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# Liquid-Liquid Extraction as an Alternative Separation Technique for Ethanol-Water Solutions

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LIQUID-LIQUID EXTRACTION AS AN ALTERNATIVE SEPARATION  
TECHNIQUE FOR ETHANOL-WATER SOLUTIONS

by

Michael Pirc

Bachelor of Science, Chemical Engineering  
University of North Dakota, 1978

A Thesis

Submitted to the Graduate Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the degree of

Master of Science

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This thesis submitted by Michael Pirc in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

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This thesis meets the standards for appearance and conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

A. William Johnson  
Dean of the Graduate School



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For Ethanol Water Solutions

Department Chemical Engineering

Degree Master of Science

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## ABSTRACT

The feasibility of liquid extraction as an economic alternative to the ternary azeotrope distillation of an ethanol-water fermentation mixture was studied. Experimentation included the determination of the attractiveness of the potential solvents "Freon" TF, 1-pentene, ethyl ether, unleaded gasoline, and #2 diesel fuel. Selectivities and distribution coefficients for these solvents were determined. Analysis included generation of a process flowsheet and the resultant energy requirements and process economics.

Unleaded gasoline was selected over #2 diesel fuel as the more attractive solvent based on the distribution coefficients, and "Freon" TF, 1-pentene, and ethyl ether were ruled out as potential solvents.

A fermentation plant incorporating a gasoline extraction process and a beer still to separate the fermentation mixture, with an ethanol recovery rate of 96 wt%, was found to yield an energy savings of 15.6% over a fermentation plant equipped with only a ternary azeotrope distillation separation process. Annual cost for this extraction scheme was found to be \$3,998,600, as compared to an annual cost of \$1,501,400 for the distillation process. Increasing the recovery rate of ethanol to greater than 99 wt% for the extraction process was suggested as a means to vastly improve its economics.

An extraction scheme that did not include the beer still to preconcentrate the alcohol was found to be uneconomical.

## CHAPTER I

### INTRODUCTION

Recent energy shortages and the unhealthy dependence of the American economy on foreign oil have spurred tremendous interest in the development of alternate energy sources. One such source, which has generated much controversy as well as study, is ethanol produced by fermentation of biomass.

Ethanol, as an alternate fuel, has two major applications. The first, which has been researched extensively by both government and private sectors, is the use of ethanol as a fuel extender for gasoline and diesel engines. Success here has been documented widely (1). Secondly, ethanol has been shown to be useful as a fuel for utility boilers and gas turbine peaking generators (2).

The production of industrial grade ethanol has been primarily based in this century on the conversion of ethylene to ethanol by direct hydration. The rapid growth of the petroleum industry in the past few decades has made, until recently, petroleum-derived ethanol the most attractive because of lower overall reactant and conversion costs. However, the recent petroleum shortages, and resultant higher ethylene costs, have again turned interest in the direction of fermentation processes.

Production of ethanol through fermentation has two inherent benefits. First, fermentation utilizes carbohydrate sources in the form



of wheat, corn, potatoes, etc. These agricultural products are renewable, whereas petroleum-based sources are not. Secondly, fermentation could be directed at "excess" crops, crops not fit for human consumption, or crops which could and would be produced given sufficient economic justification. This direction could improve the agricultural market.

Traditional fermentation processes involve four major steps. Initially, a carbohydrate source is milled, mixed with water to form a slurry, and is cooked under pressure. This preparation step serves to sterilize the mash and expose starch granules, which are stored intracellularly in plant tissues. Next, the exposed starch is converted to sugars using an enzyme known as amylase, which is derived from sprouted barley. This is known as the conversion step. Third, in the fermentation step, yeast converts the sugars into ethanol and mixture of higher alcohols commonly called fusel oils, which are present in very dilute concentrations. Concentrations of 9 to 12 vol% ethanol are usually reached in the fermentation mixture, at which point its presence inhibits the yeast fermentation action. Fermentation is carried out anaerobically.

Last, in the ethanol purification step, the fermentation mixture is centrifuged to separate the solids fraction, and the resultant liquid stream is distilled to produce 200 proof ethanol using of a ternary azeotrope distillation involving benzene. In fuel applications, the fusel oils are usually recovered in the ethanol product. Traditional fermentation processes are carried out as batch operations.

Fermentation technology has seen little advance since research

done in the 1940's by Seagrams and Son's (3, 4). This is largely because almost all ethanol production by this means is directed towards a human-consumable product, where quality control is of much greater concern than cost-effective process improvements.

The controversy surrounding the production of ethanol as an alternate energy source is centered about the economics and energy balance of the fermentation process. Because the overall plant economics are highly dependent on the cost of the feed stock, and the prices of agricultural commodities fluctuate greatly, these economics are largely a subject of conjecture. However, some reliable studies of the economics based on full-scale operating plants have been published (5).

The second source of debate, the energy balance, is based on the argument that no potential production of an alternate energy source can be justified if the product does not yield more energy than is used in its manufacture. This is precisely the discussion concerning ethanol, but the problem is complicated by lack of agreement as to what should be included in the balance. Reports both in favor and against the production of ethanol in terms of energy yield have been published (6, 7).

The energy balance of the fermentation process is controlled to a large degree by the energy expended in the ethanol-recovery process. Percentages of the total plant energy use as high as 74% have been reported (7). This can be attributed to the high energy costs associated with the change of phase of the large amount of water present in the feed stream to the distillation scheme. It is

obvious then, that an alternate separation technique which would avoid that change of phase could significantly improve the overall energy balance and notably increase the attractiveness of the fermentation production of ethanol as an alternate energy source.



## CHAPTER II

### OBJECTIVES

Liquid extraction is a possible attractive alternative for the recovery and purification of ethanol from the fermentation mixture. Theoretically, it is capable of high recovery rates and involves relatively small energy usage when carried out at ambient temperatures.

The major objective of this study was to discover a solvent to be used for the continuous countercurrent liquid extraction of ethanol from water at ambient temperature which would prove, after analysis, to be both economic and more energy-efficient than an equivalent distillation process. Other objectives included the development of a process design for the liquid extraction, and an analysis of the energy requirements and preliminary economics of the process.

All analysis of the liquid extraction process was based on comparison to the ternary water-benzene-ethanol azeotrope distillation process. These comparisons assumed equivalency between the two processes, and any differences were taken into account during economic and energy-usage comparisons. Boundaries of the process flowsheets assumed equivalent treatment of the exit streams.

A 96 wt% recovery of ethanol was the basis for the extractor design, with a capacity sufficient for a production rate of 50

million gallons of 200 proof ethanol annually. All other flowstream information was taken directly from a fermentation plant design by Hefta, Pirc, and Bader (8), as well as the complete data for the distillation scheme.



## CHAPTER III

### LIQUID EXTRACTION

#### Introduction

Liquid extraction, otherwise known as solvent extraction, is defined by Treybal as "the separation of the constituents of a liquid solution by contact with another insoluble liquid" (9). The separation occurs when the components of the original solution are distributed differently at equilibrium between the two insoluble phases. Liquid extraction belongs to a class of separation methods known as mass-transfer operations, which also include distillation, evaporation, and gas absorption.

In liquid extraction, the solution to be extracted is called the feed and the insoluble liquid with which the feed is contacted is called the solvent. The component of the feed which is distributed preferentially in the solvent phase is known as the solute. The solvent-rich phase is called the extract, and the phase rich in the residual liquid from which the solute has been removed is known as the raffinate. Traditionally, the components of the feed are denoted by "A" and "C", where C is the solute and A is the nonsolute. The solvent is denoted by "B" (9).

Liquid extraction may be carried out in a batch or continuous fashion.

After the extraction process is carried out, the solvent in the extract is almost always recovered and recycled due to high solvent costs. This also applies to the raffinate whenever practicable. Distillation is the usual means of recovery.

#### Uses for Liquid Extraction

Liquid extraction generally becomes useful whenever the economics of a given separation are particularly sensitive to energy costs, or whenever other methods of separation have failed. It has proven to be an effective substitute for crystallization, evaporation, and chemical methods of separation (10). Most often, however, liquid extraction has been used as an economic substitute for distillation.

Examples are (10):

1. separation of closely boiling liquids
2. separation of liquids with low relative volatility
3. separation of heat-sensitive substances
4. separations according to chemical type, where boiling points overlap.

#### Solvent Selection

For a solvent to be effective as an extraction agent it should exhibit several properties. Among these are (9):

1. Distribution coefficient- The distribution coefficient is defined as the ratio of the weight fraction of C in the extract versus the weight fraction of C in the raffinate. Values greater than one are desirable.

2. Selectivity- The selectivity of a solvent is a measure of its ability to selectively dissolve a large amount of solute and a minimum of the other component. This ability is defined as the ratio of the weight fraction of C versus A in the extract divided by the ratio of the weight fraction of C versus A in the raffinate. For all useful extraction operations it is necessary for the selectivity to exceed unity, and again higher values are desirable.

3. The solvent should exhibit immiscibility towards widely varying mixtures of A and C.

4. The solvent should be easily recovered from the extract. That is, the solvent should not form an azeotrope with the solute, and it should exhibit high volatility.

5. The solvent density should differ significantly from the density of the A component so that extract and raffinate phases will form rapidly.

