

PHASE EQUILIBRIA IN THE ETHANOL-WATER-GASOLINE SYSTEM

by

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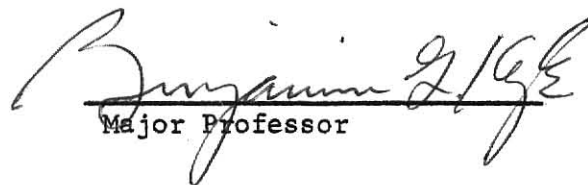
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CHAPTER I

INTRODUCTION

The ultimate role of gasohol in the energy future of the nation depends on whether its production can be made both energetically and economically appealing. However, to date all published energy and economic analyses for the production of gasohol have been predicated on the assumption that anhydrous ethanol would be produced and subsequently blended with gasoline. Because of the difficulty in obtaining anhydrous ethanol, the separational energy requirement plays a major role in determining the total processing energy (23) and thus the economic outlook for gasohol production. At Kansas State University an energy-efficient process for gasohol production has been proposed (11); however, a recent publication (12) indicates that a similar process is being studied at Purdue University. In the Kansas State University process (hereafter identified as the KSU process), instead of producing pure ethanol for blending with gasoline, the gasoline is used as an extracting solvent to extract ethanol from aqueous solution and the product of the process is gasohol. A schematic diagram of the KSU process is shown on Figure 1.1 with the major equipment items identified. The process can accept an ethanol-water feed of any concentration, but design is based on fermentation beer as the feed.

The beer (stream 1) is fed to the ethanol concentration column after being preheated by heat exchange with the bottoms of that column (stream 2). The bottoms contain very little alcohol and the distillate (stream 3) contains approximately 80 wt% ethanol (61 mol%). A reasonably low reflux ratio is required to accomplish this separation.

The concentrated aqueous ethanol solution (stream 3) enters the extraction column where it is contacted countercurrently with gasoline (stream 5). The gasoline extracts ethanol from the aqueous phase and produces a wet gasohol (stream 6) containing approximately 1 wt% water which must be removed. The spent aqueous phase leaving the extraction column (stream 4) contains considerable ethanol and is returned to the alcohol concentration column for recovery. Liquid-liquid equilibrium data show that the extraction becomes more favorable as the temperature is increased. These data are displayed on Figures 1.2 and 1.3.

The wet gasohol (stream 6) is dried by distillation in the gasohol dehydration column. The distillate (stream 7) containing ethanol, water, and gasoline is totally condensed, and separated into aqueous and gasoline phases. The aqueous phase (stream 8) is returned to an appropriate point in the extraction column for ethanol and gasoline recovery. Part of the gasoline phase (stream 9) is blended with the bottoms from this column (stream 10) to form the desired gasohol product. The rest of it is returned to the extraction column. In this process, condensing ethanol vapor from the alcohol concentration column can be used to supply heat to the gasohol dehydration column and also to preheat gasoline (stream 5) to the operating temperature of the extraction column.

Because the equilibrium distribution of ethanol between water and gasoline is not favorable for extraction by gasoline, a fairly high concentration of aqueous ethanol entering the extractor is required to produce gasohol containing 10 volume percent (11 wt%) ethanol. This is the reason why the process requires a distillation step prior to extraction with gasoline. The vapor-liquid equilibrium relationship for the

ethanol-water system is quite favorable until fairly high ethanol concentrations are reached, and therefore the distillation energy requirement for an 80 wt% distillate would be modest. Also, because of the extreme deviations from ideal solution behavior manifested by the ethanol-water-gasoline system, the dehydration of wet gasohol should be relatively easy to carry out and require very little energy.

In order to determine the feasibility of this proposed process, it is necessary to have data for the distillation of ethanol between water and gasoline. And the liquid-liquid equilibrium data are also needed to provide the solubility of water in gasoline. Since the experimental liquid-liquid equilibrium data for systems comprised of ethanol, water, and gasoline at two different temperatures have been previously determined (11), as shown on Figures 1.2 and 1.3, the objectives of this research are: 1). the application of thermodynamics and solution theory to estimate vapor-liquid equilibrium data for the design of a gasohol dehydration column, 2). design of the gasohol dehydration column, 3). energy analysis based on preliminary studies.

Because of the extreme deviations from ideal solution behavior manifested by the ethanol-water-gasoline system, we have to carefully select a suitable activity coefficient equation for this system. In Chapter II several of the more commonly used and also some of the recently developed activity coefficient equations are presented. Procedures for estimating the activity coefficient parameters from vapor-liquid equilibrium data for the ethanol-water binary system are also presented in Chapter II. Chapter III deals mainly with the procedures for estimating the activity coefficient parameters of the

UNIQUAC (universal quasi-chemical) equation (1,2) from the ethanol-water-gasoline ternary tie line data. In Chapter IV we use the UNIQUAC equation for the calculation of the equilibrium flash vaporization of ethanol-water-gasoline mixtures. In Chapter V we use the UNIQUAC equation in the plate-to-plate calculation for the gasohol dehydration column. In order to investigate the feasibility of dehydration of wet gasohol, tests with a laboratory stripping column were performed and the results are discussed in Chapter VI. Finally, design and evaluation of the KSU process are considered in Chapter VII.

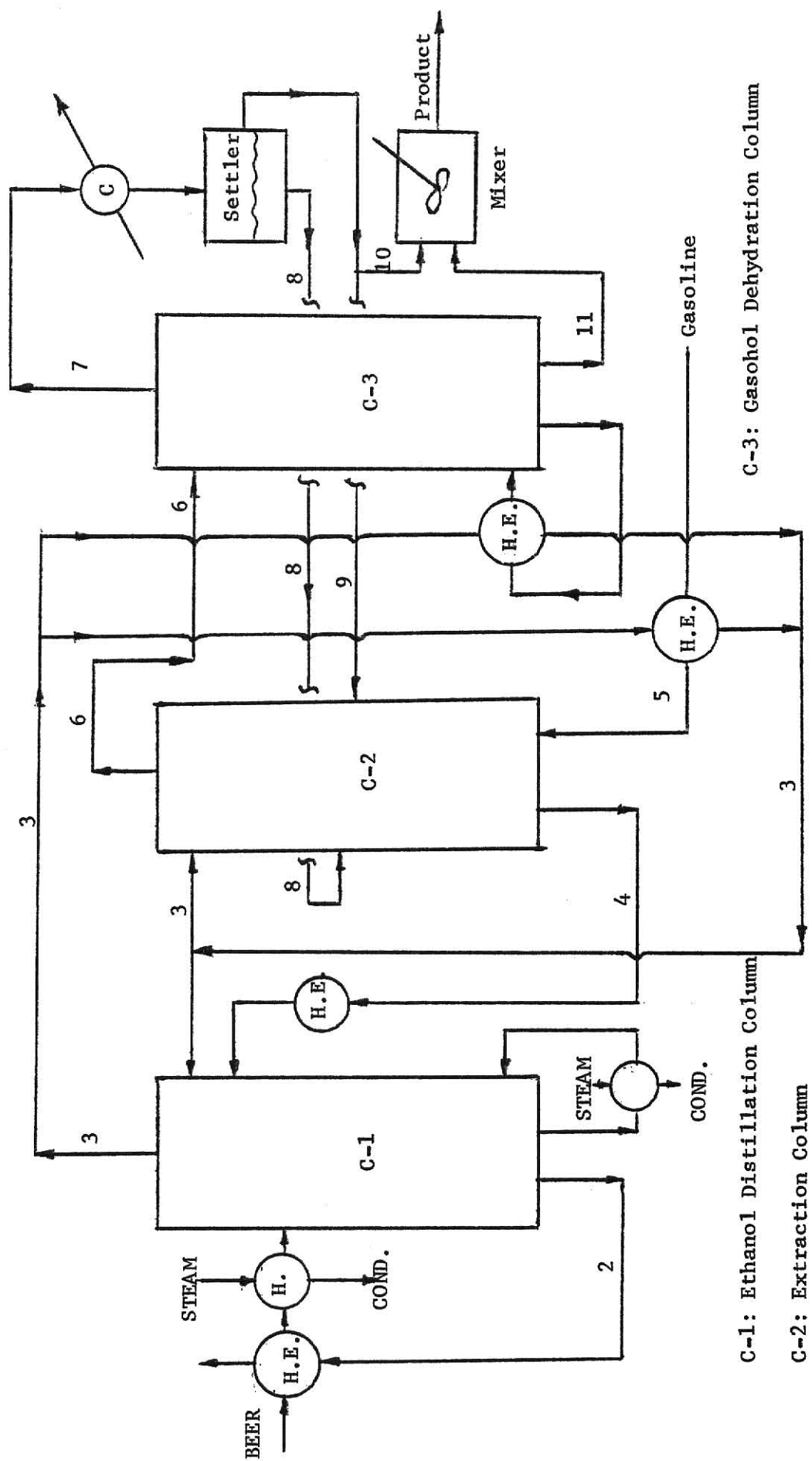


Figure 1.1 Schematic Diagram of KSU Process

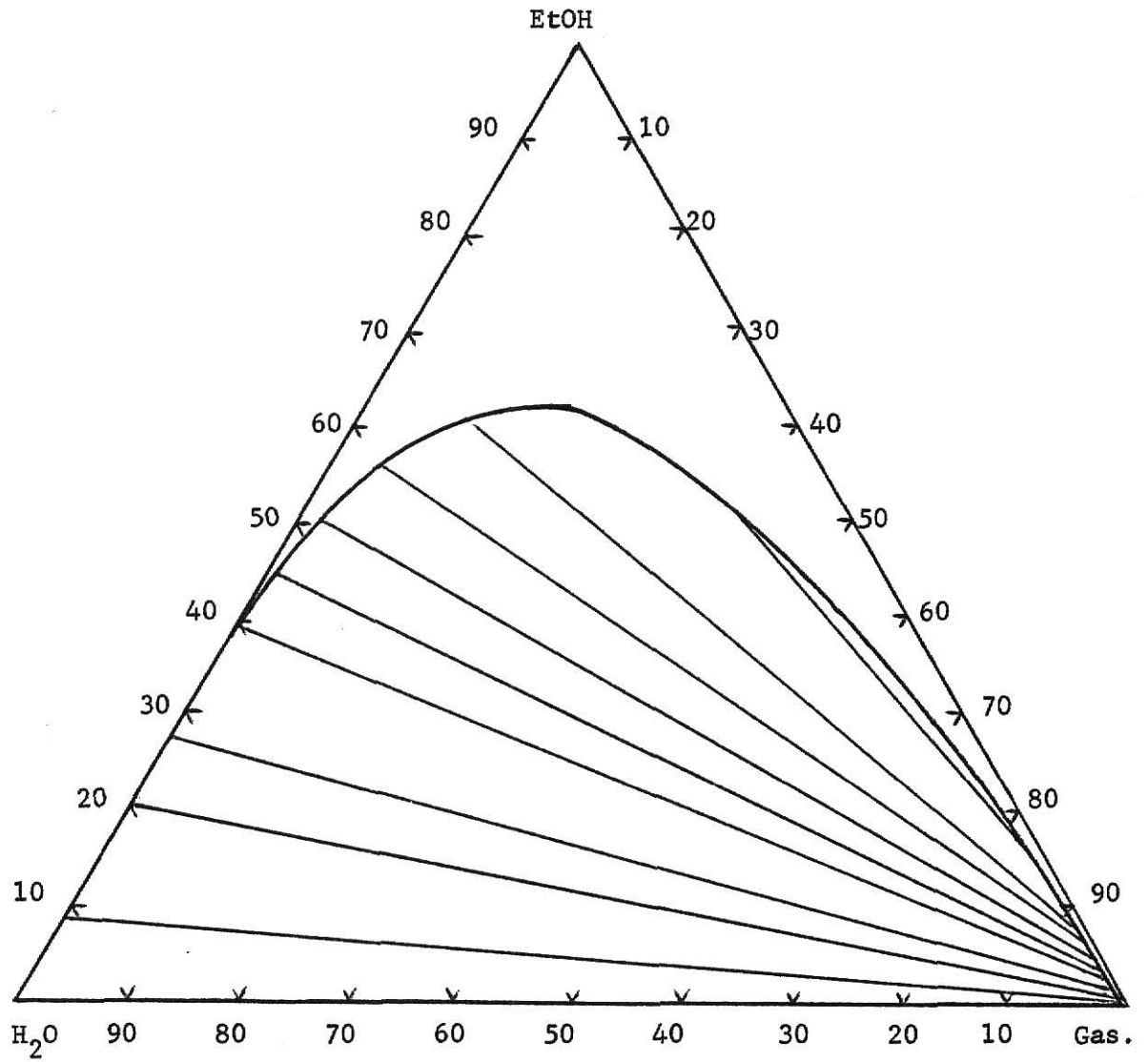


Figure 1.2 Ethanol-Water-Gasoline Phase Diagram at 50 °C (Wt.%)

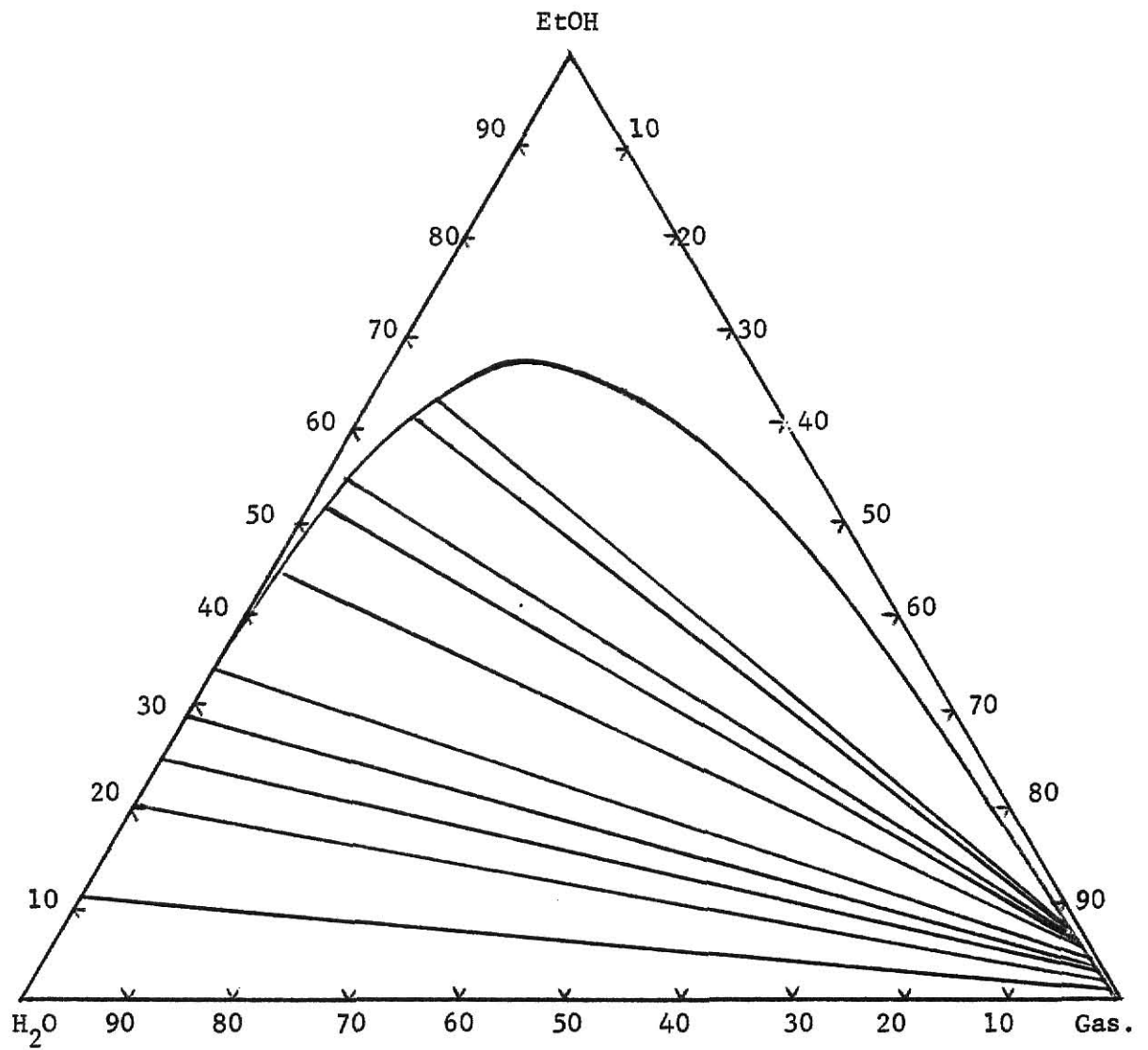


Figure 1.3 Ethanol-Water-Gasoline Phase Diagram at 25 °C (Wt.%)

CHAPTER II

ETHANOL-WATER BINARY SYSTEM

1. Introduction

In order to design the columns used in the KSU gasohol production process, we need accurate phase equilibrium data for the ethanol-water binary system and the ethanol-water-gasoline system. Since the experimental determination of phase equilibrium for the ethanol-water-gasoline system over a wide range of compositions and temperatures is expensive and time-consuming, it is desirable for us to predict the phase behavior or lessen the experimental effort by using available data. The thermodynamic concept of activity coefficient has proven to be an effective means of data reduction in phase equilibrium. For example, it has been shown that through this concept data for a binary system constituted from components of a multicomponent system can be used to reduce the data required to describe the multicomponent system. Information about the ethanol-water system can therefore be used to characterize the ethanol-water-gasoline system. Data for this binary system are plentiful in the literature and the object of this Chapter is to put this information in a usable form.

