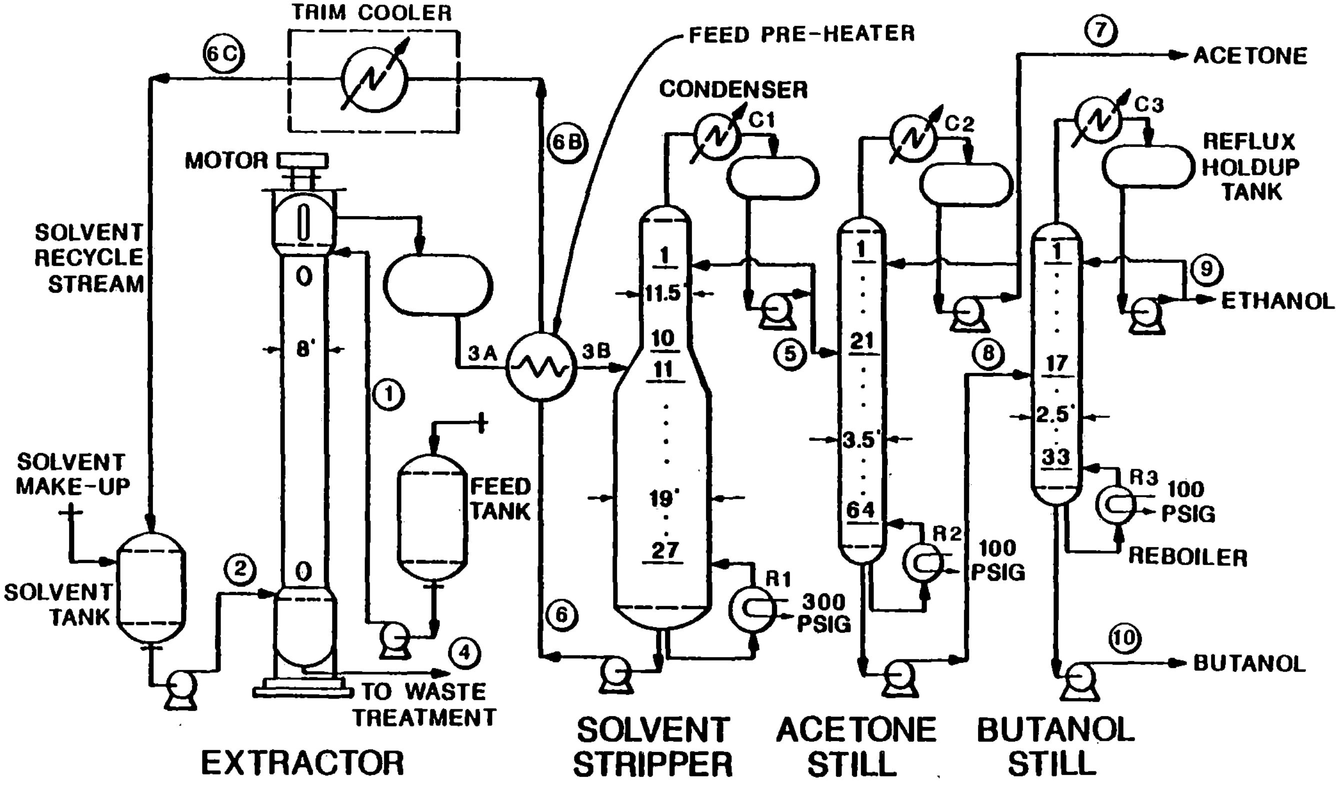

Figure 23. Schematic Flow Diagram with Stream Identification for use with Material and Energy Balances

TABLE XXII

STREAM WEIGHT COMPOSITIONS

STREAM ID NAME	1	2	4	5	7	8	9	10
Acetone	7.9E-3	--	2.91E-3	2.35E-1	9.90E-1	2.62E-6	4.34E-5	7.32E-9
Ethanol	2.3E-3	--	1.22E-3	5.10E-2	1.00E-2	6.39E-2	9.99E-1	3.99E-3
Butanol	1.63E-2	--	4.99E-4	7.13E-1	4.87E-12	9.36E-1	7.69E-5	9.95E-1
2-Ethyl-1-hexanol	--	1.00	3.96E-5	2.00E-4	2.00E-30	2.62E-1	1.61E-17	2.79E-4
Water	9.73E-1	--	9.95E-1	--	--	--	--	--
Totals (lbs/hr)	1671256	1798380	1634620	35920.6	8526.3	27394.4	1646.6	25747.7
Temperature (°F)	77	77	77	188	137	258	173	271
Pressure (psia)	14.7	14.7	24.7	14.7	14.7	24.7	14.7	24.7