6. The interfacial tension between the A-rich and B-rich phases should be high to encourage rapid coalescence.

7. The solvent should not be corrosive, and should not exhibit reactivity towards the components of the feed.

8. The solvent should be nontoxic, nonflammable, and inexpensive.

It should be noted here that only rarely do solvents meet all of these criteria, and solvent selection is often a matter of compromise.



## CHAPTER IV

### SELECTION OF EXPERIMENTAL SOLVENTS

The solvents selected for the comparison of the extraction and distillation separations, as defined in the Objectives, were chosen specifically with the assumption that a distillation operation would be used for solvent recovery. Three of the solvents to be investigated, "Freon" TF, 1-pentene, and ethyl ether, were selected on the basis of solubility of both ethanol and water, boiling point, and heat of vaporization. Secondary considerations included toxicity, flammability, and corrosiveness.

It was determined to be imperative that the solvent have a boiling point lower than that of water in order to avoid an unnecessary change of phase of the water during the solvent recovery of the raffinate. It was further desired that the solvent's boiling point be as low as possible in order to minimize energy costs during solvent recovery of both extract and raffinate streams. A low heat of vaporization of the solvent was also chosen as a desirable solvent property in order to minimize energy costs during solvent recovery of the extract.

In all of the selected solvents ethanol is highly soluble and water is highly insoluble. The boiling points of all these solvents are significantly lower than those of both ethanol and water. Also, the heat of vaporization of these solvents is much lower than that of water.

Unleaded gasoline and #2 diesel fuel were also selected as solvents for investigation. These fuels were not chosen on the basis of the above criteria, but with the idea that ethanol recovered in these solvents would be applied as a fuel-extender, and no solvent recovery would be necessary. Both of these solvents exhibit favorable solubility properties.

## CHAPTER V

### MATERIALS AND EXPERIMENTAL EQUIPMENT

Five different ternary systems were investigated in order to find their suitability as agents for the extraction of ethanol from the fermentation mixture. These five systems are:

1. water-"Freon" TF-ethanol
2. water-1-pentene-ethanol
3. water-ethyl ether-ethanol
4. water-unleaded gasoline-ethanol
5. water-#2 diesel fuel-ethanol

The solvents selected for use in the experimentation were low grade in terms of quality in order to more closely approximate what would be used in an industrial setting. This was necessary because components of the solvent present in even very small concentrations affect the equilibrium by their tendency to concentrate in the latter stages of the extraction (10). Because these solvents were of a general-use grade, no specific analysis was available.

The solvent "Freon" TF is a Dupont product and is liquid at normal ambient conditions. It is largely used as a general purpose cleaner and degreaser. It is the base compound for all other "Freon" solvents, and is the mildest solvent cleaner and has the best stability characteristics.

The 1-pentene was purchased as technical grade from Eastman-Kodak. The ethyl ether was obtained as solvent grade from Fischer Scientific Products.

Table 1 summarizes the pertinent physical properties of these three solvents.

Both the unleaded gasoline and the diesel fuel were purchased from Interstate Discount, Grand Forks, ND. Because this retailer has several suppliers, and the fuels from all suppliers are mixed, no specific analysis or source of the base fuel was available.

Generation of the equilibrium phases for the ternary systems was accomplished in identical 125 milliliter separatory funnels.

The analysis of the phases for the "Freon" TF, pentene, and ether systems was done using an Antek gas chromatograph equipped with a flame ionization detector. Integration of the peaks was done using a Fischer Recordall Series 5000 recorder.

Determination of the water content of the phases for the diesel fuel and gasoline systems was accomplished using a Karl-Fischer titration apparatus.



TABLE 1

VARIOUS PHYSICAL PROPERTIES OF "FREON" TF,  
1-PENTENE, AND ETHYL ETHER

	"Freon" TF (11)	1-Pentene (12)	Ethyl Ether (13)
Molecular Wt	187.4	70.13	74.12
Density, 77°F	1.565	0.641	0.708
Boiling Point, °F	117.6	86.0	94.3
Latent heat of Vaporization, Btu/lb	63.1	98.0	84.0
Solubility of water Wt%	0.011	--	1.10
Solubility of Ethanol	∞	∞	∞

## CHAPTER VI

### EXPERIMENTAL PROCEDURE

#### Introduction

The single purpose of the experimental work done was to determine the composition of the equilibrium phases for the systems listed above. This information allowed comparison of the different systems in terms of the distribution coefficient and selectivity of the solvents. Because of the high volatility of the solvents involved, certain compromises were made in the procedure which affected the accuracy. It is felt, however, that the methods described below were accurate enough to allow valid comparison of the different systems.

#### "Freon" TF, Pentene, and Ethyl Ether Systems

Initially, mixtures of water, solvent, and ethanol varying from 40 to 0 vol% ethanol were placed in the 125 milliliter separatory funnels and inverted approximately 50 times for 90 seconds, as recommended by Treybal (10). The resultant phases were allowed to come to equilibrium for 60 minutes. The volume of each phase was then measured, and samples of 3 to 4 milliliters were taken for gas chromatograph analysis. These samples were stored in small serum vials with rubber stoppers to minimize loss of volatile components, and were immediately frozen.

Next, the samples were analyzed by means of the gas chromatograph. Standards for the water phases of 10, 20, and 30 vol% ethanol, and a standard of 1.5 vol% for the solvent phase were used to calibrate the gas chromatograph. Injection sample sizes of 3.5 microliters were used.

The "Freon" system was analyzed using a 12 foot long, 10% FFAP on 40/60 mesh chrom T column. The column temperature was 155°C, and the nitrogen carrier gas had a flow rate of 35 milliliters per minute. The pentene and ether systems were analyzed using a 4 foot long, 0.25 inch diameter, 10% SE 30 on 70/80 mesh Anachrom ABS column. The column temperature was 90°C, with a nitrogen flow rate of 30 milliliters per minute.

#### Diesel Fuel and Gasoline Systems

Due to the large numbers of components in the unleaded gasoline and the diesel fuel and the wide boiling point range of these components, it proved impossible to resolve the ethanol peak on the gas chromatograph. Because of this, a different procedure was used for these two systems in order to determine the composition of the equilibrium phases.

Generation of the samples was identical to the above, with the exception that the initial mixtures ranged in ethanol content from 60 to 0 vol%. The water content of the solvent phase was then determined using a Karl-Fischer titration. The solvent content of the water phase was estimated by a titration with solvent until saturation of a representative water-ethanol mixture was reached.



Total closure of the mass balance was then assumed, and the composition of the equilibrium phases followed by direct calculation.

#### Analysis of the Experimental Procedure

As was mentioned previously, certain compromises were made in the experimental procedure in order to function within the framework of the highly volatile solvents. These compromises led to losses of accuracy in the experimental results. It is felt, however, that when the computational methods used in the design of the extraction column from these data and the small magnitude of these errors are taken into account, that the determination of the equilibrium phase compositions need not be of extreme accuracy. In this particular case, because the data were used only for the selection of the best solvent(s) and for a somewhat "rough" extractor design, the procedure described above is sufficient for valid comparisons.

One such compromise was the fact that results and measurements were made on a volume basis. Accurate weighing of the solvents was not feasible due to the high rate of evaporation of these solvents. Also, no satisfactory means was found for density determinations of the solvents which would have been essential to the calculations involved in the analysis of the gas chromatograph findings. The error associated with volume measurements evolves from the volume change of mixing that occurs between ethanol and water. This volume change, however, is limited to about -3.5% in the range of mixtures of 40 wt% ethanol or less. No significant volume change of mixing was seen to occur between the solvents and ethanol.

Another error arose from the tendency of the gas chromatograph columns to absorb small quantities of ethanol, reach saturation, and release bound ethanol when samples of lower ethanol concentrations were run. This affected the peaks given by the integrator. This tendency was discovered when samples of zero ethanol content were run but displayed significant ethanol peaks.

The accuracy of the analysis of the water-phase samples was affected by the absorption by the stoppers of the solvent present in very small concentrations. Here again, the high relative vapor pressure of the solvent was the cause.

A very significant loss of accuracy of analysis of all samples occurred from the lack of linearity of the flame ionization detector over ranges of concentration. Because it was necessary to determine ethanol concentrations over a range from about 45 to 0.1 vol%, an unreasonable number of calibration standards were necessary for accuracy. The problem arose because the calibration was assumed linear, and intermediate concentrations were found by interpolation.

## CHAPTER VII

### EXPERIMENTAL RESULTS AND DISCUSSION:

#### "FREON" TF, PENTENE, AND ETHYL ETHER

##### Introduction

From the analysis of the equilibrium phase samples using the gas chromatograph, the compositions of these phases were found. Tables 2 through 4 show the experimentally found compositions of the equilibrium phases for the "Freon" TF, pentene, and ethyl ether systems, respectively.

These compositions were subject to an error of analysis which resulted from errors in sample preparation, variability of the technique of injection of the sample into the gas chromatograph injection port, and variance of the gas chromatograph itself. The error associated with the above mentioned tendency of the column to retain and later release ethanol could not be measured. The variance of the gas chromatograph may be considered small in comparison to the other errors.