2. Fundamental Equation of Vapor-Liquid Equilibrium

When the vapor phase is in equilibrium with the liquid phase, the fugacity of each component in both phases is equal. Then,

$$f_1^V = f_1^L \quad (2.1)$$

where

f_i^V is the fugacity of component i in the vapor phase,
 f_i^L is the fugacity of component i in the liquid phase.

When the vapor phase obeys the ideal gas law and the liquid phase can be regarded as an ideal solution, the following equations hold:

$$f_i^V = Py_i \quad (2.2)$$

$$f_i^L = p_i^o x_i \quad (2.3)$$

and thus

$$Py_i = p_i^o x_i \quad (2.4)$$

where

P is the total pressure of the system, atm.,

p_i^o is the vapor pressure of the i -th component, atm.,

x_i and y_i are the mole fractions of the i -th component in the liquid phase and vapor phase respectively.

The vapor phase usually obeys the ideal gas law at atmospheric pressure. Accordingly, if the liquid solution to be treated is also ideal, it is possible to calculate the vapor-liquid equilibrium relation from the total pressure (P) and the vapor pressure (p^o) using equation (2.4). However, usually the liquid solution is not ideal, and the fugacity of the liquid phase is given by:

$$f_i^L = p_i^o x_i \gamma_i \quad (2.5)$$

where

γ_i is the activity coefficient of component i .

In this case, the vapor-liquid equilibrium relation can not be

calculated unless information about the activity coefficient is obtained in advance. Therefore, determination of the activity coefficient is most important for calculating the vapor-liquid equilibrium relation of non-ideal solutions.

3. Activity Coefficient Equations

In order to calculate the activity coefficient of each component in the mixture, we should know its composition dependence. There is a basic thermodynamic relation, the Gibbs-Duhem equation, which gives the necessary condition for the relation between compositions and activity coefficients at constant T and P. That is:

$$\left[\sum_{i=1}^n x_i d \ln \gamma_i = 0 \right]_{T,P} \quad (2.6A)$$

When we consider a liquid phase consisting of two components, eq. (2.6A) becomes:

$$\left[x_1 d \ln \gamma_1 + x_2 d \ln \gamma_2 = 0 \right]_{T,P} \quad (2.6B)$$

or

$$\left[x_1 (d \ln \gamma_1 / dx_1) + x_2 (d \ln \gamma_2 / dx_1) = 0 \right]_{T,P} \quad (2.6C)$$

From eq. (2.6C) we see that γ_1 and γ_2 are not independent of each other, and that at constant T and P changes in γ_1 are related to changes in γ_2 . Equation (2.6C) is a necessary condition but is not sufficient to specify a unique relationship between γ and x . There are a number of algebraic functions relating γ and x , which satisfy the Gibbs-Duhem equation and are therefore thermodynamically acceptable. However, over many years of the study of phase equilibrium several equations have been identified as having rather broad applicability and consequently have enjoyed

wide usage. Five of these equations are used here to calculate the vapor-liquid equilibrium relation of the ethanol-water binary system. They are listed below:

The Margules Equation

$$\ln \gamma_1 = x_2^2 (A_{12} + 2 (A_{21} - A_{12}) x_1) \quad (2.7A)$$

$$\ln \gamma_2 = x_1^2 (A_{21} + 2 (A_{12} - A_{21}) x_2) \quad (2.7B)$$

The Van Laar Equation

$$\ln \gamma_1 = A_{12} / (1 + A_{12}x_1 / A_{21}x_2)^2 \quad (2.8A)$$

$$\ln \gamma_2 = A_{21} / (1 + A_{21}x_2 / A_{12}x_1)^2 \quad (2.8B)$$

The Wilson Equation (27)

$$\ln \gamma_1 = -\ln(x_1 + x_2 G_{12}) + x_2 (G_{12} / (x_1 + x_2 G_{12}) - G_{21} / (x_2 + x_1 G_{21})) \quad (2.9A)$$

$$\ln \gamma_2 = -\ln(x_2 + x_1 G_{21}) + x_1 (G_{21} / (x_2 + x_1 G_{21}) - G_{12} / (x_1 + x_2 G_{12})) \quad (2.9B)$$

The dependence of the parameters, G_{12} and G_{21} , on temperature is usually taken to be

$$G_{12} = (V_1/V_2) \exp(-A_{12}/RT) \quad (2.9C)$$

$$G_{21} = (V_2/V_1) \exp(-A_{21}/RT) \quad (2.9D)$$

where V_1 and V_2 are the molar volumes of the pure liquids at absolute temperature T , and

A_{12} and A_{21} are parameters which characterize molecular interaction.

The NRTL Equation (16)

$$\ln \gamma_1 = x_2^2 \left(\tau_{21} (\exp(-2\alpha_{12}\tau_{21}) / (x_1 + x_2 \exp(-\alpha_{12}\tau_{21}))^2) + \tau_{12} (\exp(-\alpha_{12}\tau_{12}) / (x_2 + x_1 \exp(-\alpha_{12}\tau_{12}))^2) \right) \quad (2.10A)$$

$$\ln \gamma_2 = x_1^2 \left(\tau_{12} (\exp(-2\alpha_{12}\tau_{12}) / (x_2 + x_1 \exp(-\alpha_{12}\tau_{12}))^2) + \tau_{21} (\exp(-\alpha_{12}\tau_{21}) / (x_1 + x_2 \exp(-\alpha_{12}\tau_{21}))^2) \right) \quad (2.10B)$$

$$\tau_{12} = (g_{12} - g_{22}) / RT = A_{12} / RT \quad (2.10C)$$

$$\tau_{21} = (g_{21} - g_{11}) / RT = A_{21} / RT \quad (2.10D)$$

with

$$g_{12} = g_{21}$$

where

g_{ij} is the energy of interaction between a pair of molecules,
 α_{12} is characteristic of the nonrandomness of mixture.

The Modified UNIQUAC Equation (1, 2)

$$\ln \gamma_1 = \ln(\phi_1/x_1) + (z/2)q_1 \ln(\theta_1/\phi_1) + \phi_2(l_1 - l_2 r_1/r_2) - q_1' \ln(\theta_1' + \theta_2' \tau_{21}) + \theta_2' q_1' (\tau_{21}/(\theta_1' + \theta_2' \tau_{12}) - \tau_{12}/(\theta_2' + \theta_1' \tau_{12})) \quad (2.11A)$$

$$\ln \gamma_2 = \ln(\phi_2/x_2) + (z/2)q_2 \ln(\theta_2/\phi_2) + \phi_1(l_2 - l_1 r_2/r_1) - q_2' \ln(\theta_2' + \theta_1' \tau_{12}) + \theta_1' q_2' (\tau_{12}/(\theta_2' + \theta_1' \tau_{21}) - \tau_{21}/(\theta_1' + \theta_2' \tau_{21})) \quad (2.11B)$$

with

$$l_1 = (z/2)(r_1 - q_1) - (r_1 - 1.0) \quad (2.11C)$$

$$l_2 = (z/2)(r_2 - q_2) - (r_2 - 1.0) \quad (2.11D)$$

$$\phi_1 = x_1 r_1 / (x_1 r_1 + x_2 r_2), \quad \phi_2 = x_2 r_2 / (x_1 r_1 + x_2 r_2) \quad (2.11E)$$

$$\theta_1 = x_1 q_1 / (x_1 q_1 + x_2 q_2), \quad \theta_2 = x_2 q_2 / (x_1 q_1 + x_2 q_2) \quad (2.11F)$$

$$\theta_1' = x_1 q_1' / (x_1 q_1' + x_2 q_2'), \quad \theta_2' = x_2 q_2' / (x_1 q_1' + x_2 q_2') \quad (2.11G)$$

$$\tau_{12} = \exp(-A_{12}/RT), \quad \tau_{21} = \exp(-A_{21}/RT) \quad (2.11H)$$

where

z is the coordination number and is set equal to 10.0,

r is a molecular size parameter,

q is a molecular geometric external surface,

q' is a molecular surface of interaction,

A_{12} and A_{21} are parameters which characterize molecular interaction.

The parameters r , q , and q' are pure-component, molecular-structure constants depending on size and external surface areas of the molecules. Some structural parameters for the UNIQUAC equation are found in the reference (2) and are shown in Table 2.1. The pure-component constants r and q are respectively, measures of molecular van der Waals volumes and surface areas, given by Bondi (3). The original UNIQUAC equation was modified by Anderson and Prausnitz (2) in order to obtain better agreement with systems containing water or alcohols. A new parameter q' was introduced which has been obtained empirically by Anderson and Prausnitz to give an optimum fit to a variety of systems containing water and alcohols. For alcohols, the surface of interaction q' is smaller than the geometric external surface q , indicating that intermolecular attraction is determined primarily by the OH group.

4. Determination of Optimum Parameters of Equations

Parameter estimation methods are based on the selection of parameters in the chosen activity coefficient equation which minimize the deviations between measured and calculated properties. Several objective functions

can be used to measure the extent of deviations. Hirata et al. (7) have evaluated several objective functions which had been suggested in the literature and recommend the following:

$$\text{O.F.} = \sum_{i=1}^n (Q_{\text{exp}} - Q_{\text{cal}})_i^2 \quad (2.12)$$

with

$$Q = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 = G^E/RT \quad (2.13)$$

Q_{exp} is evaluated from an experimental data point and Q_{cal} is calculated from the chosen activity coefficient equation corresponding to x_1 and x_2 of the data point. The summation is over all data points. There are several computational techniques for determining the parameters which minimize the objective function. Hirata tested the following techniques:

- (A) Gaussian technique
- (B) Gradient search technique
- (C) Pattern search technique
- (D) Complex search technique

and found the Gaussian (or nonlinear least square) technique to be most suitable for using the above objective function to obtain parameters in the Wilson equation. They have determined Wilson parameters in this manner for 800 binary systems and have reported these along with a listing of experimental data and a measure of the goodness-of-fit of the Wilson equation. Here we also use the Gaussian technique to estimate the parameters in these five equations.

5. Results and Discussions

Eight sets of data are used in the determination of the optimum parameters. The vapor pressure of each component was calculated by the Antoine equation, as shown below:

$$\text{Log}_{10} p^{\circ} = A - B/(t + C) \quad (2.14)$$

where

p° is the vapor pressure of each component at the centigrade temperature t , (in mm Hg)

A , B , and C are Antoine constants.

The Antoine constants for ethanol and water are given in Table 2.2 (14). For all five equations, the calculated optimum parameters for the ethanol-water system are given in Table 2.3 and a measure of the goodness-of-fit is shown in Table 2.4. From this table it is seen that the Wilson, NRTL, and UNIQUAC equations fit the data slightly better than the Margules and Van Laar equations.

The parameters A_{12} and A_{21} in the Wilson, NRTL, and UNIQUAC equations are expected to be independent of temperature, however, Table 2.3 shows that this is not the case, nor is there any discernible trend in the dependence of these parameters on temperature. It is an observed characteristic of these equations that a wide range of parameter values will produce the same goodness-of-fit (2). Because of this parametric insensitivity it is difficult to obtain parameters that show the correct trend with temperature. Conversely, one may expect that very little goodness-of-fit's sacrificed when the prescribed temperature dependence is imposed upon the parameter estimation procedure using data at several temperatures. This was done using data at 40, 55, and 70°C.

Parameters so determined are listed under the heading "Combd" in Table 2.3. These three sets of data were chosen because they conformed most closely to the thermodynamic consistency test and because they cover the desired range of temperature. Table 2.5 shows a detailed comparison of the experimental x-y-p data with values calculated from the Wilson, NRTL, and UNIQUAC equations using parameters determined from the combined 40, 55, and 70°C data. It is expected that the parameters determined from the combined data can be used with confidence for temperatures in this range. Moderate extrapolations beyond this range should also yield acceptable results.

TABLE 2.1 SOME STRUCTURAL PARAMETERS FOR THE UNIQUAC EQUATION (1)

Components	r	q
Methanol	1.43	1.43
Acetic acid	1.90	1.80
Ethanol	2.11	1.92
Acetone	2.57	2.34
n-Hexane	4.50	3.86
n-Heptane	5.17	4.40
n-Octane	5.85	4.94
Water	0.92	1.40

SIZE PARAMETERS q' FOR WATER AND ALCOHOLS

Water	1.00	C_4 Alcohols	0.88
CH_3OH	0.96	C_5 Alcohols	1.15
C_2H_5OH	0.92	C_6 Alcohols	1.78
C_3H_7OH	0.89	C_7 Alcohols	2.71

TABLE 2.2 ANTOINE CONSTANTS FOR ETHANOL AND WATER

Components	Antoine Constants (14)		
	A	B	C
Ethanol	8.1629	1623.22	228.98
Water	7.9668	1668.21	228.00

TABLE 2.3 OPTIMUM PARAMETERS OF ACTIVITY COEFFICIENT EQUATIONS

Eq.	$^{\circ}\text{C}$	40.0	55.0	70.0	Combd	50.0	54.81	60.65	74.79	39.76
Margules eq.	A_{12}	1.669	1.817	1.850	-----	1.932	1.371	1.829	1.407	1.046
	A_{21}	0.867	0.819	0.795	-----	0.783	1.034	0.816	0.942	1.191
Van Laar eq.	A_{12}	1.749	2.034	2.103	-----	2.226	1.365	2.156	1.417	1.077
	A_{21}	0.970	0.934	0.921	-----	0.929	1.079	0.924	0.979	1.175
Wilson eq.	A_{12}	291.7	654.5	267.8	532.5	827.5	-104.	785.0	2.78	-385.
	A_{21}	863.1	829.3	986.8	852.1	807.1	1086.	831.3	1041.	1217.
NRTL eq.	A_{12}	-64.6	-144.	-21.1	-137.	-175.	184.4	-170.	64.5	481.1
	A_{21}	1155.	1458.	1198.	1414.	1588.	727.1	1577.	924.4	290.7
UNIQUAC eq.	A_{12}	-75.9	-200.	-237.	-180.	-237.	287.9	-235.	134.2	663.6
	A_{21}	649.9	1044.	1192.	959.7	1250.	147.5	1208.	292.5	-171.

* For the Wilson, NRTL, and UNIQUAC equations the units of A_{12} and A_{21} are cal/g-mole. For the Margules and Van Laar equations A_{12} and A_{21} are dimensionless.

TABLE 2.4 "THE GOODNESS OF FIT" OF ACTIVITY COEFFICIENT EQUATIONS FOR THE ETHANOL-WATER SYSTEM

Equations	40.0°C						55.0°C						70.0°C						50.0°C					
	ΔY			ΔP			ΔY			ΔP			ΔY			ΔP			ΔY			ΔP		
	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean
Margules eq.	2.30	1.06	10.3	1.41	3.70	1.80	11.7	4.74	4.10	2.05	24.3	10.6	8.6	3.54	17.0	8.06								
Van Laar eq.	1.70	0.85	10.7	1.44	5.60	1.34	13.7	3.75	5.10	1.33	24.7	7.54	11.5	3.12	16.9	7.54								
NRTL eq.	2.20	0.87	10.9	1.43	5.30	1.41	11.9	3.90	3.30	1.12	22.9	8.10	11.2	3.16	17.0	7.57								
Wilson eq.	1.70	0.72	10.8	1.70	6.10	1.01	15.1	2.89	2.30	1.07	7.10	4.50	12.2	2.76	19.3	6.54								
UNIQUAC eq.	2.20	0.82	11.0	1.47	5.70	1.28	13.3	3.57	5.10	1.23	25.4	6.90	11.9	3.03	17.9	7.34								
Range of P	75.1 - 133.8						173.3 - 280.5						362.5 - 544.5						133.0 - 225.0					
No. of data	13						13						13						9					
Reference	(14)						(14)						(14)						(9)					

Equations	54.81°C						60.65°C						74.79°C						39.76°C					
	ΔY			ΔP			ΔY			ΔP			ΔY			ΔP			ΔY			ΔP		
	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean	Max.	Mean
Margules eq.	6.60	2.28	10.3	4.85	5.60	2.07	18.5	7.44	5.60	1.93	27.9	10.8	14.2	4.64	8.90	5.02								
Van Laar eq.	6.70	2.42	10.9	5.40	9.20	2.07	30.0	7.81	5.80	2.14	29.0	12.8	14.1	4.58	6.90	4.88								
NRTL eq.	6.70	2.43	10.8	5.44	8.60	2.09	28.0	7.79	5.80	2.13	28.8	12.6	14.1	4.62	8.86	4.93								
Wilson eq.	6.80	2.58	11.2	6.02	9.30	1.96	32.5	6.59	6.10	2.39	29.9	14.5	14.0	4.69	9.00	4.97								
UNIQUAC eq.	6.40	2.41	9.80	5.20	9.20	2.03	30.9	7.60	5.60	2.25	26.7	12.8	12.4	4.54	8.30	4.46								
Range of P	192.9 - 275.9						219.0 - 362.0						469.2 - 654.0						81.4 - 131.4					
No. of data	9						11						12						16					
Reference	(27)						(9)						(27)						(27)					

$$P : \text{mm Hg} ; \Delta Y = \left| Y_{\text{exp}} - Y_{\text{cal}} \right| \times 100.0 ; \Delta P = \left| P_{\text{exp}} - P_{\text{cal}} \right|$$

TABLE 2.5 COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES
WITH A SINGLE SET OF PARAMETERS DETERMINED FROM
THE COMBINED DATA AT 40, 55, AND 70°C