TABLE XXII (CONTINUED)

STREAM ID NAME	3A	3B	6B	6C
Acetone	4.6E-3	4.6E-3	1.71E-9	1.71E-9
Ethanol	1.0E-3	1.0E-3	1.95E-10	1.95E-10
Butanol	1.44E-2	1.44E-2	4.37E-4	4.37E-4
2-Ethyl-1-hexanol	9.8E-1	9.8E-1	9.99E-1	9.99E-1
Totals (lbs/hr)	1835016	1835016	1799094	1799094
Temperature (°F)	77	360	123	105
Pressure (psia)	40.0	35.0	24.7	14.7

TABLE XXIII

SOLVENT STRIPPER COLUMN PROFILES

Tray	Temperature °F	Pressure Psia	Net Flow Rate Liquid lb-mols/hr	Net Flow Rate Vapor lb-mols/hr	Heater/Cooler Duties MM Btu/hr
1	188.2	14.7	3280		-68.92
2	227.8	15.26	3257	3811	
3	242.0	15.81	3281	3788	
4	248.8	16.37	3204	3812	
5	264.6	16.92	2920	3735	
6	306.5	17.48	2733	3451	
7	347.6	18.03	2886	3264	
8	364.3	18.59	17582	3417	
9	369.4	19.14	17904	3763	
10	373.6	19.70	18166	4085	
11	377.6	20.24	18415	4347	
12	381.5	20.81	18663	4596	
13	385.3	21.37	18907	4844	
14	388.8	21.92	19140	5088	
15	392.0	22.48	19355	5320	
16	394.8	23.03	19551	5536	
17	397.3	23.59	19729	5732	
18	399.6	24.14	19892	5910	
19	401.6	24.70		6072	113.3

TABLE XXIV

ACETONE COLUMN PROFILES

			Net Flow Rate		
Tray	Temperature °F	Pressure Psia	Liquid lb-mols/hr	Vapor	Heater/Cooler Duties MM Btu/hr
1	137.5	14.70	385.2		-7.13
2	138.5	14.93	384.4	532.3	
3	139.6	15.15	383.4	531.6	
4	140.7	15.38	382.1	530.6	
5	141.8	15.61	380.6	529.3	
6	143.0	15.84	378.7	527.8	
7	144.4	16.06	376.4	525.9	
8	145.8	16.29	373.8	523.6	
9	147.2	16.52	370.8	521.0	
10	148.8	16.75	367.4	518.0	
11	150.5	16.97	363.5	514.6	
12	152.5	17.20	358.3	510.7	
13	155.7	17.43	347.5	505.4	
14	164.0	17.65	322.5	494.7	
15	184.8	17.88	857.0	469.7	
16	187.3	18.11	852.9	473.1	
17	190.3	18.34	848.0	469.0	
18	193.7	18.56	842.9	464.1	
19	197.2	18.79	838.1	459.0	
20	200.7	19.02	834.0	454.2	
21	203.8	19.25	831.0	450.1	
22	206.5	19.47	829.0	447.1	
23	208.8	19.70	827.9	445.1	
24	210.6	19.93	827.3	443.9	
25	212.0	20.15	827.3	443.4	
26	213.2	20.38	827.6	443.4	
27	241.1	20.61	828.1	443.7	
28	215.0	20.84	828.7	444.2	
29	215.7	21.06	829.5	444.8	
30	216.4	21.29	830.3	445.6	
31	217.0	21.52	831.1	446.4	
32	217.6	21.75	832.0	447.2	
33	218.2	21.97	832.9	448.1	
34	218.7	22.20	833.8	449.0	
35	219.3	22.43	834.7	449.9	
36	219.8	22.65	835.6	450.8	
37	220.4	22.88	836.5	451.7	
38	221.0	23.11	837.3	452.6	
39	221.7	23.34	838.0	453.4	
40	222.8	23.56	838.5	454.1	
41	224.7	23.79	838.5	454.6	

TABLE XXIV (CONTINUED)

Tray	Temperature °F	Pressure Psia	Net Flow Rate Liquid lb-mols/hr	Net Flow Rate Vapor lb-mols/hr	Heater/Cooler Duties MM Btu/hr
42	228.5	24.02	838.0	454.6	
43	235.4	24.25	837.9	454.1	
44	264.2	24.47	841.7	454.0	
45	258.6	24.70		457.7	8.21