The error of analysis affecting the composition measurement was found by preparing several runs of three identical samples on which the gas chromatograph was done. The variance for a 90% confidence interval on these analysis was found to average  $\pm 26.5\%$  of the measured fraction of the solvent in the extract phase and of the



TABLE 2

COMPOSITIONS OF THE EQUILIBRIUM PHASES FOR THE

"FREON" TF SYSTEM AT 23.8°C

(all quantities in vol%)

Water Layer			"Freon" TF Layer		
Water	Ethanol	"Freon" TF	Water	Ethanol	"Freon" TF
45.6	43.3	11.1	3.7	3.3	93.0
64.7	32.7	2.6	3.1	2.0	94.9
71.7	27.4	0.9	4.3	1.0	94.7
75.2	24.1	0.7	2.5	0.6	96.9
77.2	22.4	0.4	1.8	0.4	97.8
84.3	15.1	0.6	1.0	0.3	98.7
93.8	5.9	0.3	0.2	0.1	99.7
99.7	0.0	0.3	0.1	0.0	99.9



TABLE 3

COMPOSITIONS OF THE EQUILIBRIUM PHASES FOR THE  
 1-PENTENE SYSTEM AT 25.0°C  
 (all quantities in vol%)

<u>Water Layer</u>			<u>1-Pentene Layer</u>		
Water	Ethanol	1-Pentene	Water	Ethanol	1-Pentene
52.1	38.9	9.0	3.8	3.7	92.5
59.4	35.6	5.0	4.7	2.8	92.5
63.3	34.9	1.8	3.1	1.9	95
78.0	20.8	1.2	4.0	1.4	94.6
79.1	20.2	0.7	1.1	1.3	97.6
87.9	11.8	0.3	1.5	0.9	97.6
89.8	9.9	0.3	0.8	0.4	98.8
99.5	0.3 <sup>a</sup>	0.2	0.3	0.0	99.7

<sup>a</sup>Erroneous reading caused by column dumping ethanol,  
 no ethanol was used in preparation of this sample.

TABLE 4

COMPOSITIONS OF THE EQUILIBRIUM PHASES FOR THE  
ETHYL ETHER SYSTEM AT 27.2°C

(all quantities in vol%)

<u>Water Layer</u>			<u>Ethyl Ether Layer</u>		
Water	Ethanol	Ethyl Ether	Water	Ethanol	Ethyl Ether
73.4	24.8	1.8	11.6	2.2	86.2
77.0	21.3	1.7	3.1	2.1	94.8
78.9	19.5	1.6	---	1.8	99.5 <sup>a</sup>
88.5	10.5	1.0	---	1.8	99.4 <sup>a</sup>
89.2	9.8	1.0	5.4	1.4	93.2
93.4	5.7	0.9	5.7	1.2	93.1
99.1	0.0	0.9	7.4	0.0	92.6

<sup>a</sup>Erroneously high readings.

ethanol in the raffinate phase. This is shown in the sample calculations.

The composition data were then used to determine average distribution coefficients, selectivities, and volume percent ethanol in the extract on a solvent-free basis. Table 5 summarizes these findings.

TABLE 5

SUMMARY OF DISTRIBUTION COEFFICIENTS, SELECTIVITY  
AND VOL% ETHANOL IN EXTRACT

	Freon TF	1-Pentene	Ethyl Ether
Average Distribution Coefficient	0.036	0.068	0.134
Average Selectivity	1.01	2.02	2.21
Range of Vol% Ethanol in extract on a solvent-free basis	18.2 - 47.1	37.3 - 54.2	15.9 - 40.4

Distribution Coefficient

Normally reported on a weight percent basis, the distribution coefficient was calculated on a volume basis because of the difficulties discussed earlier. As can be seen in Table 5, the average distribution coefficients ranged from 0.036 for the "Freon" TF



system to 0.134 for the ethyl ether system. These low values indicate that none of the solvents investigated here would be particularly efficient in the extraction of ethanol from water. However, although higher coefficients are desired, the extraction may still be carried out.

A statistical F-test calculation was carried out to determine if the reported distribution coefficients were significantly different. The details of this calculation is given in the sample calculations in the appendix. It was determined statistically that the distribution coefficients are significantly different.

#### Selectivity

As with the distribution coefficient, the selectivity was calculated on a volume basis. The average selectivities were found to range from 1.01 for the "Freon" TF system to 2.62 for the pentene system. These low values indicate that high solvent flow rates and large numbers of extraction stages would be needed, with correspondingly expensive equipment.

#### Ethanol Vol% in the Extract: Solvent-Free Basis

A third indicator, particularly relevant to this discussion, of the effectiveness of these solvents as extractive agents is the volume percent of ethanol in the extract on a solvent-free basis. Assuming total recovery of the solvent in the solvent-recovery scheme, this quantity would approximate the highest levels of ethanol expected to be exiting this scheme. The actual value cannot be predicted with-



out previous knowledge of the actual extractor design and the corresponding solvent flow rates. From Table 5 it can be seen that no value of the maxima of the ranges for these solvents is greater than 60 vol%. In other words, it cannot be reasonably expected that extraction with any of the above solvents will yield a product exceeding 60 vol% in purity after solvent recovery.

#### Summary

From the above findings concerning the distribution coefficients, selectivities, and volume percent ethanol in the extract, it can be estimated that none of the three solvents, "Freon" TF, 1-pentene, or ethyl ether, can be expected to make solvent extraction more attractive than the traditional distillation process.

With regard to the relative merits of the solvents, pentene appears to be the most effective solvent of the three for the extraction of ethanol from water, based on the above criteria. The low toxicity and nonflammability of "Freon" TF make it desirable from a safety standpoint.

In the final analysis, it is felt that none of these solvents warrant further study.

## CHAPTER VIII

### EXPERIMENTAL RESULTS AND DISCUSSION:

#### GASOLINE, AND DIESEL FUEL

Using the procedure described for these two systems, the compositions of the equilibrium phases were found. These compositions are summarized in Tables 6 and 7 for the gasoline and diesel fuel systems, respectively. Because of the assumption of complete closure of the mass balance, and the estimation of the volume percent solvent in the raffinate phase, these compositions can only be considered approximate. This error could not be quantified.

From the compositions found, the distribution coefficients and were calculated. The selectivities for these two systems could not be calculated directly because this calculation involves division by the percent water in the extract, which was largely found to be negligible. It can only be estimated as highly suitable for this extraction. The volume percent ethanol in the extract on a solvent-free basis is not a relevant quantity because of the use here of ethanol as a fuel extender.

The average distribution coefficients for the diesel fuel and gasoline systems were found to be 0.123 and 0.139, respectively.

Based on the above findings, the unleaded gasoline system was selected as the system for further economic study.

TABLE 6

COMPOSITIONS OF THE EQUILIBRIUM PHASES FOR THE  
UNLEADED GASOLINE SYSTEM AT 25.6°C  
(all quantities in vol%)

<u>Water Layer</u>			<u>Gasoline Layer</u>		
Water	Ethanol	Gasoline	Water	Ethanol	Gasoline
23.6	68.8	7.6	0.1	9.9	90.0
43.5	55.8	0.7	<0.1	4.8	95.2
69.0	31.0	<0.1	<0.1	4.7	95.3
83.3	16.7	<0.1	<0.1	2.2	97.8
91.7	8.3	<0.1	<0.1	1.5	98.5

TABLE 7

COMPOSITIONS OF THE EQUILIBRIUM PHASES FOR THE  
#2-DIESEL FUEL SYSTEM AT 25.6°C  
(all quantities in vol%)

<u>Water Layer</u>			<u>#2-Diesel Layer</u>		
Water	Ethanol	Diesel	Water	Ethanol	Diesel
25.1	73.0	1.9	<0.1	8.4	91.6
44.1	55.7	0.2	<0.1	6.6	93.4
69.2	30.8	<0.1	<0.1	5.2	94.8
83.0	17.0	<0.1	<0.1	1.7	98.3
91.3	8.7	<0.1	<0.1	1.0	99.0