TEMP	X1	EXPERIMENT		WILSON EQ.		NRTL EQ.		UNIQUAC EQ.	
		Y1	P	YC1	PC	YC1	PC	YC1	PC
40.0	.062	.374	75.1	.431	92.9	.433	92.7	.425	91.5
40.0	.077	.406	89.0	.459	96.9	.465	97.4	.456	96.0
40.0	.098	.450	94.6	.487	101.3	.496	102.4	.487	100.7
40.0	.128	.488	101.5	.515	105.8	.526	107.3	.517	105.5
40.0	.181	.543	109.0	.548	111.2	.556	112.6	.549	110.8
40.0	.319	.598	116.9	.602	119.6	.598	119.1	.597	118.1
40.0	.399	.628	121.0	.630	123.3	.620	121.9	.622	121.3
40.0	.511	.676	125.5	.671	127.7	.659	125.8	.663	125.5
40.0	.683	.746	130.4	.749	133.0	.744	130.9	.748	130.9
40.0	.774	.809	132.5	.802	134.9	.803	132.9	.805	132.9
40.0	.810	.829	132.8	.826	135.4	.830	133.5	.831	133.5
40.0	.875	.879	133.5	.876	135.7	.882	134.2	.882	134.3
40.0	.957	.956	133.8	.952	135.2	.956	134.5	.956	134.5
55.0	.051	.336	173.3	.382	183.7	.380	182.5	.382	183.2
55.0	.085	.428	197.8	.450	202.8	.460	205.0	.458	204.8
55.0	.106	.461	207.5	.476	210.7	.489	214.4	.486	213.7
55.0	.180	.524	227.3	.531	228.4	.545	233.5	.541	232.1
55.0	.230	.555	236.3	.556	235.1	.566	240.4	.562	239.0
55.0	.324	.589	248.2	.593	247.2	.594	249.2	.593	248.5
55.0	.429	.628	258.0	.633	257.2	.627	257.2	.628	257.1
55.0	.553	.680	267.0	.684	267.1	.675	266.1	.677	266.2
55.0	.685	.746	274.9	.750	275.5	.744	273.8	.745	274.2
55.0	.774	.801	278.4	.803	279.5	.802	277.6	.802	278.1
55.0	.810	.829	279.4	.828	280.6	.829	278.8	.828	279.2
55.0	.894	.898	280.6	.894	281.8	.897	280.3	.896	280.7
55.0	.954	.952	280.5	.950	281.2	.953	280.4	.952	280.6
70.0	.062	.374	362.5	.389	365.4	.393	366.3	.401	371.6
70.0	.095	.439	399.0	.445	395.1	.459	402.4	.463	406.4
70.0	.131	.482	424.0	.482	416.5	.501	427.9	.502	430.6
70.0	.194	.524	450.9	.524	441.3	.542	454.6	.541	455.9
70.0	.252	.552	468.0	.552	457.9	.566	468.5	.564	470.4
70.0	.334	.583	485.5	.587	487.8	.593	484.6	.592	485.8
70.0	.401	.611	497.6	.614	488.7	.615	495.1	.614	496.5
70.0	.593	.691	525.9	.700	518.9	.692	521.4	.693	523.2
70.0	.680	.739	534.3	.747	529.4	.739	530.9	.739	532.8
70.0	.794	.816	542.7	.818	539.3	.814	539.7	.813	541.3
70.0	.810	.826	543.1	.830	540.4	.827	540.7	.826	542.2
70.0	.943	.941	544.5	.941	543.6	.941	543.2	.940	543.9
70.0	.947	.945	544.5	.945	543.5	.945	543.1	.944	543.8
AVERAGE DEVIATIONS :				.010	4.02	.012	3.19	.013	2.92
MAXIMUM DEVIATIONS :				.058	17.77	.059	17.59	.051	16.44
$\Sigma (Q_{\text{exp}} - Q_{\text{cal}})^2 :$.02372		.01936		.01758	

CHAPTER III

ESTIMATION OF ACTIVITY COEFFICIENTS
IN THE ETHANOL-WATER-GASOLINE SYSTEM

1. Ternary Liquid-Liquid Equilibrium

1.1 Representation of a Ternary Liquid-Liquid System

A ternary system is usually represented on a coordinate system based on an equilateral triangle as shown in Figure 3.1a. Typical phase diagrams for two of the most frequently occurring types of ternary liquid-liquid systems are shown in Figures 3.1b and 3.1c. Figure 3.1b represents a type I system which consists of two completely miscible binaries and one partial miscible binary. The saturated solutions of the partial miscible binary, the 1-2 binary, are represented by the points A and A'. The curve ACPC'A' represents saturated ternary solutions and is known as the solubility curve or binodal curve. All mixtures outside the binodal curve exist as a single homogeneous liquid phase. However, all mixtures, for example M, within the curve separate into two liquid phases having compositions represented by the points C and C'. The line CMC' which connects the compositions of the phases that are in equilibrium is known as a tie line. The point P where the length of the tie line is equal to zero (i.e. , the two liquids become identical) is known as the plait point.

A ternary system formed from one completely miscible and two partially miscible binaries is called a type II system. A ternary phase diagram for this type of system is shown in Figure 3.1c. In this case, the heterogeneous region forms a band which extends across the triangular diagram and, of course, there is no plait point. Again tie lines such as CMC'

relate the compositions of two liquid phases in equilibrium.

Other types of ternary liquid-liquid systems exist, for example systems formed from three partially miscible binaries, systems which form three liquid phases, and systems which have two or three separate binodal curves. However, these are of little industrial interest and are seldom studied.

For the ethanol-water-gasoline system, though the gasoline is a mixture, we treat it as a single component. In this way we may regard the system as a type I ternary liquid-liquid system where component 1 refers to ethanol; component 2, water; and component 3, gasoline.

1.2 Conditions of Ternary Liquid-Liquid Equilibrium

In a ternary system containing two liquid phases and a vapor phase at equilibrium we may write:

$$f_1' = f_1'' = f_1^v \quad (3.1A)$$

$$f_2' = f_2'' = f_2^v \quad (3.1B)$$

$$f_3' = f_3'' = f_3^v \quad (3.1C)$$

where the primed and double primed superscripts refer to the liquid phases (in the E-W-G ternary, the primed superscript refers to the aqueous phase, while the double primed superscript refers to the gasoline phase) and the circumflex refers to a component in solution. At low pressure, the fugacities of component i in the vapor and liquid phases can be expressed by the following equation:

$$f_i^v = P y_i \quad (3.2A)$$

$$f_i^I = x_{is}^I \gamma_{is}^I p_i^0 \quad (3.2B)$$

$$f_i^{II} = x_{is}^{II} \gamma_{is}^{II} p_i^0 \quad (3.2C)$$

where the subscript s refers to a saturated liquid phase. Substitution of equation (3.2) into equation (3.1) results in

$$x_{1s}^I \gamma_{1s}^I p_1^0 = x_{1s}^{II} \gamma_{1s}^{II} p_1^0 = P y_1 \quad (3.3A)$$

$$x_{2s}^I \gamma_{2s}^I p_2^0 = x_{2s}^{II} \gamma_{2s}^{II} p_2^0 = P y_2 \quad (3.3B)$$

$$x_{3s}^I \gamma_{3s}^I p_3^0 = x_{3s}^{II} \gamma_{3s}^{II} p_3^0 = P y_3 \quad (3.3C)$$

2. Ternary Activity Coefficient Equations

All of the activity coefficient equations that were used in the previous chapter can be written for multicomponent mixtures and there has been considerable effort directed toward the prediction of ternary Vapor-Liquid Equilibrium (V-L-E) data from data for the three constituent binary systems. A fairly comprehensive study on 19 ternary systems (8) has demonstrated that the Wilson equation is effective for this. However, the Wilson equation fails completely for liquid-liquid equilibria even in binary systems. Though Wilson has suggested a three-parameter form of his equation which is applicable to binary liquid-liquid systems (27), it is not possible to generalize it to ternary (and higher) systems without simplifying assumptions (17). The two-parameter equations of Margules and Van Laar are applicable to liquid-liquid equilibria but usually give poor representation of such equilibria.

The three-parameter NRTL equation provides a large improvement in representation of ternary liquid-liquid equilibria using only binary parameters. However, calculated results are sensitive to the choice of the

binary parameters, especially in plait-point systems. Mutual solubility data for the 1-2 binary can be used to fix two of the 1-2 binary parameters, but the all-important choice of the third parameter remains elusive and empirical rules suggested by Prausnitz (16) appeared to be inadequate for consistently reliable results. Therefore, as shown by Renon et al (18), good presentation for ternary systems can only be obtained with extensive ternary data used to fix the nine binary NRTL parameters.

Although the UNIQUAC equation provides no major improvement over the Wilson equation for vapor-liquid equilibria in completely miscible systems, it can also represent liquid-liquid equilibria for multicomponent mixtures using only two adjustable parameters per binary. Besides, when well-defined simplifying assumptions (1) are made, the UNIQUAC model can yield any one of several well-known expressions for the excess Gibbs energy, including the Van Laar, Wilson, and NRTL equations. Therefore, the UNIQUAC equation was used in this study for estimation of activity coefficients in the ethanol-water-gasoline system.

2.1 The UNIQUAC Equation for Multicomponent Systems

The activity coefficient of component i in a multicomponent mixture containing m components by the UNIQUAC equation is:

$$\ln \gamma_i = \ln(\phi_i/x_i) + (z/2)q_i \ln(\theta_i/\phi_i) + l_i - (\phi_i/x_i) \sum_{j=1} x_j l_j - q_i' \ln(\sum_{j=1} \theta_j' \tau_{ji}) + q_i' - q_i' \sum_{j=1} (\theta_j' \tau_{ij} / \sum_{k=1} \theta_k' \tau_{kj}) \quad (3.4A)$$

where

$$l_i = z(r_i - q_i)/2 - (r_i - 1) \quad (3.4B)$$

$$\phi_i = x_i r_i / (\sum_{j=1} x_j r_j) \quad (3.4C)$$

$$\theta_i = x_i q_i / (\sum_{j=1} x_j q_j) \quad (3.4D)$$

$$\theta'_i = x_i q'_i / (\sum_{j=1} x_j q'_j) \quad (3.4E)$$

$$\tau_{ij} = \exp(-A_{ij}/RT) \quad (3.4F)$$

3. Obtaining Activity Coefficients in the E-W-G System

When considering only liquid-liquid equilibrium, equations (3.3) reduce to:

$$x_{1s}^I \gamma_{1s}^I = x_{1s}^{II} \gamma_{1s}^{II} \quad (3.5A)$$

$$x_{2s}^I \gamma_{2s}^I = x_{2s}^{II} \gamma_{2s}^{II} \quad (3.5B)$$

$$x_{3s}^I \gamma_{3s}^I = x_{3s}^{II} \gamma_{3s}^{II} \quad (3.5C)$$

In the ethanol-water-gasoline system, it can be seen from Figures 1.2 and 1.3 that for many of the tie lines the amount of gasoline in the aqueous phase is negligibly small. This allows the ternary aqueous phase to be approximated as a binary ethanol-water mixture. From the data reduction process presented in Chapter II, it is expected that good estimations of activity coefficients can be obtained for the ethanol-water binary system at 25 and 50°C. Therefore, activity coefficients for ethanol and water can be evaluated for the aqueous phase of each tie line. From the experimental tie line data and these estimated aqueous phase activity coefficients it is possible to evaluate activity coefficients of ethanol and water in the gasoline phase by application of equations (3.5)

$$\gamma_E'' = x_{Es}' \gamma_E' / x_{Es}'' \quad (3.5D)$$

$$\gamma_W'' = x_{Ws}' \gamma_W' / x_{Ws}'' \quad (3.5E)$$

In these equations γ' and γ'' are activity coefficients for the ethanol-water binary system. The tie line data can therefore be reduced to activity coefficients for ethanol and water in the gasoline phase at known mole fractions. The following objective function was used to obtain UNIQUAC parameters which fit these data:

$$FSQ = \sum_{j=1}^n \sum_{i=1}^2 (\gamma_{exp} - \gamma_{cal})_{ij}^2 \quad (3.6)$$

4. Fitting UNIQUAC Parameters in the E-W-G System

The estimation of the activity coefficient parameters of the UNIQUAC equation from the known activity coefficient data is a typical optimization calculation. There are many numerical procedures that have been proposed for finding an extremum of a given objective function, and these methods may be divided into two general classes. In one class are the methods which require the calculation of the partial derivatives of the objective function with respect to the parameters, for example, the Newton-Raphson procedure and the method of steepest descent. The second class of methods will directly minimize the objective function without having to calculate any partial derivatives. These methods are generally called search techniques. Because of the complexity of equation (3.6), the analytical expressions for the partial derivatives are extremely long and complex. The Box method (4), a search technique, was found to be an efficient method of finding the minimum of the objective function, equation (3.6). The procedures of this method are shown in the appendix A. In

the calculation we determine all 6 parameters (A 's, Equation 3.4F) from the combined E-W-G tie line data at 25 and 50°C.

4.1 Results and Discussions

The results are shown in Tables 3.1, 3.2, and 3.3. From Table 3.1, we find that the parameters A_{12} and A_{21} are different from those obtained in the previous Chapter for the ethanol-water binary system. This is expected because a different objective function and a different source of data were used. From Tables 3.2 and 3.3, we find that the deviations between experimental and calculated values are significant, however, it is expected that these parameters can be used for reasonable estimates of activity coefficients in the ethanol-water-gasoline system.

TABLE 3.1 OPTIMUM PARAMETERS OF THE UNIQUAC EQUATION FOR
ETHANOL-WATER-GASOLINE SYSTEM *

PARAMETERS	A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}
(cal/g-mloe)	22.51	546.4	233.5	1790	24510	8790

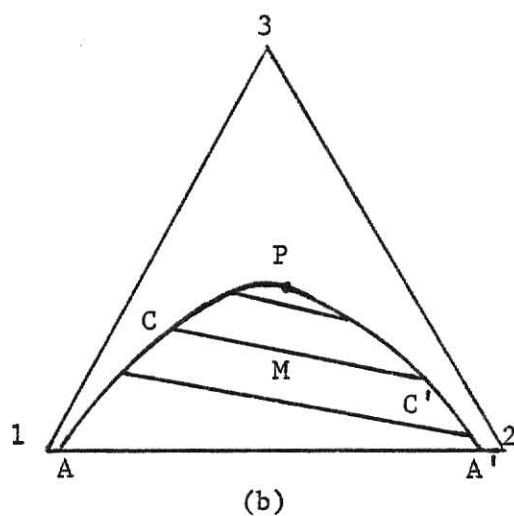
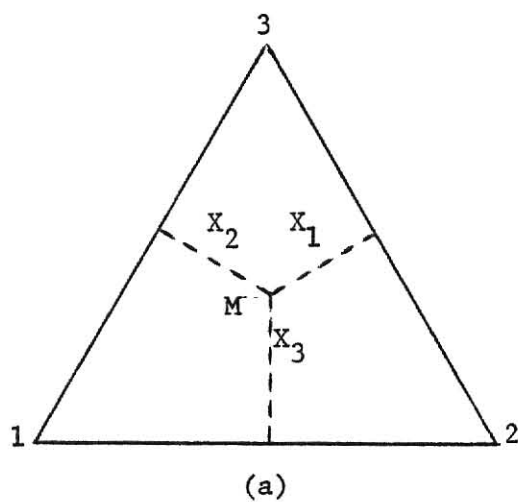
* 1: ETHANOL ; 2: WATER ; 3: GASOLINE

TABLE 3.2 COMPARISON OF EXPERIMENTAL AND CALCULATED ACTIVITY
COEFFICIENTS IN THE GASOLINE PHASE

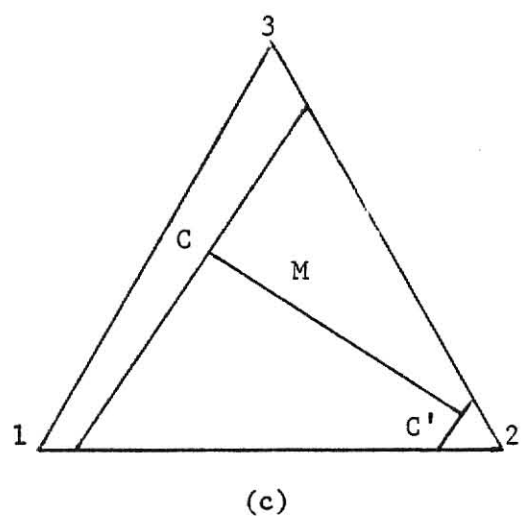
TEMP (°C)	$X''(E)$	ETHANOL GAMMA (γ)		$X''(W)$	WATER GAMMA (γ)	
		EXP.	CAL.		EXP.	CAL.
25.0	.0062	37.5	15.3	.0000
25.0	.0083	38.2	15.1	.0000
25.0	.0166	21.9	13.9	.0000
25.0	.0227	17.6	13.0	.0000
25.0	.0328	13.6	11.1	.0016	549.	347.
25.0	.0328	13.7	11.1	.0016	548.	347.
25.0	.0487	10.1	9.38	.0031	275.	214.
25.0	.0662	7.95	8.02	.0046	181.	147.
25.0	.0643	8.21	8.14	.0046	180.	152.
25.0	.0585	9.10	8.55	.0041	201.	132.
25.0	.0720	7.64	7.64	.0051	159.	133.
25.0	.0815	7.24	7.06	.0061	125.	113.
25.0	.0853	6.93	6.84	.0066	115.	107.
25.0	.1002	6.08	6.16	.0075	97.8	87.9
25.0	.1093	5.79	5.71	.0095	73.2	76.6
50.0	.0108	15.2	11.9	.0000
50.0	.0257	12.2	10.6	.0000
50.0	.0506	7.61	7.87	.0043	220.	198.
50.0	.0526	8.15	7.79	.0043	216.	191.
50.0	.0727	6.46	6.71	.0064	142.	129.
50.0	.0805	6.31	6.30	.0079	111.	111.
50.0	.0960	5.61	5.67	.0099	85.6	88.6
50.0	.1055	5.47	5.33	.0114	71.3	77.0