TABLE XXV

BUTANOL COLUMN PROFILES

Tray	Temperature °F	Pressure Psia	Net Flow Rate Liquid lb-mols/hr	Net Flow Rate Vapor lb-mols/hr	Heater/Cooler Duties MM Btu/hr
1	173.2	14.70	169.3		-3.54
2	174.6	15.15	169.6	205.0	
3	176.0	15.61	169.8	205.3	
4	177.3	16.06	170.0	205.6	
5	178.8	16.52	170.2	205.8	
6	180.5	16.97	170.1	205.9	
7	183.4	17.43	169.3	205.8	
8	189.4	17.88	166.8	205.0	
9	202.3	18.34	162.8	202.6	
10	220.9	18.79	160.9	198.6	
11	236.2	19.25	161.8	196.6	
12	244.4	19.70	532.2	197.6	
13	246.4	20.15	534.2	184.0	
14	248.6	20.61	536.3	186.0	
15	251.0	21.06	538.6	188.1	
16	253.7	21.52	541.1	190.4	
17	256.5	21.97	543.7	192.9	
18	259.3	22.43	546.5	195.6	
19	262.2	22.88	549.3	198.3	
20	264.9	23.34	552.1	201.1	
21	267.4	23.79	554.7	203.9	
22	269.7	24.25	557.2	206.6	
23	271.7	24.70		209.1	3.65

APPENDIX C

THE EXTRACTION COLUMN DESIGN AND SCALE UP PROCEDURE

The extraction scale up procedure described in this section is based on the report prepared for the U. S. Department of Energy by Radian Corporation (28).

Number of Extractors:

The diameter of the full scale column is related to the pilot plant column based on Treybal's method (41):

$$\frac{D_L}{D_S} = (\frac{Q_L}{Q_S})^{0.4}$$

where L and S denote large and small column sizes.

$$Q_s = (46.98)\ (0.832) + 43.32 = 82.91\ \frac{g}{min} = 0.182\ \frac{lb}{min}$$

set the full scale column diameter at 8 ft. Therefore,

$$(Q_L)^{0.4} = (0.182)^{0.4}\ (\frac{8}{1/12})$$

$$Q_L = 16490\ lb/min$$

The solvent and feed flows are:

$$S_L = 29972\ lb/min$$

$$S_F = 28754\ lb/min$$

hence;

$$\text{number of extractor} = \frac{S_F + S_L}{Q_L} = 3.51 \approx 4$$

Number of Theoretical Stages:

The number of theoretical stages, based on a countercurrent plug flow assumption, can be set forth as (27):

$$n = \frac{\ln[(X_F/X_R)\ (K\ S/F - 1) + 1]}{\ln(K(S/F))} - 1 = 1.93$$

For the full scale column based on butanol,

$$(N)_L = \frac{\ln[(0.0163/0.0005)(6.09)*(39.08/43.32) - 1) + 1]}{\ln[6.09 * (39.08/43.32)]} - 1 = 1.93$$

For the pilot plant column based on butanol,

$$(n)_S = \frac{\ln[(0.0163/0.0001)\ (6.09 * 0.9023 - 1) + 1]}{\ln(6.09 * 0.9023)} - 1 = 2.86$$

Effective Height of the Pilot Plant Column:

From Figure 14,

$$H_{eff} = (20.5" + 19.5") - 2.5" = 37.5" = 3.125 \text{ ft}$$

Note: the inlet of the solvent stream is to a packing section. This section contributes negligible mass transfer, therefore, the effective column height should not include this packing height.

Height Equivalent to a Theoretical Stage (HETS):

The height of the column required to make the separation equivalent to one theoretical stage is given by (28):

$$\text{HETS} = \frac{H_{eff}}{n}$$

For the pilot plant column,

$$(\text{HETS})_S = \frac{37.5}{2.86} = 13.11 \text{ in}$$

For the full scaled column, HETS can be scaled up by Scheibel's method (31):

$$\frac{(\text{HETS})_L}{(\text{HETS})_S} = \left(\frac{D_L}{D_S}\right)^{0.5}$$

As a result,

$$(\text{HETS})_L = 13.11'' \left(\frac{8}{1/12}\right)^{0.5} = 128.45'' \text{ per stage}$$

Height of the Mixing and the Packing Zones:

The mixing and packing zone heights can be scaled up as follows (35):

$$\frac{(H_{mix})_L}{(H_{mix})_S} = \left(\frac{D_L}{D_S}\right)^{0.5}$$

and,

$$\frac{(H_{packed})_L}{(H_{packed})_S} = (\frac{D_L}{D_S})^{0.5}$$

Application of the above equations results:

$$(H_{mix})_L = 0.5\ (\frac{8}{1/12})^{0.5} = 4.9 \simeq 5.0 \text{ in}$$

$$(H_{packed})_L = 2.75\ (\frac{8}{1/12})^{0.5} = 26.94 \simeq 27 \text{ in}$$

Therefore the height of one stage is:

$$H_{stage} = H_{packed} + H_{mix}$$

$$H_{stage} = 27 + 5 = 32 \text{ in}$$

Total Extraction Height:

The extraction section of the column is:

$$H_{ext} = HETS * n$$

$$(H_{ext})_L = (128.45)\ (1.93) = 247.91 \text{ in}$$

Number of Actual Stages:

$$(N)_L = \frac{H_{ext.}}{H_{stage}} = \frac{247.91}{32} = 7.75 \simeq 8 \text{ stages}$$

Total Column Height:

$$(H)_{total} = N * H_{stage} + H_{packed} = (8)\ (32) + 27 = 283 \text{ in} \approx 24 \text{ ft}$$

Column Internal Parameters:

The impeller diameter and height is correlated by (29):

$$(\frac{d_i}{D})_S = (\frac{d_i}{D})_L \qquad \text{and,}$$

$$(\frac{h_i}{H_{mix}})_S = (\frac{h_i}{H_{mix}})_L$$

where d_i and h_i are the impeller diameter and height, respectively. For column parameters of this study:

$$(d_i)_L = (\frac{0.53}{1/12})\ (8) = 50.88 \approx 4.25 \text{ ft}$$

$$(h_i)_L = (\frac{5/32}{0.5})\ (5) = 156 \text{ in}$$

Power Input Requirement:

The energy required to disperse the liquid phases is given by Scheibel (31):

$$P = K \frac{d_i^{\,5}\ \rho\ N^3}{g_c}$$

where,

$$K = 9.74\ (B)^{0.495}\ \left(\frac{h_i}{d_i}\right)^{1.33\ B^{-0.108}}$$

B = number of impeller blades

N = rotational speed of impeller in rev/sec

ρ = mean density in lb/ft^3

Evaluate the constant, K:

$$K = 9.74\ (4)^{0.495}\ \left(\frac{5/32}{0.53}\right)(0.133)\ (4)^{-0.108} = 16.82$$

Therefore,

$$(P)_S = \frac{(16.82)\ (0.53/12)^5\ (61.2)\ (8)^3}{32.3} = 2.75\ \mathrm{x}10^{-3}\ \frac{\text{lbf-ft}}{\text{sec}}$$

The power required per unit volume is given by:

$$(P/V)_S = \frac{(P)_S}{\frac{\pi}{4}\ D^2\ H_{mix}} = \frac{2.75\ \mathrm{x}\ 10^{-3}}{\frac{\pi}{4}\ (\frac{1}{12})^2\ (\frac{0.5}{12})} = 12.10\ \frac{\text{lbf}}{\text{ft}^2\text{-sec}}$$

The scale up correlation is:

$$(P/V)_S = (P/V)_L$$

where,

$$V_L = \frac{\pi}{4}\ D_L^2\ (H_{mix})_L = \frac{\pi}{4}\ (8)^2\ (\frac{5}{12}) = 20.94\ \text{ft}^3$$

Therefore,

$$P_L = (P/V)_S\ V_L = (12.10)\ (20.94) = 253.42\ \frac{\text{ft-lbf}}{\text{sec}}$$

$$P_L = (253.42)\ (\frac{0.7457}{550}) = 0.3436\ \text{kw}$$

$$P_L = (0.3436)\ (3600)\ (24)\ (325) = 9.65 \times 10^6\ \text{kJ/yr}$$

VITA 2

Alireza Memaran Dadgar

Candidate for the Degree of

Doctor of Philosophy

Dissertation: DESIGN AND ECONOMIC ASSESSMENT OF LIQUID-LIQUID EXTRACTION FOR THE RECOVERY OF THE CLOSTRIDIUM FERMENTATION PRODUCTS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in Zahdan, Iran, August 6, 1957, the son of Mr. and Mrs. A. M. Dadgar. Married to Billie A. Bowersock, November 22, 1986.

Education: Graduated from Mehran High School, Zahdan, Iran, in May 1975; received Bachelor of Science in Chemical Engineering degree from Oklahoma State University in 1981; received Master of Science degree from Oklahoma State University in 1983; Completed requirements for the Doctor of Philosophy degree in Chemical Engineering at Oklahoma State University in December, 1986.

Professional Experience: Employed as a teaching assistant with Oklahoma State University, 1981-1986; employed as a graduate researcher (AMOCO Fellowship) with Oklahoma State University, 1982-1986.