## CHAPTER IX

### PROCESS DESIGN

#### Introduction

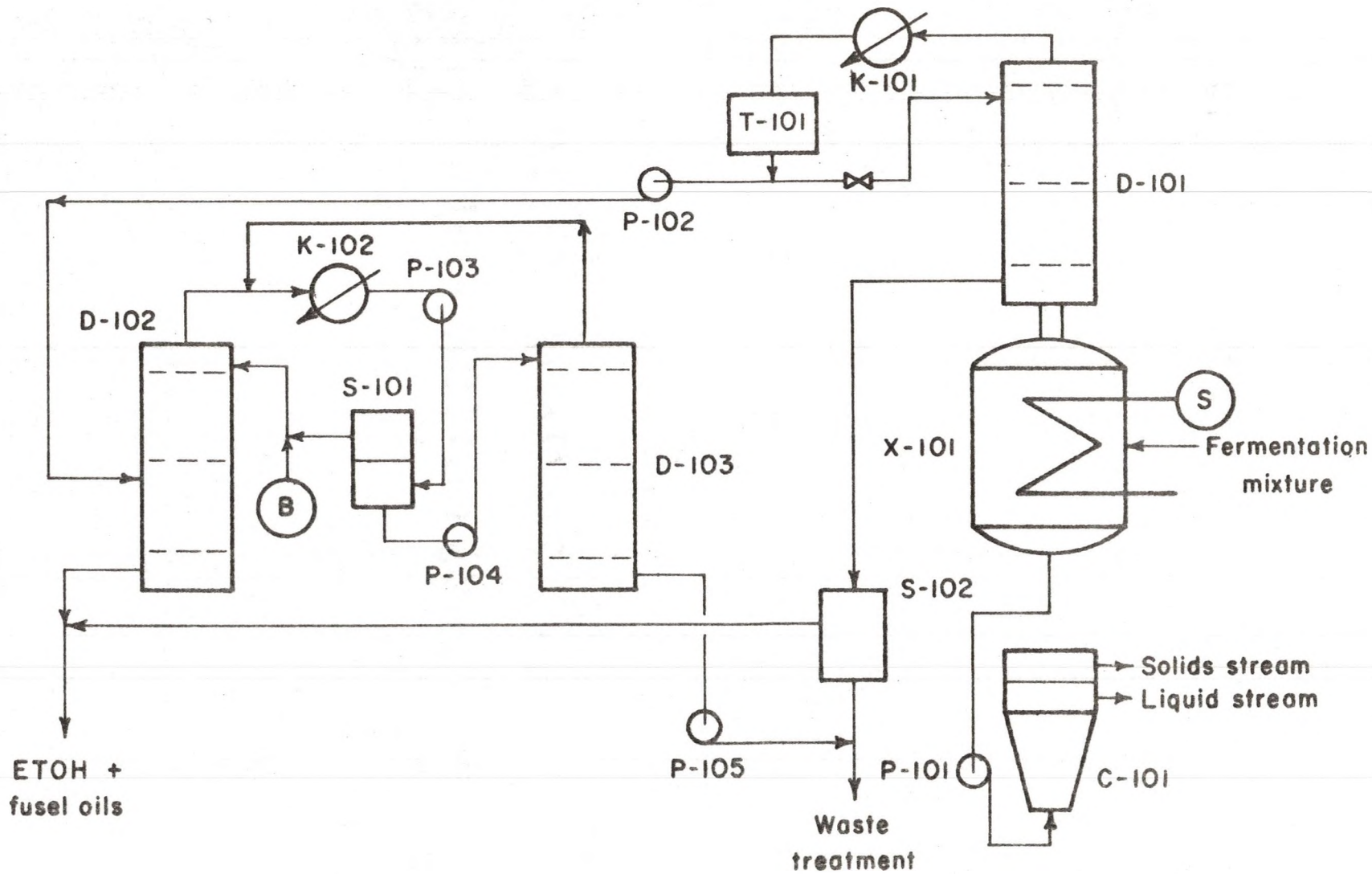
The solvent extraction process described here was designed to extract the exit stream from the fermentation section of a plant producing 50 million gallons of ethanol annually. The design of this plant incorporated fully-continuous processing, with an exit concentration of ethanol in the fermentation mixture of 7.0 wt%. Details of the design can be found in literature (8).

Unleaded gasoline was selected above as the extraction solvent for this study. In usual extraction processes, solvent is recovered and recycled. Only make-up solvent enters the process. This type of process applies to solvents like "Freon" TF, pentene, and ether. However, because of the high energy costs that would stem from solvent recovery with gasoline as the solvent, and the fact that the gasoline-ethanol extract is a desirable product with no further need for processing, the extraction flowschemes described below are single-pass. That is, the gasoline solvent is not recycled and passed through the extractor only once.

#### Ternary Azeotrope Distillation

Figure 1 is a flowsheet of the distillation process. In this

Figure 1 . Ternary azeotropic distillation scheme.



process, the fermentation mixture enters the beer still, X-101, and is concentrated to 76 wt% ethanol. The residual stream exits into a centrifuge, C-101, which separates the solids and liquid streams for further processing. The overhead stream from X-101 is injected directly into the concentration column, D-101, which further concentrates the ethanol vapors. The ethanol-rich overhead from D-101 is combined with the benzene stream, forming the feed stream for the ternary azeotrope column, D-102.

The overhead from D-102 in the ternary azeotrope of water, ethanol, and benzene, and the bottoms product is anhydrous ethanol. This overhead is condensed and separated into a benzene and water phase in S-101. The benzene phase is the feed benzene for D-102, and the water phase is feed for the column D-103, which acts as a rectifying column. The overhead from D-103 is ternary azeotrope and is combined with the overhead from D-102. The bottoms of D-103 contain 0.01 mole% ethanol and are discarded (14).

The decanter S-102 separates the bottoms of D-101 which contain water and insoluble fusel oils. Here, the fusel oils are mixed with the final ethanol product.

#### Solvent Extraction Process

Because both energy requirements and economics of the extraction and distillation processes were compared, two different solvent extraction processes were examined. One process retains the use of the beer still, while the second extracts the fermentation stream directly after solids separation. These two processes will be here-



after referred to as Case 1 and Case 2, respectively.

Figure 2 gives the flowsheet for Case 1. As in the distillation scheme, the fermentation mixture enters the beer still, X-101, and the overhead product at 76 wt% ethanol is pumped to the solvent extraction tower, E-101. The mash slurry is sent to centrifuge C-101, where the solids and liquid stream are separated for further processing. The solvent is pumped to E-101 from the solvent storage tank T-101. A recovery of 96 wt% of the ethanol was assumed for the extraction. The extract exits the extractor at about 11 wt% ethanol and is pumped to storage and/or distribution.

The raffinate stream, at approximately 1000 ppm gasoline concentration, can be treated in the biological ponds used for the treatment of normal plant wastes. When mixed with the normal waste streams, the mixture is diluted to 36 ppm gasoline, with an increase in volume over the original flowrate of 3.8%. This level of gasoline concentration was assumed treatable by biological means (15). The material balance for Case 1 is given in Table 8.

The flowsheet for Case 2 is given in Figure 3. The fermentation mixture enters centrifuge C-101 and is separated into a solids stream at 65 wt% moisture and a liquid stream. For simplicity, it was assumed that no loss of ethanol from the liquid stream resulted from this separation. The liquid stream is pumped to the solvent extraction tower E-101, where again 96 wt% recovery of ethanol is assumed. The gasoline solvent is pumped from storage in S-101 to the extractor, and the extract stream, at about 2.0 wt% ethanol, is sent to storage and/or distribution.



Figure 2 . Gasoline extraction scheme ( w / beer still ).