TABLE 3.3 COMPARISON OF EXPERIMENTAL AND CALCULATED ACTIVITY COEFFICIENTS IN THE AQUEOUS PHASE

TEMP (°C)	X' (E)	ETHANOL		X' (W)	WATER	
		GAMMA EXP.	(γ) CAL.		GAMMA EXP.	(γ) CAL.
25.0	.0576	4.04	4.21	.9423	1.01	1.01
25.0	.0924	3.43	3.50	.9075	1.02	1.03
25.0	.1183	3.08	3.07	.8812	1.04	1.05
25.0	.1421	2.81	2.71	.8574	1.05	1.06
25.0	.1841	2.43	2.33	.8144	1.08	1.11
25.0	.1898	2.38	2.29	.8090	1.09	1.11
25.0	.2445	2.03	1.91	.7529	1.13	1.18
25.0	.2920	1.80	1.67	.7033	1.19	1.25
25.0	.2955	1.79	1.64	.6989	1.19	1.26
25.0	.3035	1.76	1.60	.6901	1.20	1.28
25.0	.3383	1.63	1.49	.6538	1.24	1.34
25.0	.4232	1.40	1.25	.5582	1.37	1.55
25.0	.4256	1.39	1.24	.5551	1.37	1.56
25.0	.4661	1.31	1.17	.5084	1.44	1.69
25.0	.5152	1.23	1.11	.4524	1.54	1.85
50.0	.0372	4.25	4.48	.9627	1.00	1.00
50.0	.0927	3.29	3.55	.9072	1.02	1.03
50.0	.1302	2.84	2.81	.8692	1.04	1.05
50.0	.1639	2.52	2.47	.8354	1.06	1.08
50.0	.2041	2.22	2.11	.7937	1.09	1.12
50.0	.2526	1.94	1.81	.7431	1.14	1.19
50.0	.2989	1.74	1.58	.6933	1.19	1.26
50.0	.3694	1.51	1.35	.6152	1.28	1.41



Type I system



Type II system

Figure 3.1 Ternary Phase Diagram

CHAPTER IV

FLASH CALCULATION

1. Introduction

In the KSU gasohol production process, there is approximately 1 wt% water in the wet gasohol, which must be removed. There are two possible methods to remove the water. One is by flash vaporization, the other is by distillation. Here we will study the possibility of dehydration of wet gasohol by flash vaporization.

2. Basic Equations

Consider the case of flash vaporization at the pressure P , suppose there are F moles of liquid entering with component mole fractions denoted by z , and there are L moles of liquid and V moles of vapor leaving with mole fractions x and y respectively. If these two exit streams are in equilibrium, we can obtain the following equations:

$$y_i = K_i x_i \quad (4.1)$$

$$F = L + V \quad (4.2)$$

$$Fz_i = Lx_i + Vy_i \quad (4.3)$$

where the quantity K_i is referred to as the equilibrium ratio for the component i and can be calculated and correlated as a function of T , P , and liquid composition as follows:

When the vapor and liquid phases of a mixture are in equilibrium for each component i we can write:

$$Py_i \hat{\phi}_i = f_i^L x_i \gamma_i \quad (4.4)$$

so

$$K_i = y_i/x_i = f_i^L \gamma_i / P \hat{\phi}_i \quad (4.5)$$

At low pressure, $\hat{\phi}_i = 1.0$ and $f_i^L = p_i^o$, so equation (4.5) becomes:

$$K_i = y_i/x_i = (p_i^o/P) \gamma_i = K'_i \gamma_i \quad (4.6)$$

where p_i^o is the vapor pressure of pure component i at T , and K'_i is the vapor-liquid equilibrium ratio of pure component i at T and P . Letting f denote the flash ratio (equal to V/F), and solving the equations (4.1), (4.2), and (4.3) for x , we obtain:

$$x_i = z_i / (K_i V/F + L/F) = z_i / (K_i f + 1.0 - f) \quad (4.7)$$

So for a given feed (z 's), K values and fraction flashed (f), we can calculate x and y by use of equations (4.1) and (4.7).

Gasoline is a "continuum" or mixture of an "infinite" number of components. However, it may be approximated as a multicomponent mixture of a finite number of hypothetical components. This kind of representation of the continuum may be done by taking equal size cuts, say 20, on the True Boiling Point (TBP) curve. Each of these narrow cuts is characterized by its mean boiling point. This method of representing a continuum by a finite number of hypothetical components simulates a smooth TBP curve by a series of plateaus. The larger the number of hypothetical components, the more accurate the representation. Increased accuracy is purchased with the expense of increased calculation detail. The determination of the mean boiling point and the K' value of each hypothetical component is shown in the following section.

3. Determination of K Values

In the determination of a K value for each component, we have to first obtain the γ and K' values for each component.

3.1 K Values of Ethanol and Water

From equation (4.6), we find that the K' values of ethanol and water can be obtained by dividing the vapor pressure (p^0) by the system total pressure (P). The vapor pressures of ethanol and water at different T are expressed by equation (2.14) (i.e., the Antoine equation).

Since we can estimate the γ 's values of ethanol and water at different temperatures and compositions of the E-W-G mixtures by the UNIQUAC equation with parameters obtained in the previous chapter, we can combine this with equations (2.14) and (4.6) and determine their K values.

3.2 K Values of the Gasoline Components

Determination of the K value of a hypothetical component of gasoline is more complicated. At first we assume that each hypothetical component has the same activity coefficient as that of gasoline remembering that gasoline was regarded as a single component in the calculation of the activity coefficients for the ethanol-water-gasoline system. This assumption will be discussed later.

The procedure for determining the K' value of each gasoline component is as follows:

- 1). The molar TBP curve, Figure 4.2, was obtained from the ASTM curve, Figure 4.1, using procedures developed by Edmister (25). The data for these figures are shown in Table 4.2. The gasoline used in this study was supplied by Getty Refining and Marketing

Company of El Dorado, Kansas. The ASTM distillation and other property data were determined by them and appear in Table 4.1.

- 2). As shown on Figure 4.2, the molar TBP curve was divided into 20 equal molar increments. Each increment represents a hypothetical component and is characterized by the average boiling point.
- 3). Using methods developed by Edmister (26), the K' values of the hypothetical components were estimated at 120 and 180 °F. These estimations were found from correlations based on boiling point that were established for paraffin hydrocarbons. Table 4.3 lists the mean boiling point and the K' values at 120 and 180 °F for the twenty hypothetical components of the gasoline.

Values of K' at other temperatures were interpolated or extrapolated by the following equation:

$$\text{Log}_{10} K'_i = AA_i + BB_i / (t + 460.0) \quad (4.8)$$

The UNIQUAC equation with the parameters in Table 3.1 provides the activity coefficient of gasoline, γ_G . We now wish to estimate the activity coefficients for each of the twenty hypothetical components, γ_{Gi} 's. To do this we define:

- \hat{a}_G - the activity of the gasoline,
- x_G - the mole fraction of the gasoline in the E-W-G system,
- \hat{a}_{Gi} - the activity of a hypothetical component of gasoline,
- x_{Gi} - the mole fraction of a hypothetical component of gasoline in the E-W-G system.

For an ideal solution the activities are equal to the mole fractions and because the gasoline mole fraction will usually be fairly high in the

mixtures we study, it is not unreasonable to assume that the Raoult's Law applies to the gasoline and write:

$$\hat{a}_G = x_G \quad (4.9)$$

and

$$\hat{a}_{Gi} = x_{Gi} \quad (4.10)$$

now since $x_G = \sum x_{Gi}$, we may write

$$\hat{a}_G = \sum \hat{a}_{Gi} \quad (4.11)$$

When activities are expressed in terms of activity coefficients we have:

$$x_G \gamma_G = \sum x_{Gi} \gamma_{Gi} \quad (4.12)$$

If the assumption is made that all γ_{Gi} are equal we obtain:

$$x_G \gamma_G = \gamma_{Gi} \sum x_{Gi} \quad (4.13)$$

or

$$\gamma_G = \gamma_{Gi} \quad (4.14)$$

The equality of activity coefficient of each gasoline component is suggested by Regular Solution Theory (10) (see Appendix B) and can be shown to be consistent with the Gibbs-Duhem equation.

For the ternary E-W-G system, the Gibbs-Duhem equation requires:

$$\left[x_E d \ln \gamma_E + x_W d \ln \gamma_W + x_G d \ln \gamma_G = 0 \right]_{T,P} \quad (4.15)$$

The above relationship is insured by the use of the UNIQUAC equation, However, when gasoline is considered a mixture we must write:

$$\left[x_E d \ln \gamma_E + x_W d \ln \gamma_W + \sum x_{Gi} d \ln \gamma_{Gi} = 0 \right]_{T,P} \quad (4.16)$$

This requires

$$x_G d \ln \gamma_G = \sum x_{Gi} d \ln \gamma_{Gi} \quad (4.17)$$

but since we have assumed

$$\gamma_G = \gamma_{G1} = \gamma_{G2} = \dots = \gamma_{Gi} = \dots = \gamma_{G20} \quad (4.18)$$

we may write

$$d \ln \gamma_G = d \ln \gamma_{Gi} \quad (4.20)$$

and equation (4.17) reduces to

$$x_G = \sum x_{Gi}$$

Thus, the assumption of $\gamma_G = \gamma_{Gi}$ is compatible with the Gibbs-Duhem equation and is therefore thermodynamically acceptable.

4. Procedure of Calculation

From equation (4.7), it is seen that the x 's depend on K 's which in turn depend on T , P , and x 's (because γ 's are function of x 's and T). Hence, the calculations must be done by trial and error and are fairly complicated. The mole fraction of gasoline in the wet gasohol feed is 0.778 and when the flash ratio is below 20%, the mole fraction of gasoline in the liquid phase is found not to be substantially different from the feed. In this case, the activity coefficient of gasoline ranges between 1.1 and 1.4. So we assume it to be 1.25 for the first trial. The procedure of calculation is as follows:

- 1). use the K'_{350} data at 120 and 180 °F to evaluate AA_i and BB_i in equation (4.8) for each gasoline component,
- 2). assume γ_G (denoted by γ_G^* , and initially assumed to be 1.25),
- 3). assume T , (say, $T = 80$ °F),
- 4). use equation (4.6) to evaluate K'_i at the temperature T , and then evaluate K_i from equation (4.6),
- 5). use equation (4.7) to evaluate x_i for each gasoline component,
- 6). evaluate x_G ($x_G = \sum x_{Gi}$). If $1.0 < x_G$, go back to step 3 and change the temperature T ,
- 7). assume x_E (denoted by xx_E), then evaluate xx_W ($= 1.0 - x_G$)

- xx_E),
- 8). evaluate the activity coefficients for ethanol, water, and gasoline at temperature T , pressure 730 mm Hg, and composition xx_E , xx_W , and x_G , by the UNIQUAC equation,
 - 9). use equation (2.14) to evaluate the vapor pressures of ethanol and water at temperature T ,
 - 10). use equation (4.6) to evaluate K_E and K_W ,
 - 11). use equation (4.7) to evaluate x_E and x_W ,
 - 12). compare xx_E with x_E and xx_W with x_W . If they are not equal, set $xx_E = x_E$ and $xx_W = x_W$, then go back to step 8. Repeat steps 8, thru 12 till $x_E = xx_E$, and $x_W = xx_W$,
 - 13). If the sum of x_E , x_W , and x_G isn't equal to unity, go back to step 3 and change the temperature T ,
 - 14). check γ_G evaluated in step 8 with γ_G^* assumed in step 2, if $\gamma_G = \gamma_G^*$, then we have answer, if not, then go back to step 2, and repeat these calculations till $x_E = xx_E$, $x_W = xx_W$, and $\gamma_G = \gamma_G^*$.

The calculations were carried out on a PDP-11 minicomputer under operator's control. After an unsuccessful trial the necessary adjustments were made by the operator.

5. Calculations and Results

Fifteen different flash vaporization ratios of wet gasohol operated at 730 mm Hg pressure were calculated. The results of five of them are shown in Table 4.4. These calculations indicate that it is impossible to dehydrate the wet gasohol to the desired water content by flash vaporization.

TABLE 4.1 ASTM DISTILLATION DATA OF AN UNLEADED REGULAR GASOLINE *

Gravity, API	63.9
Reid Vapor Pressure	10.5
Lead, gm/gal	0.003
Gum, ASTM, mg/100 ml	0.2
RSH, ppm	5.0
Research Octane No.	85.4
Motor Octane No.	77.8
Distillation, D86	
IBP	92
5%	106
10%	115
20%	128
50%	188
90%	350
95%	399
EP	425
Recovery %	97.0
Residue %	1.4
Loss %	1.6

* Supplied by Getty Refining and Marketing Company, Eldorado, Ks.

TABLE 4.2 COMPARISON OF ASTM DATA TO MOLAR TBP DATA FOR THE GASOLINE OF TABLE 4.1

ASTM DATA		TBP DATA		
Vol.% off	Mean B.P.	Vol.% off	Mean B.P.	Mol.% off
0	92	0	33	0
10	106	10	63	13.1
30	140	30	121	36.6
50	188	50	188	57.7
70	250	70	265	76.1
90	350	90	372	92.5
100	425	100	457	100.0

TABLE 4.3 MEAN BOILING POINT AND K' VALUES OF EACH HYPOTHETICAL GASOLINE COMPONENT

Pseudo component	Mean B.P. (°F)	K'(120)	K'(180)
1	38	3.872	9.900
2	48	3.300	8.460
3	59	2.816	7.560
4	71	2.244	6.165
5	84	1.848	5.175
6	97	1.461	4.230
7	110	1.179	3.420
8	125	.8712	2.655
9	139	.6336	2.070
10	155	.4840	1.553
11	170	.3432	1.193
12	187	.2422	0.864
13	204	.1804	0.653
14	222	.1285	0.491
15	242	.0862	0.351
16	267	.0502	0.221
17	299	.0277	0.119
18	331	.0143	0.067
19	372	.0049	0.025
20	425	.0012	0.007

TABLE 4.4 RESULTS OF FLASH VAPORIZATION CALCULATION FOR WET GASOHOL

FEED (m.f.) : Z(E) = 0.1957, Z(W) = 0.0261, Z(G) = 0.7782						
FLASH	(MOL.%) :	4.0	8.0	12.0	16.0	20.0
EQUIL. T.	(°F) :	110.70	113.20	115.72	118.30	121.30
LIQUID	X(E) :	0.1980	0.1994	0.1997	0.1985	0.1951
PHASE	X(W) :	0.0243	0.0223	0.0202	0.0180	0.0156
(m.f.)	X(G) :	0.7776	0.7782	0.7801	0.7835	0.7892
VAPOR	X(E) :	0.1423	0.1543	0.1673	0.1813	0.1984
PHASE	X(W) :	0.0703	0.0705	0.0701	0.0693	0.0686
(m.f.)	X(G) :	0.7881	0.7756	0.7627	0.7494	0.7330

* m.f. : mole fraction

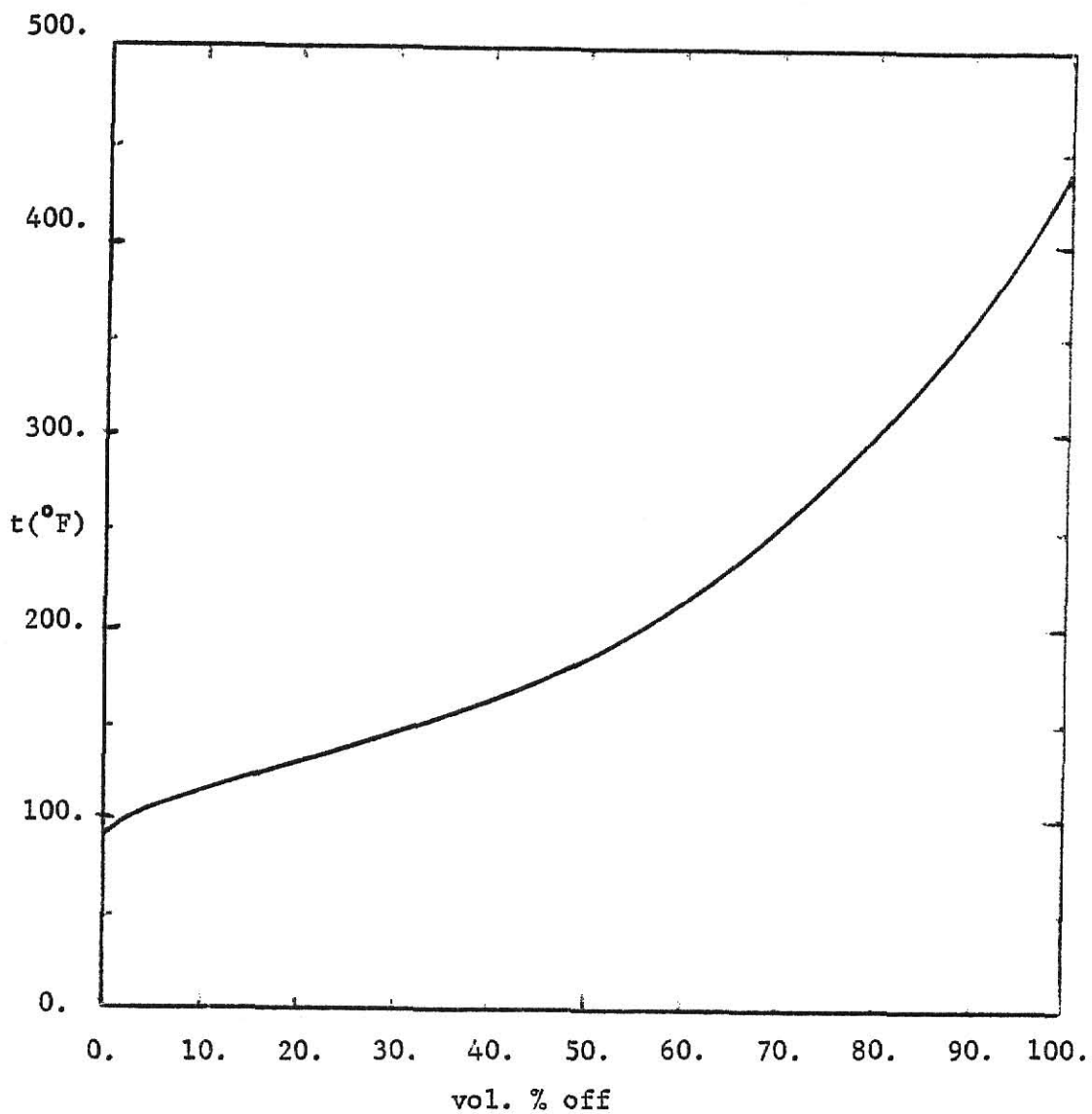


Figure 4.1 Volumetric ASTM Curve of an Unleaded Regular Gasoline
(See Table 4.1)

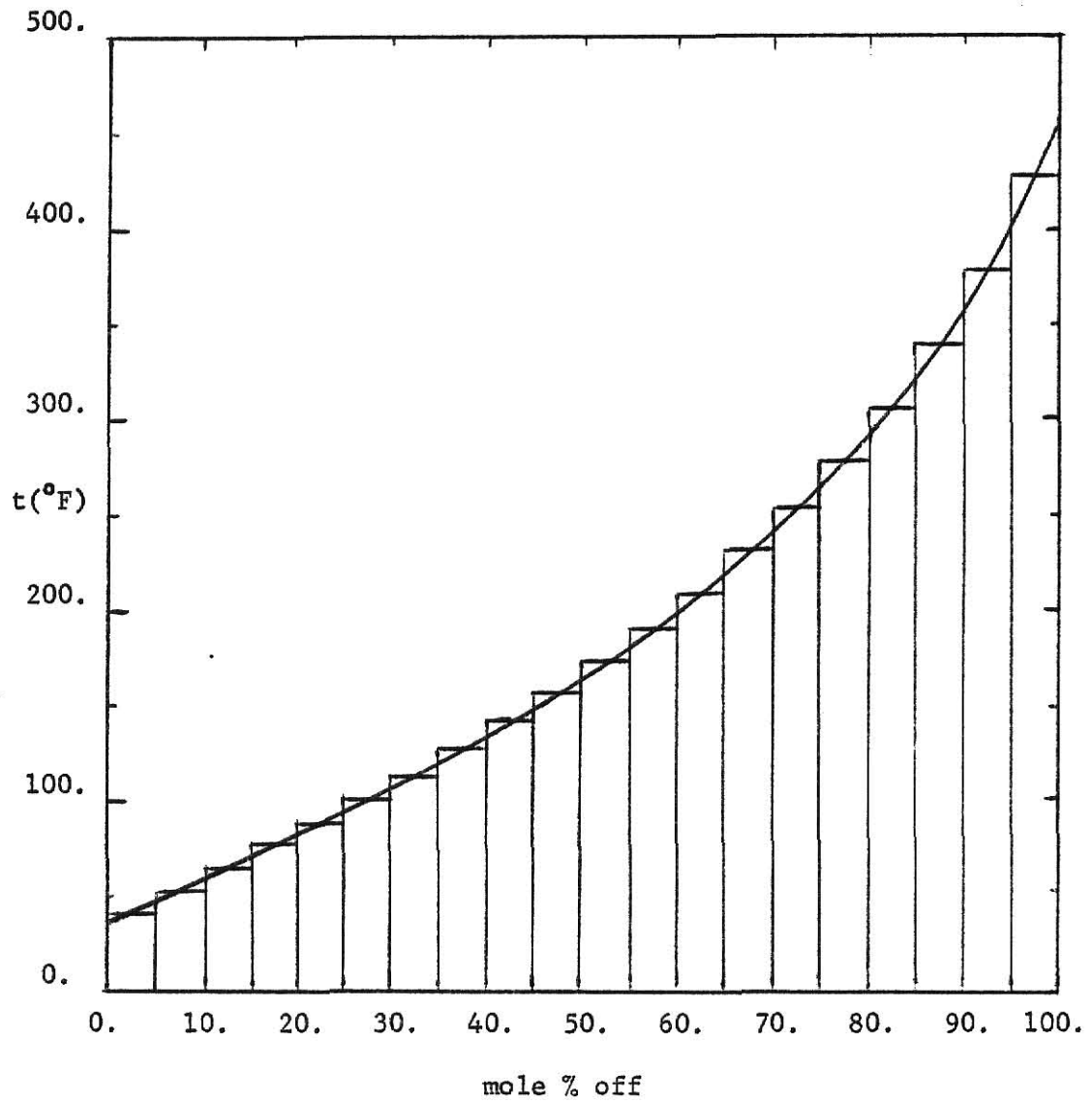


Figure 4.2 Molar TBP Curve of an Unleaded Regular Gasoline

CHAPTER V

PLATE-TO-PLATE CALCULATIONS

FOR A MULTICOMPONENT DISTILLATION COLUMN

1. Introduction

Fundamentally, the estimation of the number of theoretical plates involved for the separation of a multicomponent mixture involves exactly the same principles as for binary mixtures. Thus, the operating-line equations for each component in a multicomponent mixture are identical in form with those for binary mixtures. The procedure is exactly the same; i.e., we start with the composition of the liquid at any position in the column, then we calculate the composition of the vapor which is in equilibrium with this liquid, and by applying the appropriate operating line for the section of the column in question to each component, the liquid composition on the plate above is then determined, and the operation is repeated from plate to plate up the column.

Naturally, the estimation of the number of theoretical plates required for the separation of a complex mixture is more difficult than that for a binary mixture. In the case of a two-phase binary system, once the total pressure and one component in either phase are fixed, the temperature and the composition of the other phase are hence immediately fixed (i.e., at a given total pressure, a unique or definite relationship between y and x allows the construction of the y - x curve). But in the case of a multicomponent mixture of n components, in addition to the pressure, we have to fix $(n-1)$ concentrations before we can completely define the system. This means that for a given component of this kind of mixture the y - x relationship is a function not only of the physical characteristics of the other

components but also of their relative amounts. Therefore, instead of a single y - x relationship for a given component, there are an infinite number of such relationship depending on the relative amounts of the other components present. This necessitates a large amount of equilibrium data for each component in the presence of various proportions of the others, and, except in the special cases in which some generalized rule (such as Raoult's law) applies, these are usually not available, and it is very laborious to obtain them. However, there are three methods of simplification that are usually adopted. The first one employs the relative volatility and is used for systems, particularly those consisting of chemically similar substances, where the relative volatilities of the components remain constant or vary little over a wide range of temperature and pressure. The second one, particularly useful for multicomponent mixtures of hydrocarbons in the petroleum industry, employs the simple relation $y = Kx$. These K values have been measured for a wide range of hydrocarbons at various P . The third one employs the activity coefficients such as Wilson equation (27), NRTL equation (16), or UNIQUAC equation (1,2) to calculate the multicomponent equilibrium data. These equations are reliable and permit calculation of the vapor-liquid equilibrium relationship of a multicomponent system once the parameters have been determined from experimental data.

Here we use a combination of the last two methods and use the UNIQUAC equation with the parameters listed in Table 3.1 to predict the activity coefficients for the ethanol, water, and gasoline under different T and P . As stated in Chapter IV, we assume that each hypothetical component of the gasoline has the same activity coefficient and that the vapor phase is an ideal gaseous solution, so we can calculate the K values (the actual

vapor-liquid distribution ratios) as follows:

$$K_E = (p_E^o / P) \gamma_E \quad (5.1)$$

$$K_W = (p_W^o / P) \gamma_W \quad (5.2)$$

$$K_i = K'_i \gamma_i \quad (5.3)$$

where

K_E = the actual vapor-liquid distribution ratio of ethanol in the mixture,

K_W = the actual vapor-liquid distribution ratio of water in the mixture,

K_i = the actual vapor-liquid distribution ratio of the hypothetical component i of gasoline in the mixture,

K'_i = the vapor-liquid distribution ratio of the hypothetical component i of gasoline,

P = the total pressure of the system, mm Hg.,

p_E^o = the saturated vapor pressure of the ethanol, mm Hg.,

p_W^o = the saturated vapor pressure of the water, mm Hg.,

γ_E = the activity coefficient of ethanol in the mixture,

γ_W = the activity coefficient of water in the mixture,

γ_i = the activity coefficient of gasoline in the mixture.

2. Number of Plates Required in a Distillation Column

There are four streams that are involved in the transfer of heat and material across a plate, as shown in Figure 5.1

Plate n receives liquid flow L_{n+1} of composition $X_{n+1,i}$ from plate $n+1$ above, and vapor flow V_{n-1} of composition Y_{n-1} , from plate $n-1$ below.

plate n supplies liquid flow L_n of composition $X_{n,i}$ to plate $n-1$, and vapor flow V_n of composition $Y_{n,i}$ to plate $n+1$.

The action of this plate is just to bring about contact so that the vapor leaving the plate reaches equilibrium with the liquid on the plate. The streams L_{n+1} and V_{n-1} cannot be in equilibrium and during the interchange process on this plate, some of the more volatile components are vaporized from the liquid L_{n+1} , decreasing its concentration to $X_{n,i}$ and some of the less volatile components are condensed from V_{n-1} , increasing the vapor concentration to Y_n . The heat which is used to vaporize the more volatile components from the liquid is supplied by partial condensation of the vapor V_{n-1} . Thus the resulting effect is that the more volatile components are passed from the liquid running down the column to the rising vapor, while the less volatile components are transferred in the opposite direction.

2.1 The Lewis-Matheson Method

Several methods have been proposed for the design of a multicomponent distillation column, but fundamentally they are based on Sorel's method (24). One of the best is that due to Lewis and Matheson (13). This is the application of Sorel's method together with the usual simplifying assumptions for multicomponent mixtures. The same operating line equations as used for binary mixtures are employed to determine the relation between the vapor composition and the composition of liquid on the plate above. This calculation together with vapor-liquid equilibrium data will be sufficient for the determination of the number of theoretical plates for given conditions.

Consider a unit which is operating as shown in Figure 5.2, so that a feed F is distilled to give a top product D and a bottom product W , with $X_{f,i}$, $X_{d,i}$, and $X_{w,i}$ as the corresponding mole fractions of component i . The vapor V_t rising from the top plate is condensed, and part of it is returned as liquid at its boiling point to the column as reflux, the remainder

being withdrawn as top product.

A material balance above plate n (indicated by the loop I in Figure 5.2) gives:

$$V_n = L_{n+1} + D \quad (5.4)$$

Expressing this balance on component i , we have:

$$V_n Y_{n,i} = L_{n+1} X_{n+1,i} + D X_{d,i}$$

Thus

$$Y_{n,i} = (L_{n+1}/V_n) X_{n+1,i} + (D/V_n) X_{d,i} \quad (5.5)$$

In the section above the feed plate, this equation gives a relation between the composition of the vapor rising to a plate and the composition of the liquid on that plate. With the assumption of equal molar flow, we can replace L_{n+1} by L , V_n by V , and write:

$$Y_{n,i} = (L/V) X_{n+1,i} + (D/V) X_{d,i} \quad (5.6)$$

Similarly, taking a material balance for the total stream and for the component i for the bottom part of the column (indicated by the loop II in Figure 5.2), and noting that $L_m = \bar{L}$, and $V_m = \bar{V}$, we write:

$$\bar{L} = \bar{V} + W \quad , \quad Y_{m,i} \bar{V} = \bar{L} X_{m+1,i} - W X_{w,i}$$

or

$$Y_{m,i} = (\bar{L}/\bar{V}) X_{m+1,i} - (W/\bar{V}) X_{w,i} \quad (5.7)$$

This is similar to equation (5.6), and gives the corresponding relation between the compositions of the vapor rising to a plate and the liquid on the plate, for the section below the feed plate. These two equations are the equations of the operating lines for the multicomponent distillation

calculation.

In order to calculate the change in composition from one plate to the next, we use the equilibrium data to find the composition of the vapor above the liquid, and the operating line to calculate the composition of the liquid on the next plate. This method can then be repeated up the column, using equation (5.7) for section below the feed plate, and equation (5.6) for section above the feed plate.

3. Procedure of Calculation

3.1 The Degrees of Freedom for a Distillation Column

In order to calculate the number of theoretical plates for our multi-component distillation column, we have to know the degrees of freedom for our system. The degrees of freedom involved in a distillation system can be evaluated (5) by applying 1). the law of conservation of matter, 2). the law of conservation of energy, and 3). the second law of thermodynamics. These laws together with phase rule can be applied to each plate, the still, and the condenser in a distillation column and the over-all degrees of freedom for the system determined.

Considering the rectifying column consisting of a total condenser, a reboiler, a feed plate, n theoretical plates above the feed plate, the degrees of freedom for a system involving C components has been shown to be (5)

$$C + 2m + 2n + 10 \quad (5.8)$$

The variables used for these degrees of freedom are usually chosen from the ones summarized in Table 5.1. Theoretically, the choice of variables is completely independent, but in practically all distillation calculations, some of those given in the table are ordinarily fixed. For example, it is usual to define the composition and the condition of the feed,

the operating pressure of each plate, and the heat gain or loss to or from each plate and the condenser. Referring to Table 5.1, these four items add up to $C + 2m + 2n + 6$, so there are four variables that still should be assigned. In most case, to facilitate the design calculation the reflux ratio is fixed, and in general it is desirable to carry out the separation specified with the minimum number of theoretical plates (i.e., the ratio of n/m is such that the total number of the plates shall be a minimum, and this effectively fixes one additional variable). So there are only two remaining variables which can be fixed, and the choice of these is dictated by the essential nature of the operation to be performed in the column. In the case of a binary mixture, the choice of these two independent terminal concentrations obviously gives the complete compositions of the distillate and residue, and makes the design calculations easy and straightforward. However, in the case of multicomponent mixtures the problem is more complex and, in general, the complete composition of neither the residue nor the distillate can be determined by using the two additional factors to fix two terminal conditions.

In this case, it is necessary to estimate the complete composition of either the product or the residue, and then proceed with the calculations until the desired degree of separation is attained. If the calculated product and residue compositions satisfy a material balance for each component, the estimated composition is correct. However, if a material balance is not satisfied by any one of the components, it is necessary to readjust the composition and repeat the calculation until the material balances are all satisfied simultaneously.

For the dehydration column in the KSU gasohol production process, there are no plates above the feed plate because the feed is saturated with water

, and equilibrium calculations have shown that the vapor in equilibrium with the feed will split into two liquid phases on condensing. So the dehydration column is just a stripper. For a stripper consisting of a total condenser, a reboiler, a feed plate, and m perfect plates below the feed plate, the degrees of freedom are (5)

$$C + 2m + 8 \quad (5.9)$$

The variables from which degrees of freedom may be chosen are summarized in Table 5.2.

3.2 The Light Key and Heavy Key Components

In selecting these two terminal concentrations, it is desirable to choose components that will give a significant control of separation desired and, at the same time, that will appear in appreciable amounts in both the bottoms and the distillate. Because these controlling components are so important in determining the design calculations, they have been termed the "key components". In other words, they are the key to the design problems. In the development of design equations, it is found that it is much more convenient to identify two key components, the light key component and the heavy key component. The former is the more volatile component whose concentration is desired to control in the bottoms; the latter is the less volatile component which is specified in the distillate. Most practical equations which have been developed for the minimum number of theoretical plates at total reflux, the optimum feed-plate location, and the minimum reflux ratio, have involved the terminal concentrations of the key components (22), so it is very important to select the key components carefully.

However, certain difficulties are involved: 1). the design specifications may be such that the key components are not obvious and 2). these design equations often require the concentrations of both key components in the distillate and bottoms as well as the concentrations of some of the other components. Hence the difficulties of choosing the key components and estimating the complete distillate and bottoms compositions are often the most difficult parts of a multicomponent design calculation.