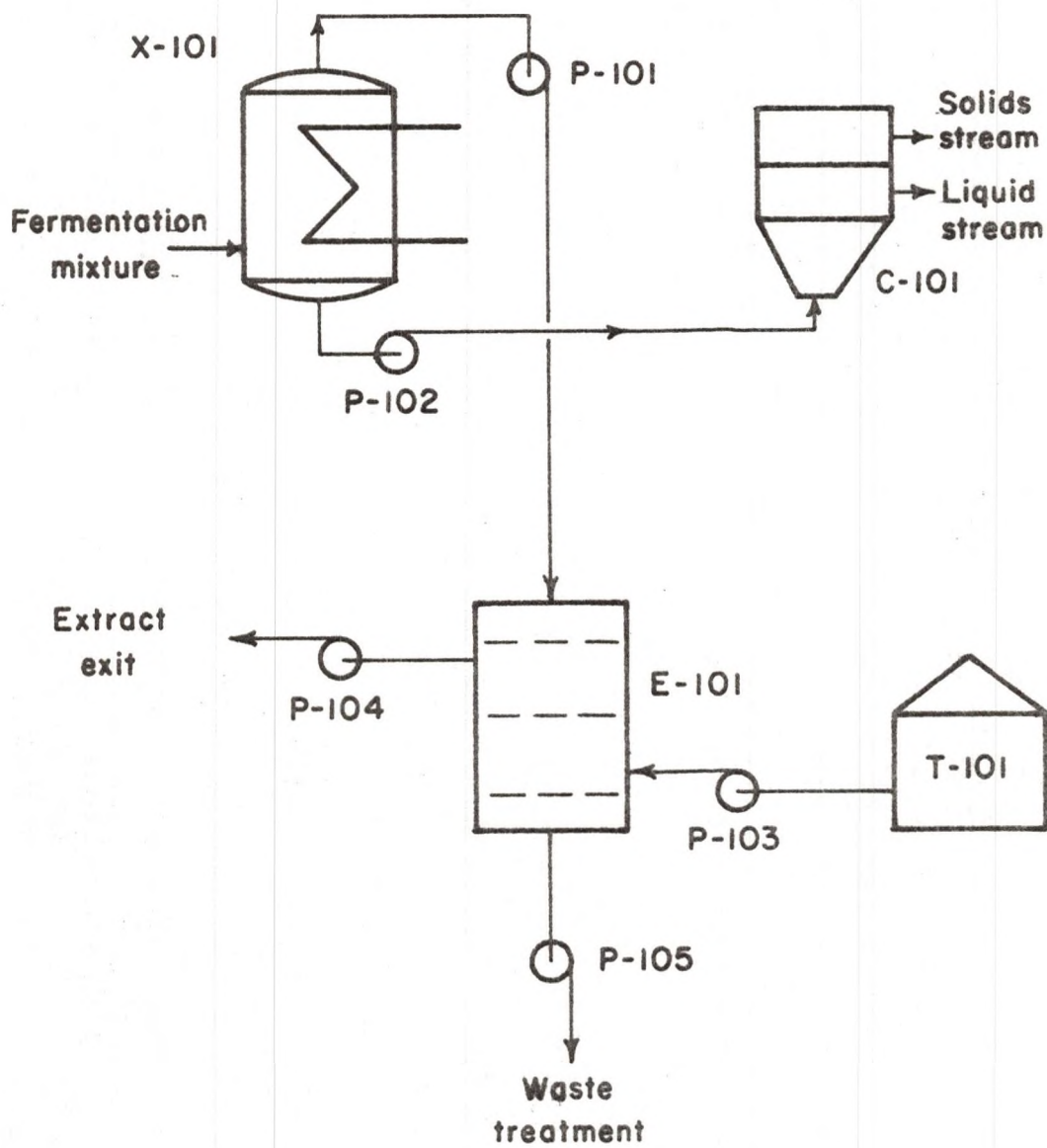
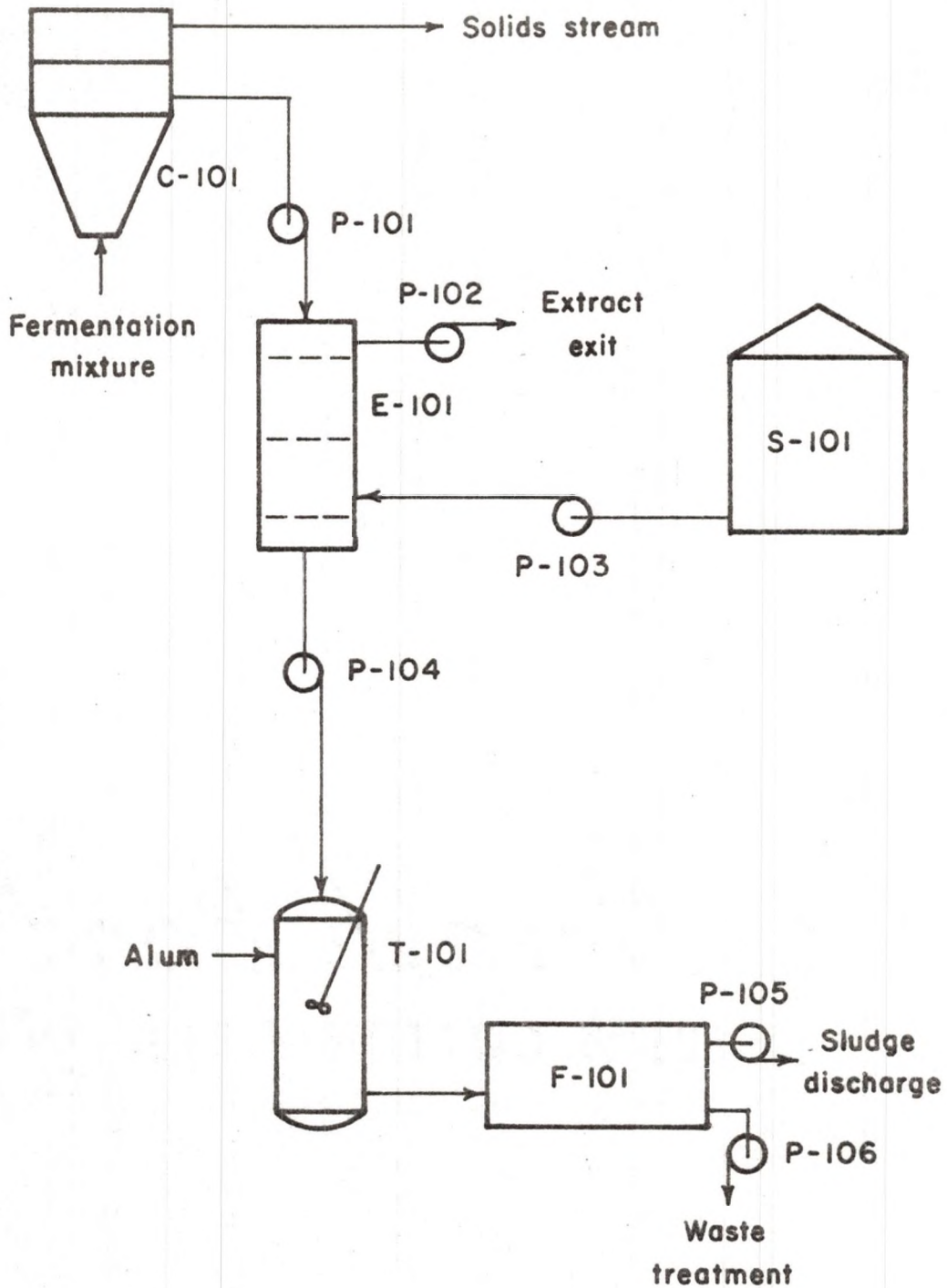


TABLE 8

## STREAM COMPOSITION FOR CASE 1 (W/BEER STILL)

Stream Description	All quantities in lbs/hr					
	Water	Ethanol	Fusel Oils	Solids	Gasoline	Total
Fermentation Mixture	502,471	41,796	3,443	46,362	0	594,072
From X-101 to C-101	489,244	0	0	46,362	0	535,606
From X-101 to E-101	13,227	41,796	3,443	0	0	58,466
From T-101 to E-101	0	0	0	0	323,127	323,127
Extract Exit	367	40,124	3,433	0	323,112	367,046
Raffinate Exit	12,860	1,672	0	0	15	14,547

Figure 3 . Gasoline extraction scheme (w/o beer still).



The raffinate stream from the extractor, at 1000 ppm gasoline, is of such a high flow rate to require separate treatment facilities. Both coagulation and dissolved-air flotation will be used for this treatment, as recommended in literature for petroleum-contaminated streams (16). The coagulation tank, T-101, uses alum at 200 ppm concentration as the coagulation agent. The alum forms a hydrate with the water, upon which suspended gasoline collects. This stream is then pumped to the air flotation tank F-101, where the mixture is saturated with tiny air bubbles which cause the alum hydrate-gasoline complex to float to the surface of the tank for removal (15). This process is assumed 96% efficient at the removal of gasoline contaminant, and the treated stream exists at approximately 40 ppm gasoline. This stream is pumped to biological waste treatment.

Table 9 gives the material balance for Case 2.

#### Equipment Design

Tables 10 and 11 are the equipment lists for proposed processes Case 1 and Case 2, respectively. All required equipment the size of a pump or larger is listed here, with their equipment numbers, items required, and description. Only the extent of design necessary to estimate the cost of the equipment was done.

The centrifuges used to separate the solids and liquid streams were sized based on the mass flow rates through them. The design of the beer still was based on capacity, and taken from literature (17).

The extractors were designed by York Process Equipment Company. This design was based on the mass flow rates, the average distribution



TABLE 9

## STREAM COMPOSITION FOR CASE 2 (W/O BEER STILL)

Stream Description	All quantities in lbs/hr						Total
	Water	Ethanol	Fusel Oils	Solids	Gasoline	Alum	
Fermentation Mixture	502,471	41,796	3,443	46,362	0	0	594,072
Solids Stream	86,101	0	0	46,362	0	0	132,463
From C-101 to E-101	416,370	41,796	3,443	0	0	0	461,609
From S-101 to E-101	0	0	0	0	1,988,150	0	1,988,150
Extract Exit	0	40,124	3,443	0	1,987,732	0	2,031,299
From E-101 to T-101	416,370	1,672	0	0	418	0	418,460
From T-101 to F-101	416,370	1,672	0	0	418	84	418,544
Sludge Discharge	0	0	0	0	402	84	486
To Waste Treatment	416,370	1,672	0	0	16	0	418,058

TABLE 10

## LIST OF EQUIPMENT FOR CASE 1 (W/BEER STILL)

Item No.	No. Required	Description
X-101	1	Beer Still, 3 Ft high 9 Ft diam.
C-101	1	Centrifuge, Filter continuous vibratory screentype, 60 tons/hr, 150 HP motor
E-101	1	Extraction column, 20 stages, 10 Ft diam, 35 Ft high, 50 HP impeller
F-101	6	Floating roof solvent storage tank, $2.97 \times 10^6$ gal. capacity each, total 2 weeks storage
P-101	1 and 1 spare	Centrifugal Pump, 30 Ft head, 152 gal/min, 3 HP
P-102	1 and 1 spare	Centrifugal Pump, 20 Ft head, 1062 gal/min, 15 HP
P-103	1 and 1 spare	Centrifugal Pump, 50 Ft head, 884 gal/min, 15 HP
P-104	1 and 1 spare	Centrifugal Pump, 50 Ft head 1005 gal/min, 20 HP
P-105	1 and 1 spare	Centrifugal Pump, 80 Ft head 29 gal/min, 1 HP

TABLE 11

## LIST OF EQUIPMENT FOR CASE 2 (W/O BEER STILL)

Item No.	No. Required	Description
C-101	1	Centrifuge, Filters continuous vibratory screentype, 67 tons/hr, 170 HP
E-101	3	Extraction column, 72 stages, 14 Ft diam, 135 Ft high, 50 HP impeller
S-101	15	Floating-roof solvent storage tank, 3.00 x 10 <sup>6</sup> gal capacity each total 1 week storage
T-101	1	Coagulation tank system, alum coagulant, 1.20 MGD capacity
F-101	1	Dissolved air-flotation unit, 3000 gpd/sq Ft loading 25-50% recycle rate
D-101	1 and 1 spare	Centrifugal Pump, 30 Ft head, 922 gal/min, 20 HP
P-102	6 and 3 spare	Centrifugal Pump, 50 Ft head, 926 gal/min, 20 HP
P-103	6 and 3 spare	Centrifugal Pump, 50 Ft head, 906 gal/min, 20 HP
P-104	1 and 1 spare	Centrifugal Pump, 20 Ft head, 836 gal/min, 10 HP
P-105	1 and 1 spare	Centrifugal Pump, 20 Ft head, 1.3 gal/min, 1 HP
P-106	1 and 1 spare	Centrifugal Pump, 80 Ft head, 835 gal/min, 40 HP

coefficient for the system, and the ethanol recovery rate of 96 wt%. The extractors were designed as countercurrent continuous multistage towers, and a solvent to feed rate of 5.9 was established.