The problem can generally be simplified in cases where the separation between adjacent components is essentially complete, the two independent variables can be chosen as the concentration of the more volatile of the two in the bottoms and as the concentration of the less volatile component in the distillate. These adjacent components then become the key components, and the composition of the distillate and the bottoms can be determined completely enough for the design calculations by simple material balances. This is because usually the components more volatile than the light key component will be negligible in the bottoms, and the components heavier than the heavy key will be negligible in the distillate. However, if the degree of separation is low and/or there are several components of nearly the same volatility in the range in which the separation is being made, the selection of the two key terminal concentrations will generally not give enough information to allow the complete terminal compositions to be calculated by simple material balances. In such cases, it is necessary to estimate the terminal concentrations of the other distributed components and then check this estimation by proceeding with the usual stepwise plate-to-plate calculations. If such plate-to-plate calculations give a consistent over-all result, the estimated values are satisfactory; if the results are

inconsistent, new values must be estimated and the calculations repeated. A useful estimation of the distributions of components in continuous multi-component distillation has been proposed by Hengstebeck (21).

4. Plate-to-plate Calculations for the Gasohol Dehydration Column

The wet gasohol from the extractor contains approximately 0.56 wt% (2.61 mol%) water, and is to be dried by distillation in the gasohol dehydration column. The water contained in the gasohol product is asked to be less than 0.1 wt% (0.5 mol%). In order to proceed with the calculations, some variables must be specified and some assumptions must be made. The variables which are usually fixed are:

- 1). complete composition of feed; $X(E) = 0.1957$, $X(W) = 0.0261$, $X(G) = 0.7782$. This is the saturated gasoline phase from the extractor,
- 2). condition of the feed; saturated liquid at its boiling point.
- 3). operating pressure over each plate and the still and condenser ; 730 mm Hg.,
- 4). heat gain or loss to or from each plate; adiabatic operation.

Referring to Table 5.2, these four items add up to $C + 2m + 5$, so there are three variables that still should be assigned. These will be:

- 1). the ratio of the liquid flow rate to the vapor flow rate,
- 2). the number of plates below the feed plate,
- 3). the bottom product to be 100 moles (i.e., use 100 moles of the residue as the basis).

4.1 Procedure of Calculations

The procedure of the calculations is as follows:

- 1). assume a complete composition of the bottom product,

- 2). assume a temperature, and use equations 5.1, 5.2, and 5.3 to calculate the values of Y 's,
- 3). if the sum of Y 's is not equal to unity, a new temperature is assumed, and steps 2 and 3 are repeated until the sum of the mole fractions of all the components in the vapor (Y 's), so calculated, add up to 1,
- 4). by use of the operating line equation (equation 5.7) calculate the liquid composition of the next plate,
- 5). repeat steps 2 and 3 to find the equilibrium temperature and the composition of the vapor which is in equilibrium with the liquid on that plate, and then step 4 until plate m is reached,
- 6). continue to calculate the values of $X_{n+1,i}$'s to see if the mole fractions of ethanol and water in the liquid phase of plate of $m+1$ are in the range of the feed composition, and each hypothetical component has the same mole fraction. If the answer is no, a new complete composition of the bottom product is assumed, and steps 2 thru 6 are repeated until the answer is yes.

In step 2 we need the K values of ethanol, water, and each of the hypothetical components. The calculation of these quantities has been shown in Chapter IV.

4.2 Results and Discussions

These plate-to-plate calculations are made by use of the PDP-11 mini-computer. The computing program is shown in Appendix C. The calculation results are shown in Tables 5.3 and 5.4, and plotted in Figures 5.3 and 5.4. For the case shown, the concentration of ethanol is higher than required,

and the concentration of water is lower than required, so that part of the gasoline phase of the distillate may be blended with the bottom product to form the desired gasohol product. Some other calculations are also made as shown in Table 5.5 and 5.6. From Table 5.5, we can see that when the feed composition and the flow ratio of liquid to vapor are fixed, if the number of the plates is increased, the concentration of ethanol in the bottom product will increase and that of water will decrease. From Table 5.6, we can see that when the feed composition and the number of the plates are fixed, if the flow ratio of liquid to vapor is increased (less heat is added to the reboiler), the concentration of water in the bottom product will increase, while that of ethanol will increase to some maximum then decrease. So the optimum design of this stripper is function of the numbers of the plates, the flow ratios of liquid to vapor and composition of feed.

Because this system exhibits regions of partial miscibility a major concern is that there be only one liquid phase, the gasoline phase, on a plate. The computed liquid compositions on each plate were checked against the ternary liquid-liquid equilibrium data and none were found to lie in the two-liquid-phase region.

TABLE 5.1 DISTILLATION COLUMN VARIABLES

Types of Variables	No. of Variables Fixed
Complete composition of feed	(C-1)
Condition of feed	2
Operating pressure over each plate and in still and condenser	$m + n + 3$
Operating temperature on each plate and in still and condenser	$m + n + 3$
Heat gain or loss to or from each plate and condenser	$m + n + 2$
Heat supplied to still	1
Composition of two product streams	2(C-1)
Relative quantity of two products streams ...	1
No. of plates above feed	1
No. of plates below feed	1
Relative quantity of feed returned to top plate to overhead product	1

TABLE 5.2 STRIPPING COLUMN VARIABLES

Types of Variables	No. of Variables Fixed
Complete composition of feed	(C-1)
Condition of feed	2
Operating pressure over each plate and in still and condenser	$m + 3$
Operating temperature on each plate and in still and condenser	$m + 3$
Heat gain or loss to or from each plate	$m + 1$
Heat removed from condenser	1
Heat supplied to still	1
Composition of two product streams	2(C-1)
Relative quantity of two product streams ...	1
No. of plates below feed	1
Relative quantity of feed returned to top plate to overhead product	1

TABLE 5.3 RESULTS OF PLATE-TO-PLATE CALCULATIONS FOR THE GASOLIN DEHYDRATION COLUMN
(MOLE FRACTION OF SELECTED COMPONENTS IN THE LIQUID PHASE)

Plate	T(°F)	X(E)	X(W)	X(1)	X(2)	X(3)	X(4)	X(6)	X(8)	X(11)	X(15)	X(19)
0	145	.22220	.00225	.00039	.00103	.00250	.00750	.02460	.03970	.05110	.05650	.05820
1	131	.28099	.00772	.00123	.00287	.00628	.01614	.04074	.05042	.04691	.04150	.03905
2	124	.24105	.01166	.00307	.00629	.01223	.02674	.05250	.05489	.04416	.03999	.03893
3	120	.22309	.01641	.00608	.01083	.01856	.03447	.05422	.04949	.04162	.03941	.03890
4	117	.21325	.02115	.01074	.01662	.02495	.03947	.05170	.04568	.04041	.03918	.03889
5	113	.20631	.02481	.01773	.02372	.03110	.04206	.04791	.04302	.03977	.03905	.03889
6	111	.19900	.02582	.02707	.03123	.03564	.04149	.04328	.04077	.03917	.03890	.03887
Feed	108	.19565	.02606	.03937	.03907	.03876	.03928	.03948	.03932	.03880	.03882	.03886

X : mole fraction ; $\bar{L}/\bar{V} = 3.0$

TABLE 5.4 RESULTS OF PLATE-TO-PLATE CALCULATIONS FOR THE GASOLIN DEHYDRATION COLUMN
(MOLE FRACTION OF SELECTED COMPONENTS IN THE VAPOR PHASE)

Plate	T(°F)	Y(E)	Y(W)	Y(1)	Y(2)	Y(3)	Y(5)	Y(7)	Y(9)	Y(11)	Y(15)	Y(19)
0	145	.39856	.01867	.00290	.00654	.01383	.05438	.07671	.06082	.03854	.01150	.00074
1	131	.27874	.03048	.00844	.01681	.03169	.09329	.10066	.05921	.03029	.00697	.00039
2	124	.22487	.04473	.01745	.03044	.05067	.11153	.09574	.04690	.02265	.00523	.00030
3	120	.19535	.05895	.03415	.04779	.06986	.11606	.08383	.03854	.01903	.00454	.00026
4	117	.17452	.06994	.05242	.06909	.08830	.11234	.07275	.03364	.01712	.00415	.00023
5	113	.15259	.07297	.08041	.09162	.10191	.10104	.06191	.02952	.01530	.00371	.00021
6	111	.14255	.07369	.11715	.11515	.11127	.08847	.05416	.02699	.01421	.00347	.00019

Y : mole fraction ; $\bar{L}/\bar{V} = 3.0$

TABLE 5.5 COMPOSITION OF BOTTOM PRODUCT FOR
DIFFERENT NUMBERS OF PLATES *

No. of plates	3	4	5	6	7
X(E)	0.2170	0.2197	0.2211	0.2223	0.2234
X(W)	0.0042	0.0034	0.0027	0.0022	0.0018
X(G)	0.7788	0.7769	0.7762	0.7755	0.7748
Feed Composition: X(E) = 0.1957; X(W) = 0.0261; X(G) = 0.7782					

* $\bar{L}/\bar{V} = 3.0$

TABLE 5.6 COMPOSITION OF BOTTOM PRODUCT UNDER
DIFFERENT VALUES OF \bar{L}/\bar{V} *

Ratio of \bar{L}/\bar{V}	2.0	2.5	3.0	3.5	4.0
X(E)	0.1944	0.2191	0.2222	0.2209	0.2174
X(W)	0.0000	0.0003	0.0023	0.0075	0.0111
X(G)	0.8056	0.7806	0.7755	0.7716	0.7715
Feed Composition: X(E) = 0.1957; X(W) = 0.0261; X(G) = 0.7782					