The solvent storage tanks were sized based on storage capacity. They are of the floating roof-storage type because of safety considerations.

The design of the coagulation unit is based on capacity and a 200 ppm alum concentration (18). The dissolved-air flotation system design was based on surface hydraulic loading, of which an average value of 3000 gallons per day per square foot was assumed (18).

All pumps, motors, and starters were sized from a nomograph given in literature (19). This design was based on an assumed pressure head and a 60% pump efficiency. Allowance was taken for spare pumps, motors, and starters.



## CHAPTER X

### ENERGY REQUIREMENTS

#### Introduction

The energy balances discussed below for the azeotrope distillation and the two extraction processes examine both the individual energy requirements of the processes and complete plant requirements, that is, complete ethanol production plants (as described above) which have incorporated each of the above three separation schemes. Horsepower requirements for all equipment such as impellers, and pumps are taken into account. Steam heating requirements are noted, as are energy values of lost ethanol product and solvent gasoline.

Energy payback will be defined as the energy value in the ethanol recovered divided by the energy required to produce and recover the ethanol. Here, lost solvent was counted as an energy requirement, whereas lost ethanol was reflected by the reduced total energy value of the product.

The percent energy savings is defined as the difference between the energy usage of a distillation-equipped plant and an extraction-equipped plant, divided by the energy requirement of the distillation-equipped plant. For this calculation, lost ethanol is counted as an energy usage for equivalency.

Electrical requirements were converted to Btu/hr units assuming a 60% motor efficiency and a 33% power plant efficiency. The energy values of ethanol and gasoline were taken to be 75,600 Btu/gal. and 115,000 Btu/gal., respectively (7).

#### Ternary Azeotrope Distillation

All values given here were obtained from previous work (8).

Energy requirements for the distillation process included 158.7 million Btu/hr for steam to the beer still and the three columns, and 173 horsepower for all pumps and the centrifuge C-101. Additionally, 175,940 gal/hr of cooling water was required for condensers K-101 and K-102. This totals, without cooling water, 160.9 million Btu/hr.

The energy requirements for the rest of the plant were 389.5 million Btu/hr, giving a complete plant total of 550.4 million Btu/hr. The energy value of the product was 519.2 million Btu/hr, and the energy payback was found to be 94.3%.

#### Case 1 (w/beer still)

The energy requirements for this extraction process were: 51.3 million Btu/hr steam requirements for the beer still (8), 253 horsepower for the pumps, extractor and centrifuge. The value of lost energy was found to be 20.8 million Btu/hr in ethanol and 0.3 million Btu/hr in lost gasoline solvent.

Energy payback was found to be 112%, and energy savings was found to be 15.6%.

## Case 2 (w/o beer still)

For this process, horsepower requirements were found to total 681 horsepower, assuming 70 total horsepower for T-101 and the recycle and aspirator pumps for F-101. Lost ethanol totals were as above, 20.8 million Btu/hr, and the energy value of the lost gasoline was found to be 7.9 million Btu/hr.

Energy payback was found to be 123%, with energy savings at 22.4%.



## CHAPTER XI

### ECONOMIC ANALYSIS

#### Introduction

The solvent extraction processes were designed as equivalent substitutes for the ternary azeotrope distillation traditionally used. In other words, all required equipment and energy costs, and certain direct and annual costs were considered in order to make the three processes equivalent. Operation and maintenance cost for additional equipment that could be quantified were also included. All other indirect costs, start-up expenses, manufacturing costs, and general expenses were considered to be equivalent for all three processes. This assumption is based on two observations. First, the distillation and extraction processes would be integrated as only part of an entire ethanol production plant, where many of the above costs reflect support facilities and expenses for the plant as a whole. Secondly, any differences between the distillation and extraction processes in regard to many of the above costs could not be accurately quantified.

#### Purchased Equipment Costs

The estimated purchased equipment cost for all required equipment for the ternary azeotrope distillation process are given in Table 12. These costs were obtained from the previous plant design (8), and



TABLE 12

## ESTIMATED PURCHASED EQUIPMENT COSTS - AZEOTROPE DISTILLATION

Item No.	Description	No. Req'd	Cost/Item	Total Cost
X-101	Beer Still	1	\$ 44,600	\$ 44,600
C-101	Centrifuge	1	154,800	154,800
D-101	Rectifying Column	1	264,500	264,500
K-101	Condensor for D-101	1	18,100	18,100
T-101	Reflux Drum	1	2,900	2,900
D-102	Azeotrope Column	1	232,400	232,400
K-102	Condensor for D-102	1	23,200	23,200
S-101	Azeotropic Separator	1	13,400	13,400
D-103	Benzene-Recovery Column	1	22,000	22,000
S-102	Fusel Oil-Water Separator	1	7,500	7,500
P-101, 105	Pumps	10	1,400	14,100
		Total		\$797,500

were updated to July 1979 costs by the Marshall-Stevens' cost index for chemical process industry equipment (20). All total costs include shipping estimated at 5% of the purchased equipment cost (PEC), and tax estimated at 4%.

Tables 13 and 14 list the estimated purchased equipment costs for all required equipment for Case 1 and Case 2, respectively. All total costs are in July 1979 dollars, and include 5% shipping and 4% tax.

The costs for the beer still for Case 1 and for the centrifuges for both Cases 1 and 2 were obtained from the previous design (9). The costs for the extractor towers were obtained from York Process Equipment Company (21). These costs are total extractor costs and include fabrication, baffles, drive unit, shell, impellers, stuffing box, support bearings, and manways.

The extractor tower designs were not optimized and cost estimates were for budget purposes only and were conservative on the high side. Also it was suggested that further experimentation could result in more liberal stage efficiencies, again reducing cost (21).

The costs for the solvent storage tanks were obtained from nomographs (17), and were updated from January 1967 to July 1979 costs by using the Marshall and Stevens' index (22).

The cost for the coagulation system was obtained from literature (18). Included in the purchased equipment cost is two proportioning feeders, tanks, pumps, and 30 days bulk storage for coagulation chemicals. Costs for the air-flotation system were obtained from nomographs (18), and include all tanks and internals, air-pressurizing

TABLE 13

## ESTIMATED PURCHASED EQUIPMENT COSTS - CASE 1 (W/BEER STILL)

Item No.	Description	No. Req'd	Cost/Item	Total Cost
X-101	Beer Still	1	\$ 44,600	\$ 44,600
C-101	Centrifuge	1	154,800	154,800
E-101	Extraction Column	1	227,400	227,400
T-101	Solvent Storage Tank	6	221,200	1,327,200
P-101	Centrifugal Pump <sup>a</sup>	2 <sup>b</sup>	1,100	2,200
P-102	Centrifugal Pump	2	2,500	5,000
P-103	Centrifugal Pump	2	2,400	4,800
P-104	Centrifugal Pump	2	2,600	5,200
P-105	Centrifugal Pump	2	1,300	<u>2,600</u>
		Total		<u>\$1,773,800</u>

<sup>a</sup>Includes motor and starter costs.

<sup>b</sup>Includes spare pump, etc.

TABLE 14

## ESTIMATED PURCHASED EQUIPMENT COSTS FOR CASE 2 (W/O BEER STILL)

Item No.	Description	No. Req'd	Cost/Item	Total Cost
C-101	Centrifuge	1	\$171,700	\$ 171,700
E-101	Extraction Column	3	909,700	2,729,100
S-101	Solvent Storage Tank	15	257,900	3,868,500
T-101	Coagulation Tank System	1	23,100	23,100
F-101	Dissolved Air-Flotation Unit	1	139,900	139,900
P-101	Centrifugal Pump <sup>a</sup>	2 <sup>b</sup>	2,500	5,000
P-102,3	Centrifugal Pump	18	2,600	46,800
P-104	Centrifugal Pump	2	2,400	4,800
P-105	Centrifugal Pump	2	800	1,600
P-106	Centrifugal Pump	2	3,400	<u>6,800</u>
			Total	<u>\$6,997,300</u>

<sup>a</sup>Includes motor and starter costs

<sup>b</sup>Includes spare pump, etc.



equipment, recycle equipment, valves, and piping. Both of the above costs for the coagulation and air-flotation systems were obtained as installed costs, in July 1972 dollars. The purchased equipment costs were determined using estimates for installation costs recommended by literature (17). These costs were then updated using the Marshall and Stevens' cost index (23).

All pump costs were estimated from a nomograph (24), and were updated to July 1979 costs from third quarter 1968 costs using the Marshall and Stevens' cost index (22). Motors and starters costs were obtained as July 1979 costs from a local retailer (25).