* No. of Plates = 6

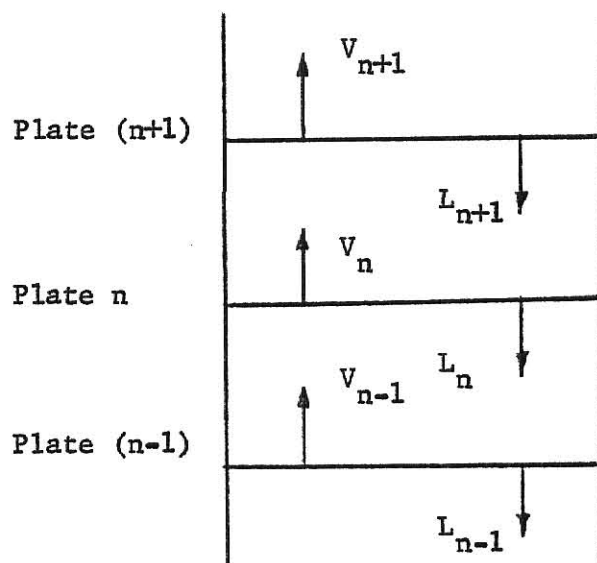


Figure 5.1 Material Balance over a Plate

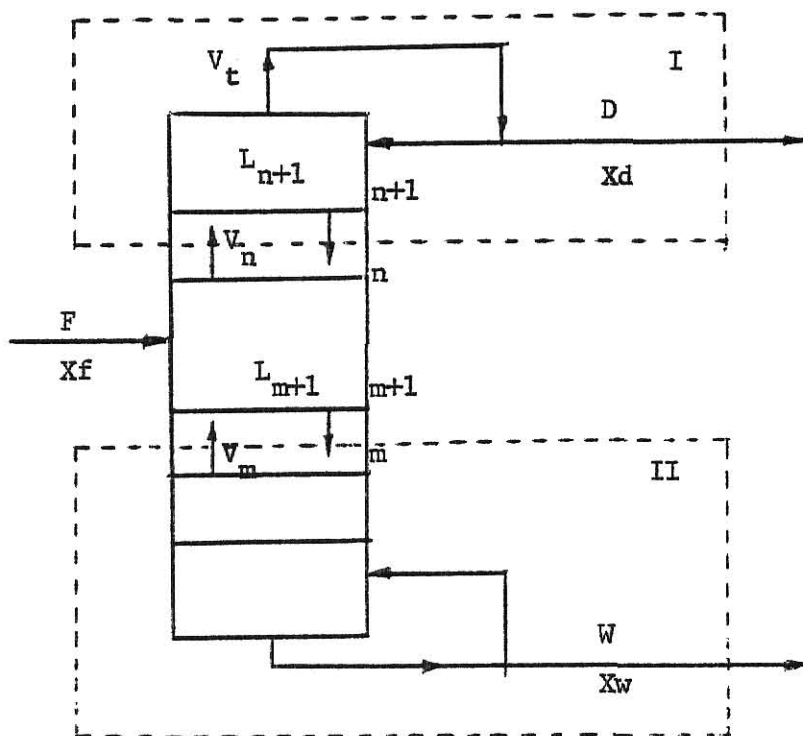


Figure 5.2 Material Balances at Top and Bottom of Plates

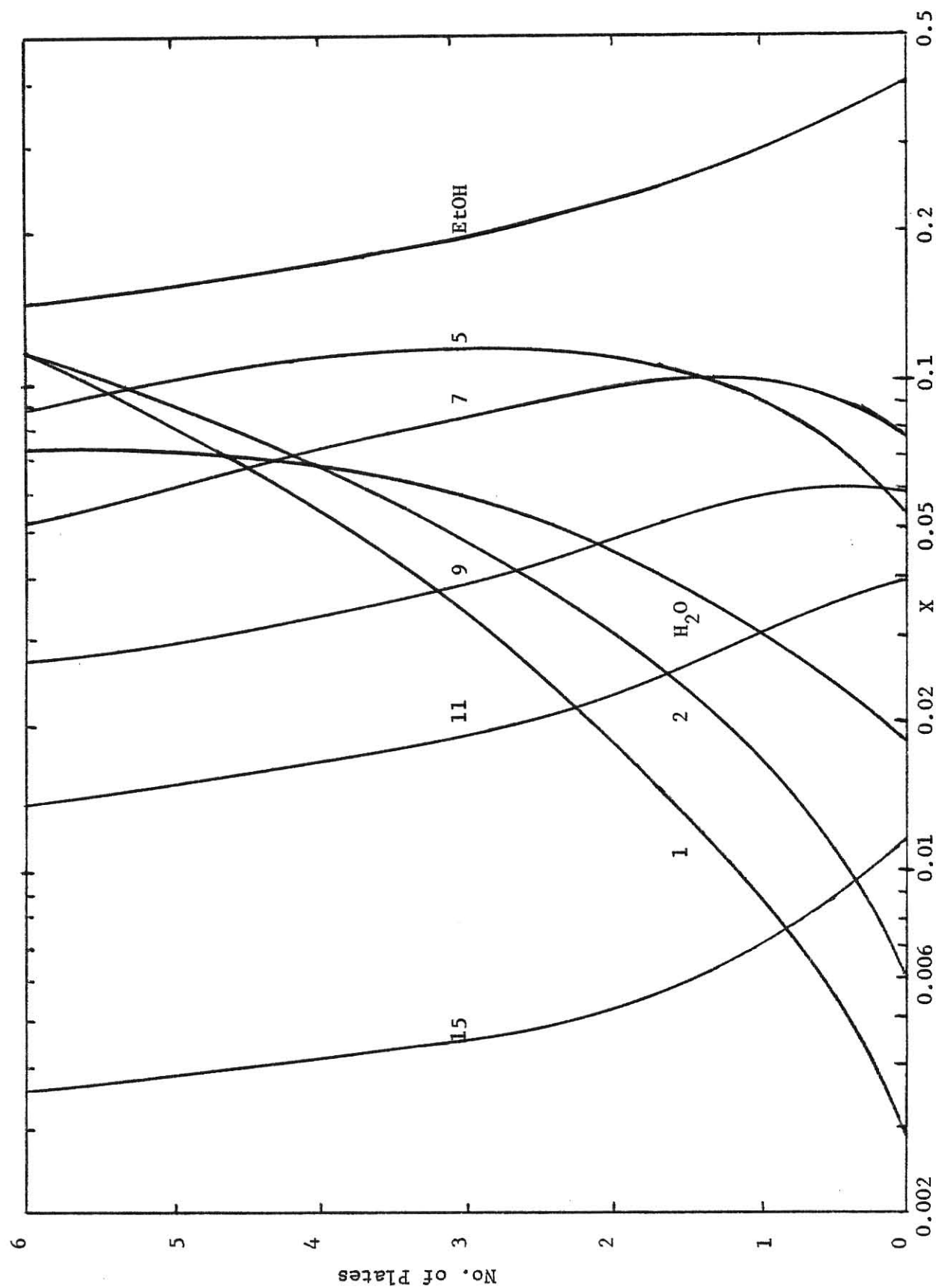


Figure 5.3 Mole Fractions of Some Components in the Vapor Phase

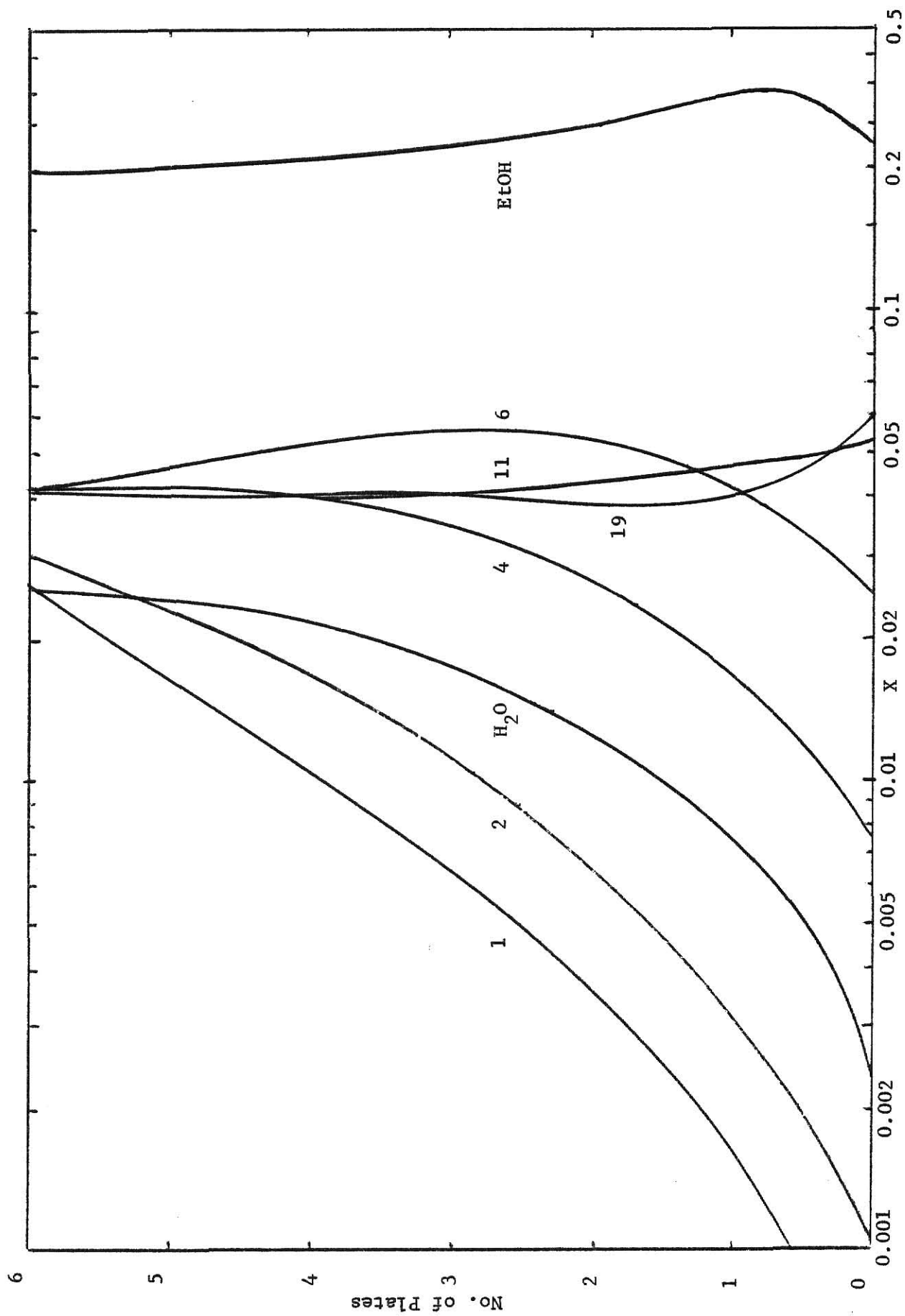


Figure 5.4 Mole Fractions of Some Components in the Liquid Phase

CHAPTER VI

GASOHOL DEHYDRATION TEST

1. Introduction

In order to test the possibility of dehydration of wet gasohol by distillation, an apparatus was set up as shown in Figure 6.1. It was a bubble-cap distillation column with 11 plates. The column was made of glass and was one inch in diameter with one bubble cap per tray. In accordance with the calculations of Chapter V, the column was operated as a stripping column. The wet gasohol was fed to the column through a flow meter. The feed was regulated manually to keep the flow rate constant. The vapor from the top plate was totally condensed and collected. The bottom residue was withdrawn to keep the liquid level in the boiling flask constant. The concentrations of water in the feed, distillate, and residue were measured by use of a Beckman Model KF-3 Aquameter. Before the experiment was conducted, the over-all efficiency of the column was measured, and the vapor rates corresponding to different heat inputs were also measured.

2. Overall Efficiency of the Column

In order to measure the overall efficiency of the column, the methylcyclopentane-benzene binary system was chosen. The vapor-liquid equilibrium data at 760 mm Hg pressure are listed in Table 6.1 (1). The indices of refraction of methylcyclopentane-benzene mixtures at different compositions at 20 °C are also listed in Table 6.1. Several different compositions of methylcyclopentane-benzene mixtures were distilled with total reflux. The compositions of the distillate and the bottom residue were measured by refractive index and the number of ideal stages for the separation was then deter-

ined by use of the method of McCabe and Thiele. The overall efficiency of the column was found by definition as follows:

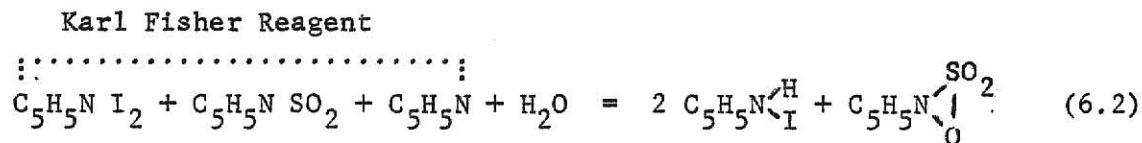
$$\frac{\text{the no. of ideal stages}}{\text{the no. of actual stages}} = \text{overall efficiency of the column} \quad (6.1)$$

The results are shown in Table 6.2, and a sample calculation is illustrated on Figure 6.2. We can see that the overall efficiency of the column is between 55 and 64 % and that the column contains between 6 and 7 stages.

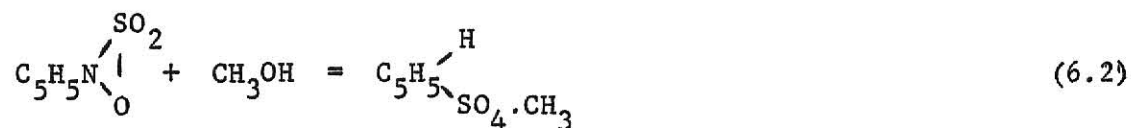
3. Determination of Water Content in Liquid Samples

The concentrations of water in the feed, distillate, and residue are about 0.6, 1.6, and 0.05 wt% respectively. In order to measure the water content precisely, a Beckman Model KF-3 Aquameter was used. The measurements are based on the Karl Fisher titration, in which the reagent reacts quantitatively with water in the sample to give a sharp chemical change (titration end point) that is detected electrometrically by the instrument. Titrations are completed automatically, eliminating the need for human judgement used conventionally in recognizing titration end point by subtle color changes.

In a titration, a standard reagent is added from a burette to a solution containing the sample till an end point, or moisture-free state is reached. The main reactions that appear to take place in methanol solution are:



and



When the end point is approached, the resistance of the solution decreases and is sensed by a platinum electrode which, in turn, cause a delivery valve to stop flow of the reagent. Simultaneously, a timer is activated to initiate a timing cycle that may be any length up to 60 seconds. The timing cycle is incorporated to prevent false end points caused by side reactions or slow release of moisture, from stopping the titration before it is completed. After the time delay the end point is rechecked.

At the end of a titration, the amount of reagent required to bring the sample to a moisture-free state is read directly from the graduated burette. With this information, and by knowing the titer of the reagent, the water content of the sample can be calculated.

The titer is used to define how many milligrams of water a milliliter of reagent represents.

4. Experimental Procedure

4.1 Preparing Karl Fisher Reagent

The titer of undiluted Karl Fisher (KF) reagent is typically 3 to 7 mg of water per ml of reagent, while the water contents in the feed, distillate, and residue are about 0.6, 1.6, and 0.05 wt% (or 4.5, 12.2, and 0.38 mg of water per ml of solution) respectively. Therefore, it is desirable to dilute the KF reagent to a titer range from 1.0 to 1.5 by blending it with a special diluent. Both the KF reagent and the diluent were obtained from the Fisher Scientific Company.

4.2 Preparing Anhydrous Solution

Sample materials analyzed with the Beckman Model KF-3 Aquameter must be immersed in an anhydrous or moisture-free titrating solution. It is necessary to titrate for an anhydrous solution only at the beginning of a series of analyses, since the completion of one reaction gives a moisture-free solution for the next. The anhydrous solution is prepared by titrating about 20 - 25 ml of water-methanol solution containing approximately 2 milligrams of water per milliliter of solution to an end point.

4.3 Standardizing KF Reagent with Sodium Tartrate Dihydrate

Because a fine grained sodium tartrate dihydrate contains 15.66 wt% water under all conditions in the laboratory, it serves as an excellent primary standard for determining the titer of KF reagent. The procedure of standardizing the KF reagent is as follows:

- 1). Weigh out approximately 200 milligrams of sodium tartrate dihydrate, then pour this sample into anhydrous solution in the reaction beaker, and record the exact amount of sodium tartrate dihydrate added,
- 2). Titrate the solution and record volume of KF reagent used to reach end point.

The titer of KF reagent is then calculated as follows:

$$\begin{aligned}
 & \frac{0.1566 \times \text{milligrams of sodium tartrate dihydrate added}}{\text{volume of reagent used for titration (ml)}} \\
 & = \text{titer of the reagent} \qquad \qquad \qquad (6.4)
 \end{aligned}$$

This value can be used in subsequent titrations to determine the moisture content of unknown samples and to establish the titer of the secondary standard, water-methanol solution.

4.4 Standardizing KF Reagent with Water-Methanol Solution

The titer of the KF reagent is checked once or twice daily with water-methanol solution. The water content of the water-methanol solution is determined once a week. The procedure of determining the titer of the water-methanol solution is as follows:

- 1). Immediately after standardizing the KF reagent with sodium tartrate dihydrate, titrate approximately 10 to 15 ml of water-methanol solution, taking careful note of the exact volume of water-methanol added,
- 2). The burette reading at end point represents volume of KF reagent equivalent to water-methanol added.

The moisture content of the solution is then calculated as follows:

$$\begin{aligned}
 & \frac{(\text{mg H}_2\text{O/ml reagent}) \times (\text{ml reagent added})}{\text{ml water-methanol added}} \\
 &= \text{mg H}_2\text{O/ml water-methanol} \qquad (6.5)
 \end{aligned}$$

4.5 Preparing Wet Gasohol

Wet gasohol was prepared by blending 2,358.8 grams of unleaded gasoline, 286.0 grams of anhydrous ethanol, and 15.0 grams of water. In order to make sure of obtaining a saturated mixture, five more grams of water were added. By this way, we obtained a very small amount of aqueous phase (about 15 ml) at the bottom of the mixture. The water content in

this gasohol as measured by the KF-3 Aquameter was 4.71 mg water/ml solution (or 0.628 wt%).

4.6 Operation of Dehydration Column

The procedure for operating the dehydration column is as follows:

- 1). Add 150 - 200 ml of wet gasohol into the boiling flask, adjust the heat supply and operate the column at total reflux until the light hydrocarbons and most of the water are stripped from the liquid in the flask. As long as water is in the system the condensed vapors will form two liquid phases. The condenser head was constructed so that the aqueous phase (the heavy phase) would be collected and could be withdrawn while the hydrocarbon phase (the light phase) overflowed and returned to the column. The column was operated at total reflux until the aqueous phase no longer formed.
- 2). Next, feed in the wet gasohol at a constant rate. Collect the distillate, and withdraw the bottom product from the boiling flask to keep the liquid level constant,
- 3). Every 10 minutes, record the reading of temperature at the bottom, the amounts of the distillate collected and the bottom product withdrawn until the system reaches the steady state. Steady state is assumed when the temperature of the liquid in the boiling flask is unchanged.
- 4). Measure the water content in the bottom product, when sufficient quantity is collected.

5. Results and Discussions

We ran the experiment twice, and the gasoline used was different from that used previously whose properties were shown in Chapter IV. The properties of the new gasoline are shown in Table 6.3. For the first run a steady state was not reached. This could be because we put too much wet gasohol (about 280 ml) in the boiling flask and didn't reflux the system to remove water before starting the feed. For the second run, we put only 150 ml of wet gasohol in the boiling flask. Before we fed the wet gasohol into the dehydration column, we withdrew 55 ml to keep the liquid in the boiling flask around 90 ml throughout the experiment. We also recorded the total volume of wet gasohol used, the rate of the distillate collected and the temperature change of the liquid in the boiling flask throughout the experiment. The detailed data are shown in Appendix D and summarized in Table 6.4.

The data obtained indicated that the system reached steady state for the second run. The flow rate of the feed was 4.49 ml/min (or 3.287 gram/min), the distillate was collected at the rate of 1.60 ml/min (or 1.082 gram/min), and the bottom product was withdrawn at the rate of 2.29 ml/min (or 1.845 gram/min). Thus, 0.369 gram/min of gasoline was unaccounted for and the material balance closure was 89%. The ratio \bar{L}/\bar{V} was calculated from liquid volumetric flows based on the assumption of equal liquid molar volumes for the overhead and bottom products. This ratio was calculated to range from 2.3 to 2.7 during this run.

There is a great deal of uncertainty associated with the calculated value of \bar{L}/\bar{V} . The assumption of equal liquid molar volumes would be reasonable if there were little difference between the overhead and

bottom compositions. Except for the water content these compositions were not measured, but a value of 125°C for the boiling temperature of the bottoms indicates that quite a few of the lighter components of the gasoline were stripped out. The calculations of Chapter V showed some stripping of these components, but predicted a boiling temperature of 67°C . Because this fractionation of the gasoline would result in the the liquid molar volume of the bottom product surpassing that of the overhead product, the calculated values of \bar{L}/\bar{V} could be too large.

Liquid-phase water concentration profiles calculated for seven ideal stages and three values of \bar{L}/\bar{V} by the method described in Chapter V are tabulated in Table 6.4. Observe that for seven ideal stages and $\bar{L}/\bar{V} = 2.8$ a bottoms water content of 0.016 wt% was calculated. In view of the tenuousness of the calculated \bar{L}/\bar{V} , it seems reasonable to state that within the experimental uncertainty the test values of 0.016 to 0.018 wt% water for 6 to 7 ideal stages with \bar{L}/\bar{V} between 2.3 and 2.7 tend to confirm the calculations. In any event, the experimental results show that dehydration of wet gasohol by stripping is possible. It should also be noted that during both runs only one liquid phase was observed on the trays or in the boiling flask.

TABLE 6.1 DATA FOR THE METHYLCYCLOPENTANE-BENZENE SYSTEM (6)

Mole Fraction of Methylcyclopentane		Relative Volatility	Boiling Point at 760 mm Hg	Refractive Index of Known Mixture	
Liquid	Vapor	α	$^{\circ}\text{C}$	x	n
0.0297	0.0526	1.814	79.64	0.0547	1.49333
0.1080	0.1668	1.653	77.62	0.1343	1.48432
0.1751	0.2533	1.598	76.62	0.1616	1.48120
0.3017	0.3870	1.461	74.85	0.2095	1.47553
0.3806	0.4598	1.385	74.00	0.3857	1.45794
0.4450	0.5179	1.340	73.43	0.4851	1.44896
0.5031	0.5673	1.295	---	0.6159	1.43820
0.5737	0.6255	1.241	72.84	0.7486	1.42749
0.6434	0.6795	1.175	72.06	0.7871	1.42486
0.7206	0.7442	1.128	71.79	0.8316	1.42175
0.7855	0.7986	1.083	---	0.8435	1.42138
0.8224	0.8299	1.054	71.54	0.9366	1.41452
0.8441	0.8499	1.046	---		
0.8721	0.8754	1.030	---		
0.9030	0.9034	1.005	71.47		
0.9180	0.9174	0.992	71.53		
0.9295	0.9287	0.988	---		
0.9373	0.9360	0.978	71.65		
0.9450	0.9442	0.985	71.68		
0.9518	0.9503	0.968	71.80		
0.9613	0.9602	0.971	---		

TABLE 6.2 OVERALL EFFICIENCY OF THE COLUMN

Time Run	1 Hour			2 Hours			3 Hours			4 Hours		
	B	T	N	B	T	N	B	T	N	B	T	N
1	.127	.640	6-7	.105	.563	6-7	.075	.550	6-7	.045	.488	6-7
2	.148	.600	6-7	.095	.590	6-7	.088	.555	6-7	.062	.530	6-7
3	.205	.623	5-6	.180	.640	6-7	.162	.662	7-8	.140	.630	6-7
Overall Efficiency of the Column = 55 - 64 %												
* B: Bottom; T: TOP; N: No. of Ideal Stages												

TABLE 6.3 ASTM DISTILLATION DATA OF THE GASOLINE USED
IN THE DEHYDRATION TEST *

Gravity, API	60.1
Reid Vapor Pressure	11.3
Lead, gm/gal	0.001
Gum, ASTM, mg/100 ml	0.2
RSH, ppm	2.8
Research Octane No.	91.1
Motor Octane No.	84.1
Distillation, D86	
IBP	87
5%	110
10%	124
20%	155
50%	232
90%	336
95%	372
EP	398
Recovery %	96.0
Residue %	1.1
Loss %	2.9

* Supplied by Getty Refining and Marketing Company
ElDorado, Ks

TABLE 6.4 THE WATER CONTENTS IN THE BOTTOM PRODUCT AT
DIFFERENT OPERATING TIMES *

Time (minutes)	0	11	60	90	130	157	final
	Feed	B-1	B-2	B-3	B-4	B-5	B-6
Sol. added (ml)	2.50	5.00	20.0	50.0	50.0	50.0	50.0
KFR added (ml)	7.80	6.05	4.35	4.15	4.40	3.95	3.40
No. of titrations	3	3	3	1	1	1	1
mg water/ml sol.	4.71	1.83	.328	.125	.133	.120	.103
wt%	.628	.244	.044	.017	.018	.016	.014

* $\bar{L}/\bar{V} = 2.28 - 2.71$; The titer of KFR = 1.51

TABLE 6.5 LIQUID PHASE WATER COMPOSITION* PROFILES
CALCULATED FOR A COLUMN WITH SEVEN IDEAL
STAGES UNDER VARIOUS \bar{L}/\bar{V}