#### Fixed Costs

Only those fixed costs which were considered to vary between the distillation and two extraction processes described were taken into account. These costs included installation, insulation, instrumentation, and piping. All fixed costs for the above processes were estimated either directly or indirectly as percentages of the respective purchased equipment costs, by guidelines given in literature (17). These costs are given in Table 15.

Because of the use of benzene, the azeotrope distillation process was designed as fully automatic (8), and instrumentation costs were estimated as large at 25% of the total purchased equipment cost. Piping, too, was expected to be fairly complex, and was estimated at 50%.

Because the Case 2 extraction process was designed to operate at ambient temperatures, no insulation costs are included. Insulation

TABLE 15

## FIXED COSTS FOR THE AZEOTROPE DISTILLATION, CASE 1, AND CASE 2

A) Azeotrope distillation, PEC <sup>a</sup> = \$797,500	
1. Installation (30% PEC)	\$ 239,300
2. Insulation (8% PEC)	63,800
3. Instrumentation (25% PEC)	199,400
4. Piping (50% PEC)	398,800
	Total \$ 901,300
.....	
B) Case 1 (w/beer still), PEC = \$1,773,800	
1. Installation	
a. Beer Still, X-101 (30% IPEC <sup>b</sup> )	\$ 13,400
b. Centrifuge, C-101 (20% IPEC)	31,000
c. Extraction Column, E-101	5,000
d. Solvent Storage Tank, T-101 (20% IPEC)	265,400
e. Centrifugal Pump, P101,5 (20% IPEC)	4,000
	\$ 318,800
2. Instrumentation (15% PEC)	266,100
3. Piping (25% PEC)	443,500
	Total \$1,028,400
.....	
C) Case 2 (w/o beer still), PEC = \$8,634,700	
1. Installation	
a. Centrifuge, C-101 (20% IPEC)	\$ 34,300
b. Extraction Column, E-101	21,000
c. Solvent Storage Tank, S-101 (20% IPEC)	773,700
d. Coagulation Tank System, T-101 (43% IPEC)	9,900
e. Dissolved Air-Float. Unit, F-101 (43% IPEC)	60,200
f. Centrifugal Pump, P-101,6 (20% IPEC)	13,000
	\$ 912,100
2. Instrumentation (15% PEC)	1,295,200
3. Piping (40% PEC)	3,453,900
	Total \$5,661,200

<sup>a</sup>Purchased equipment cost total.

<sup>b</sup>Individual purchased equipment cost.

costs for the Case 1 beer still were also neglected. All solvent extraction towers are received fully fabricated, and only erection costs were included. All other installation costs for Cases 1 and 2 were estimated independently for increased accuracy from literature recommendations (17). Piping costs for Case 2, because of much higher flow rates, were estimated at 40% rather than 25% as in Case 1.

#### Capital Investment

The only additional costs considered here were those for the expanded waste facility in Case 2. The additional wastewater generated by this flowscheme was 418,460 lbs/hr, with a gasoline concentration of 40 ppm. This represented an increase of 108% over the original (distillation) flowrate. The additional capital investment in the treatment facility was estimated at \$662,800 based on the flow rates and the established cost of the original facility from literature (8).

The equivalent capital investment will be defined here as the necessary investment of capital into equipment, fixed costs, and additional facilities in order to make the distillation and extraction processes equal for economic comparison. Based on this, the equivalent capital investment for the azeotrope distillation was found to be \$1,698,800. The equivalent capital investment for Case 1 and Case 2 were found to be \$2,802,200 and \$12,658,500, respectively.

#### Annual Costs

The annual costs for all three processes are summarized in Table 16.



TABLE 16

## ANNUAL COSTS FOR THE AZEOTROPE DISTILLATION, CASE 1, AND CASE 2

---

A) Azeotrope Distillation	
1. Energy costs	
a. Steam generation, \$7.00/ton lignite, shipped	\$ 933,800
b. Cooling costs, \$0.15/1000 gal	208,100
c. Electrical costs, \$0.01927/KWH (26)	32,700
	<u>\$1,174,600</u>
2. Cost of lost ethanol, \$1.55/200 proof gal (27)	2,200
	<u>\$1,176,800</u>
.....	
B) Case 1 (w/beer still)	
1. Energy costs	
a. Steam generation	\$ 301,800
b. Electrical Costs	47,800
	<u>349,600</u>
2. Cost of lost ethanol	3,100,000
3. Cost of lost solvent, \$0.70/gal gasoline	13,600
	<u>\$3,463,200</u>
.....	
C) Case 2 (w/o beer still)	
1. Energy costs	
a. Electrical costs	\$ 128,600
2. Cost of lost ethanol	3,100,000
3. Cost of lost solvent	378,900
4. Cost of coagulant, \$7.90/100 lbs alum (27)	52,300
5. Main. and operation of T-101, (18)	29,000
6. Main. and operation of F-101 (18)	7,000
	<u>\$3,695,800</u>

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These costs included energy costs, costs of lost solvent and ethanol in the wastewater, maintenance and operation costs of additional equipment that could be quantified, and cost of coagulant. Because safety requirements would minimize process losses of benzene, ethanol, and gasoline solvent, these costs were neglected.

All annual costs are based on 328.5 days/year operation.

#### Total Equivalent Annual Cost

The total equivalent annual cost will be defined as the annual cost which takes into account the capital investment in equipment and facilities, the fixed costs, and the annual costs in order to make the distillation and extraction processes equal for economic comparison.

The equivalent capital investment was converted to an annual cost assuming a minimum acceptable rate of return of 15%, an equipment service life of 11 years (17), and a salvage value of zero.

Table 17 summarizes the economic findings for all three processes. It can be seen that the total equivalent annual costs for the azeotrope distillation, and Case 1 and Case 2 extractions were found to be \$1,501,400, \$3,998,600, and \$6,114,500, respectively.

It is obvious from these figures, then, that neither extraction process as designed is economically attractive as an alternative to azeotropic distillation. However, the total equivalent annual cost of the Case 1 extraction process is largely due to the loss of ethanol in the wastewater. Higher recovery rates could be attained merely by increased numbers of stages in the extractor tower.

TABLE 17

## ECONOMIC SUMMARY

	Azeotropic Distillation	Case 1 (w/beer still)	Case 2 (w/o beer still)
Purchased Equipment Total	\$ 797,500	\$1,773,800	\$6,997,300
Fixed Costs Total	901,300	1,028,400	5,661,200
Equivalent Capital Investment	1,698,800	2,802,200	12,658,500
Annual Equivalent Capital Investment	324,600	535,400	2,418,700
Annual Costs Total	1,176,800	3,463,700	3,695,800
Total Equivalent Annual Cost	\$1,501,400	\$3,998,600	\$6,114,500

As was mentioned above, a basis for this study was a recovery rate of 96 wt% of ethanol in the extractor. It is estimated that a recovery rate of 99 wt% could be attained by an additional extractor investment of 15% of the original cost (28). Using these figures, and the calculational procedure as before, the total equivalent annual cost was found to be \$1,682,700. This figure is only approximate, and does not take into account additional energy costs of the extractor, its additional installation costs, or minor alterations in flow rates.

## CHAPTER XII

### CONCLUSIONS

Based on test results and observation, the results of this investigation are:

1. "Freon" TF, 1-pentene, and ethyl ether are not effective solvents for the extraction of ethanol from water.
2. The volume percent ethanol in the extract on a solvent-free basis is a quantity that should be examined in the selection of a solvent for the extraction of ethanol from water.
3. Solvents possessing a low distribution coefficient (like gasoline) generally will not be an attractive alternative to distillation unless concentration of the ethanol-water feed is accomplished prior to the extraction step. This is due to the high flow rates of the solvent and the necessity for large wastewater treatment facilities.
4. Extraction processes yield a significant energy savings over azeotropic distillation in the separation of ethanol from water.
5. The economics of extraction are particularly sensitive to the ethanol recovery rates.
6. Ethanol recovery rates of less than about 99 wt% are uneconomical.
7. For single-pass extraction processes, the capital investment in solvent storage tanks can be significant.



8. The extraction process described above as Case 1 is a possible economically attractive alternative to distillation if ethanol recovery rates greater than 99 wt% are achieved.

## CHAPTER XIII

### RECOMMENDATIONS

The results of this investigation are preliminary in nature.

Suggestions for further work are:

1. Investigation should be done to find possible attractive mixed solvents.
2. More accurate equilibrium phase data should be determined for the water-gasoline-ethanol system, including temperature dependence.
3. More accurate cost estimation should be performed for the extraction system described above as Case 1.
4. Study should be done to determine the optimum economical recovery rate of ethanol.
5. The economic impact of combining a large source of gasoline solvent, such as a distributor, and a fermentation plant equipped with an extraction recovery scheme should be studied. Eliminating the need for capital investment in solvent storage facilities should significantly improve the extraction economics.

APPENDICES

APPENDIX A

SAMPLE CALCULATIONS FOR DETERMINATION OF EQUILIBRIUM PHASE  
COMPOSITION, DISTRIBUTION COEFFICIENT, SELECTIVITY,  
COMPOSITION ERROR, STATISTICAL F-TEST, ENERGY  
REQUIREMENTS, PURCHASED EQUIPMENT COST,  
AND TOTAL EQUIVALENT ANNUAL COST



Sample calculation for determining the composition of the equilibrium phase from the integrator readout.

Pentene Sample:

- A. Known composition of standard is 97 vol% pentene, 1.5 vol% ethanol, 1.5 vol% water. Respective counts are 2287 and 300 for pentene and ethanol. Water is not detected by flame-ionization detector. Extract sample counts are 2180 and 740 for pentene and ethanol.

$$\text{Pentene vol\%} = (2287/2180) 97 = 92.5\%$$

$$\text{Ethanol vol\%} = (840/300) 1.5 = 3.7\%$$

$$\text{Water vol\%} = 100 - 92.5 - 3.7 = 3.8\%$$

- B. Known composition of standard is 2.0 vol% pentene (270 cts.), 30 vol% ethanol (5203 cts.), and 68 vol% water. Raffinate sample counts are 1220 and 6750 for pentene and ethanol.

$$\text{Pentene vol\%} = (122/270) 2.0 = 9.0\%$$

$$\text{Ethanol vol\%} = (6750/5203) 30 = 38.9\%$$

$$\text{Water vol\%} = 100 - 38.9 - 9 = 52.1\%$$

Sample calculation for the determination of the distribution coefficient from above data:

$$\begin{aligned} \text{Distribution Coefficient} &= \frac{\text{vol\% ethanol in extract}}{\text{vol\% ethanol in raffinate}} \\ &= 3.7/38.9 = 0.095 \end{aligned}$$

These are averaged for all samples over the operating range of extraction concentrations.

Sample calculation for the determination of the selectivity from the above data:

$$\begin{aligned} \text{Selectivity} &= \frac{(\text{vol\% ethanol in extract})/(\text{vol\% water in extract})}{(\text{vol\% ethanol in raffinate})/(\text{vol\% water in raffinate})} \\ &= \frac{3.7/3.8}{38.9/52.1} = 1.30 \end{aligned}$$

These are averaged for all samples over the operating range of extraction concentrations.

Sample calculation for the determination of the vol% ethanol in the extract on a solvent-free basis.

$$\text{Ethanol vol\%} = 3.7\%, \text{water vol\%} = 3.8\%$$

$$\begin{aligned} \text{Ethanol vol\% on} \\ \text{Solvent-free basis} &= \frac{3.7}{3.8+3.7} = 49.3\% \end{aligned}$$

Sample calculation for the determination of the error of sample composition.

Counts of solvent in extract samples:

a.	1910	b.	2320	c.	2740	d.	2940
	1900		2340		2780		2930
	1880		2370		2810		3000

Counts of ethanol in raffinate samples:

e.	2280	f.	3400	g.	2380
	2340		3340		2330
	2350		3440		2350

Note: These values vary from set to set because they were taken from a range of ethanol concentration, with both "Freon" TF and pentene solvents.

The confidence interval was defined by literature (29):

$$C.I. = \bar{x} \pm t_{.90, (n-1)} \left( \frac{s^2}{n} \right)$$

Where  $\bar{x}$  = mean value

$$t_{.90, (n-1)} = t\text{-value at } 90\% \text{ confidence level} = 1.886$$

n = number of samples in set (3)

$$s_{\bar{x}}^2 = s^2/n \text{ where } s^2 \text{ is variance of set}$$

Findings were:

	SAMPLE SET							
	a.	b.	c.	d.	e.	f.	g.	Avg.
$\bar{x}$	1897	2343	2776	2957	2323	3393	2353	--
$s_{\bar{x}}^2$	78	211	411	478	478	844	211	--
$((t_{.90, (2)} s_{\bar{x}}^2) / \bar{x}) 100\%$	7.7	17.0	27.9	30.5	38.8	46.9	16.9	26.5%

Sample calculation for F-test:

Sample distribution coefficients:

	<u>"Freon" TF</u>	<u>Pentene</u>	<u>Ethyl Ether</u>
	0.076	0.095	--
	0.061	0.079	--
	0.036	0.054	0.089
	0.025	0.067	0.099
	0.018	0.064	0.092
	0.020	0.076	0.171
	0.017	0.040	0.210
Average:	$\mu_1=0.036$	$\mu_2=0.068$	$\mu_3=0.134$

$$H_0: \mu_1 = \mu_2 = \mu_3 \quad A_0: \mu_1 \neq \mu_2 \neq \mu_3$$

The test F-value was taken from literature (29):

$$F = \frac{\sum_{i=1}^k n_i (\bar{x}_{i.} - \bar{x}_{..})^2 / (k-1)}{\frac{\sum_{i=1}^k \sum_{j=1}^n (x_{ij} - \bar{x}_{i.})^2 / \sum_{i=1}^k (n_i - 1)}$$

Where k = number of populations (3)

n = number of samples in population

$x_{ij}$  = a given sample

$\bar{x}_{i.}$  = a population mean

$\bar{x}_{..}$  = overall mean

$$F = 0.0159/0.00103 = 15.45$$

From F-tables, at 95% confidence level,

$$F_{.95,2,17} = 3.6, \quad F > F_{.95,2,17}: \text{reject } H_0$$



Sample calculation showing the energy requirement calculations for case 1:

A. Horsepower requirements:

E - 101	-	50 HP
C - 101	-	150 HP
Pumps	-	<u>53 HP</u>
		253 HP

Assume: 60% motor efficiency  
33% power plant efficiency

Known: 1 HP = .7457 KW  
1 KW = 3414 Btu/hr

$$(253 \text{ HP} / .60) (.7457 \frac{\text{KW}}{\text{HP}}) = 198.6 \text{ KW}$$

$$(198.6 \text{ KW} / .33) (3414 \frac{\text{Btu/hr}}{\text{KW}}) = 2.055 \text{ million Btu/hr}$$

B. Steam requirements:

X-701 - 51.30 Btu/hr (8)

C. Lost product, solvent energy:

Basis 6874 gal ethanol and fusel oils/hr

Known: 75,600 Btu/gal ethanol (7)  
115,000 Btu/gal gasoline (7)  
96% recovery of ethanol

$$\begin{aligned} \text{Lost ethanol energy} &= (.04) (6350.8 \frac{\text{gal ethanol}}{\text{hr}}) (75,600 \frac{\text{Btu}}{\text{gal ethanol}}) \\ &= 20.8 \text{ million Btu/hr} \end{aligned}$$

Basis: 15 lb/hr lost gasoline

$$\begin{aligned} \text{Lost gasoline energy} &= (15 \frac{\text{lb gasoline}}{\text{hr}}) (\frac{1}{(.73)(8.341)} \frac{\text{gal}}{\text{lb gasoline}}) \\ &\quad (115,000 \frac{\text{Btu}}{\text{gal}}) \\ &= .28 \text{ million Btu/hr} \end{aligned}$$

## D. Energy payback:

Defined as (product energy recovered/ total energy requirement)100%

Known: Total energy of rest of plant is  
389.5 million Btu/hr (8)

Recovered energy:

(.96)(6874 gal ethanol + Fusel oils/hr)(75,600 Btu/hr) =  
498.9 million Btu/hr

Energy payback:  $\left( \frac{498.9}{389.5 + 0.3 + 51.3 + 2.6} \right) 100\% = 112\%$

## F. Percent Energy Savings:

Known: Total energy usage of distillation process is  
550.4 million Btu/hr (8)

Energy savings =  $\frac{550.4 - (389.5 + 0.3 + 51.3 + 2.6 + 20.8)}{550.4} = 15.6\%$

Sample calculation showing calculation of Case 1 solvent storage tank design, purchased equipment cost, and installation.

A. Basis: 323,127 lbs/hr gasoline flow

Assume: 2 weeks storage capacity

Known: 0.73 specific gravity for gasoline

$$(323,127 \frac{\text{lbs}}{\text{hr}}) (\frac{24 \text{ hrs}}{\text{day}}) (\frac{14 \text{ days}}{2 \text{ weeks}}) (\frac{1 \text{ Ft}^3}{62.4 \text{ lbs}}) (\frac{7.481 \text{ gals}}{\text{Ft}^3}) (\frac{1}{.73})$$

$$= 1.783 \times 10^7 \text{ gals/2 wk storage}$$

assume 6 tanks,  $2.97 \times 10^6$  gal. capacity

B. From (17), cost per tank of floating-roof

Storage type is \$90,000, January 1967 cost using Marshall-Stevens'

$$\text{Index (22), July 1979 cost} = (\$90,000/\text{tank}) (\frac{577}{256}) = \$202,900$$

Shipping estimated at 5% = \$ 10,200

Tax estimated at 8% = \$ 8,100

Purchased Equipment Cost = \$221,200

C. From (17), installation for tanks estimated at 20% of the purchased equipment cost:

Installation cost/tank - \$44,200

Sample calculation showing the annual cost calculation for Case 1.

Known: Total annual costs are \$3,463,200

Total equivalent capital investment is \$2,802,200

Assume: 15% minimum rate of return

11 yr service life of equipment

Zero salvage

$$\text{Total Equivalent Annual Cost} = (P-L) \frac{\text{CRF}}{i-n} + L_i + AC \quad (30)$$

Where P = Capital investment

L = Salvage value

CRF = Capital recovery factor - .19107

i = Minimum rate of return

n = Service life

AC = Total Annual cost

With zero salvage this simplifies to:

$$\text{T.E.A.C.} = (\$2,802,200) \frac{\text{CRF}}{.15-11} + \$3,463,200$$

$$= \$535,400 + 3,463,200$$

$$= \$3,998,600$$



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