Plates No. Values of \bar{L}/\bar{V}	4	3	2	1	0 **
2.6	0.151	0.086	0.047	0.027	0.006
2.8	0.267	0.175	0.107	0.067	0.016
3.0	0.420	0.314	0.210	0.144	0.039

* Weight Percentage ; ** Bottom

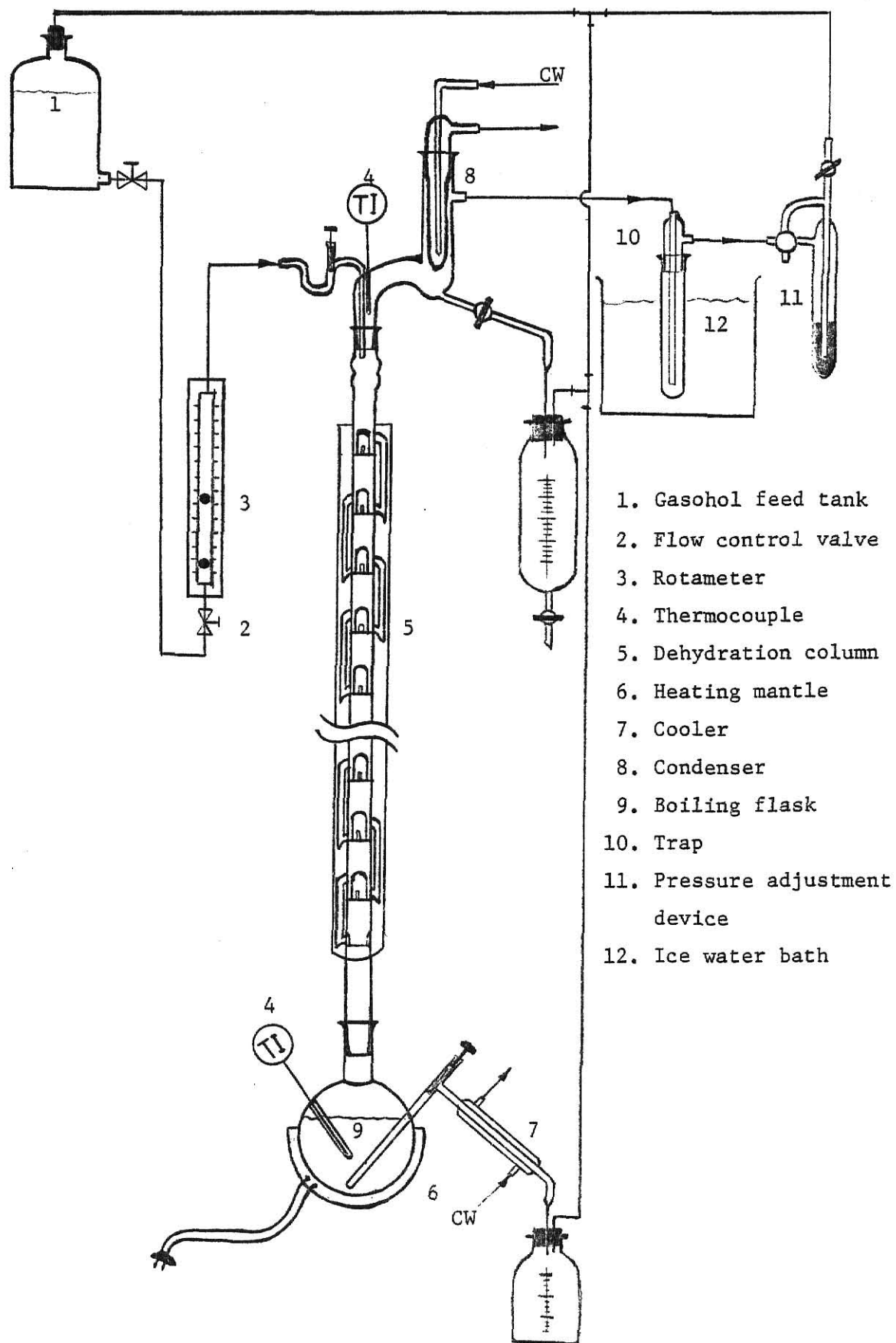


Fig. 6.1 Flow diagram of dehydration equipment

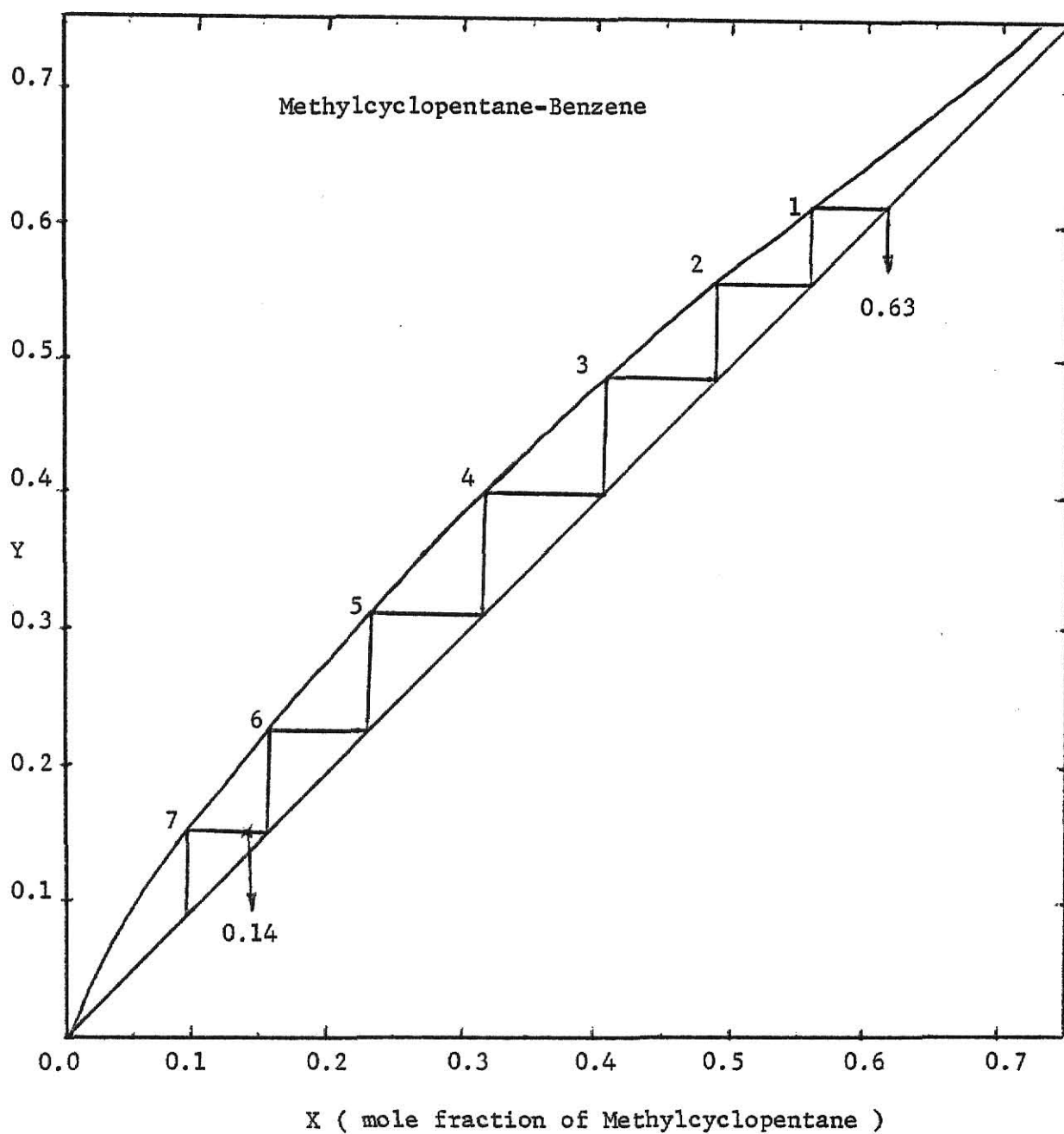


Figure 6.2 Determination of number of ideal stages by the McCabe-Thiele method. Run No. 3 (4 hours)

CHAPTER VII

DESIGN AND EVALUATION OF KSU SEPARATION PROCESS

1. Introduction

In this chapter, we delineate a design for the KSU process which is detailed on Figure 7.1. An energy analysis is also performed. Although the design was not optimized, it was found that the energy requirement for producing gasohol by the KSU process is significantly less than that by the presently-used process. This lower energy requirement results in the cost for producing gasohol by the KSU process being slightly lower than that by the presently-used process in which gasohol is produced by blending gasoline with anhydrous ethanol.

2. Design of KSU Separation Process

2.1 Description

As shown in Figure 7.1, the process is divided into three parts - distillation of ethanol, extraction of ethanol, and dehydration of wet gasohol.

In the distillation of ethanol, the numbers of ideal plates required to concentrate the ethanol from a feed concentration of 7.3 wt% to 80 wt% under different operating pressures has been determined by the McCabe-Thiele method. The results are shown in Table A.1 and Figure A.1. Since the numbers of ideal plates under different operating pressures were almost the same, the column was designed to operate at 75 psia pressure so that the heat released by condensing the distillate might be used to supply that required by the reboiler of the dehydration

column.

First, the ethanol solution (from fermentation) is preheated by heat exchanger with the bottoms of the ethanol column in E-1, then further heated by steam in E-2 to its boiling point (284°F). The raffinate from the bottom of the extraction column is preheated by steam condensate in E-3 from 122°F to its boiling point (270°F). For the energy recovery, part of the distillate is condensed in the reboiler (E-8) of the dehydration column and part is condensed in E-7 to heat the gasoline which is used as a solvent in the extraction column from room temperature to 122°F . The rest is condensed in E-5 by cooling water. All the condensed distillate is collected in a storage tank (T-3), then part is pumped to the distillation column as reflux. The rest is further cooled to 122°F and pumped to the extraction column. All the steam condensate is collected in T-2 for energy recovery.

In the extraction of ethanol, the cooled ethanol solution (61 mol% ethanol) is pumped to the top of the extraction column where ethanol's extracted countercurrently with gasoline. The extract (the wet gasohol) is stored in T-6, then pumped to the dehydration column for the removal of water.

For dehydration, the wet gasohol is pumped from T-6 to the top of the dehydration column. The distillate is condensed in E-9 and collected in T-7. The storage tank is so constructed that it serves as a settler which allows the two liquid phases to separate. The aqueous phase is pumped to the extractor for ethanol and gasoline recovery. Part of the gasoline phase's pumped to the mixer and blended

with the bottom product to obtain the desired gasohol product. The rest of the gasoline phase is then pumped to the extraction column. The bottom product is cooled in E-10 to room temperature before it is pumped to the mixer. The heat required by the dehydration column is supplied by condensing part of the distillate from the ethanol distillation column.

2.2 Specifications of Major Equipment

The process design was based on the production of 200 million gallons of gasohol per year which is equivalent to producing 20 million gallons per year of ethanol. The major equipment items shown in Figure 7.1 are those which required to produce gasohol from beer. The equipment required to produce the beer from grain is beyond the scope of our study.

The major equipment items are roughly specified. The specifications of the columns are shown in Table 7.1 and the detailed calculations are shown in Appendix F.

3. Energy Analysis of KSU Process

To date, gasohol has been produced by blending gasoline with anhydrous ethanol. However, ethanol and water form a minimum boiling azeotrope at ordinary conditions (for example, at 760 mm Hg pressure, the azeotrope composition is 95.6 wt% ethanol). In order to obtain anhydrous ethanol, dilute ethanol solution (beer) is concentrated approximately to its azeotropic point, then used as feed to an azeotropic or an extractive distillation column which furnishes dry ethanol. Because of the unusual shape of the ethanol-water vapor-liquid equilibrium diagram, the energy required per pound of distillate increases slowly as the ethanol

concentration in the distillate increases to about 90 wt%. Above 90 wt%, it increases greatly (14).

However, in the KSU process, the ethanol from a feed concentration of 6 to 12 wt% (beer) is concentrated only to 80 wt%. Then the ethanol is extracted with gasoline to form wet gasohol. Finally, the wet gasohol is dehydrated to the desired water content in the dehydration column. Because of the extreme deviations from ideal solution behavior, water is quite volatile and the dehydration of wet gasohol requires very little energy. From the flow sheet of this process (Figure 7.1), we see that steam is used only in the reboiler and feed heater of the ethanol distillation column. In the calculation of the heat required to produce one pound of gasohol product, the process was not designed to optimize energy recovery. Also, the heat loss from the surface of distillation column was assumed to be 10%. A reflux of 2.0 (about 1.20 x the minimum) was used in the ethanol distillation column.

The energy required to produce one pound of gasohol by the KSU process was calculated to be 229 Btu (or 1,509 Btu/gal gasohol). However, the energy used in conventional distillation producing anhydrous ethanol is estimated at 52,000 Btu/gal ethanol (or 5,200 Btu/gal gasohol, or 7,891 Btu/lb ethanol) (15). The difference is 3,691 Btu/gal gasohol and with a unit fuel cost of \$1.43 per million Btu, the production cost of gasohol by the KSU process is \$0.0053 per gallon less than the conventional distillation process.

4. Conclusion

From the above analysis, we see that the production of gasohol

by the KSU process is cheaper than that by the conventional distillation process. Although the differential cost of gasohol is only \$0.0053 per gallon, the KSU process would save \$1,060,000 for 200 million gallons per year gasohol production.

TABLE 7.1 SPECIFICATIONS OF THE COLUMNS

	Distillation Column	Extraction Column	Dehydration Column
Diameter (ft)	6	7	6
Height (ft)	52	51	36
No. of Plates	23	--	10
No. of Columns	1	2 *	1
* in series			

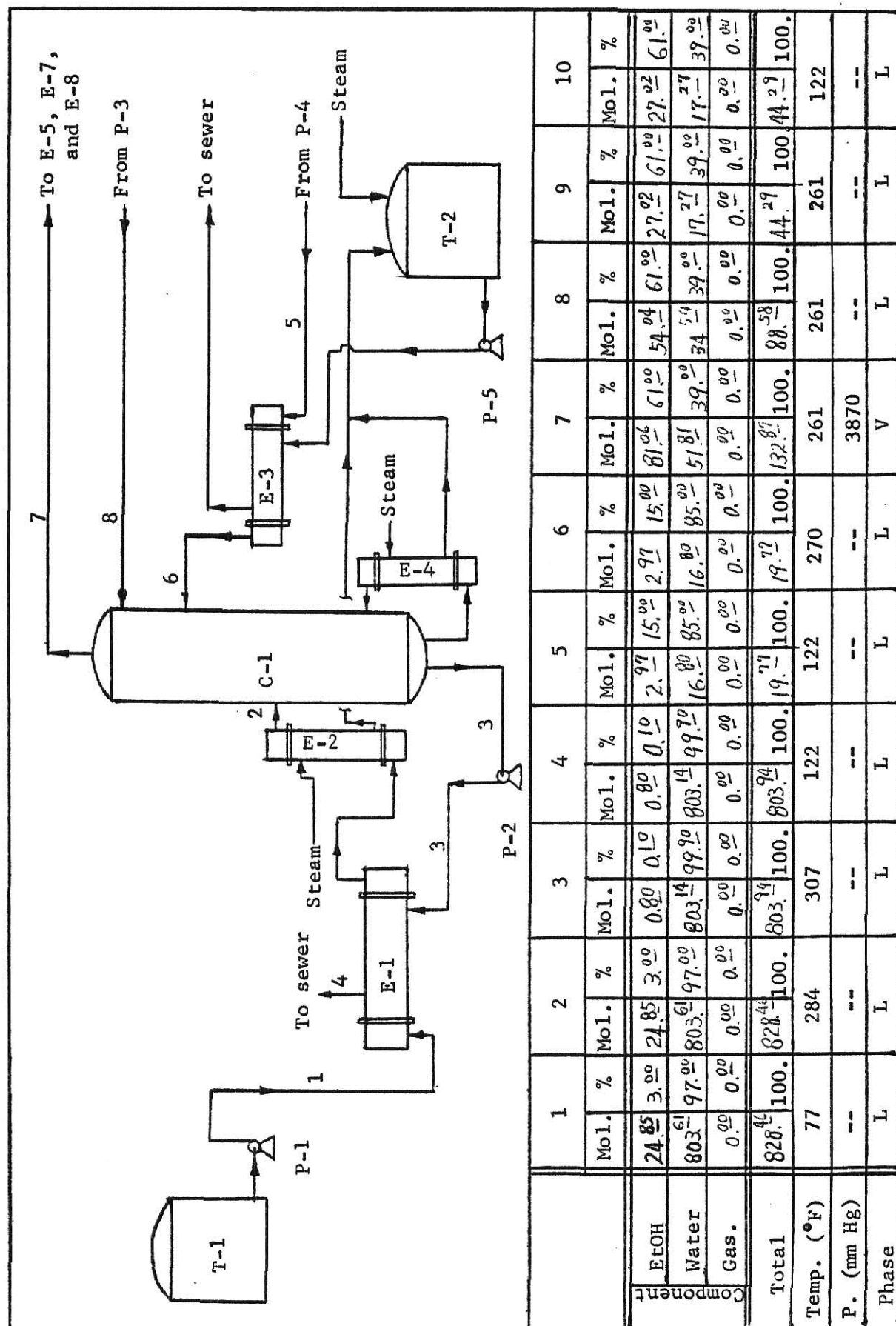


Figure 7.1a Flow sheet of KSU process with material balance (I)

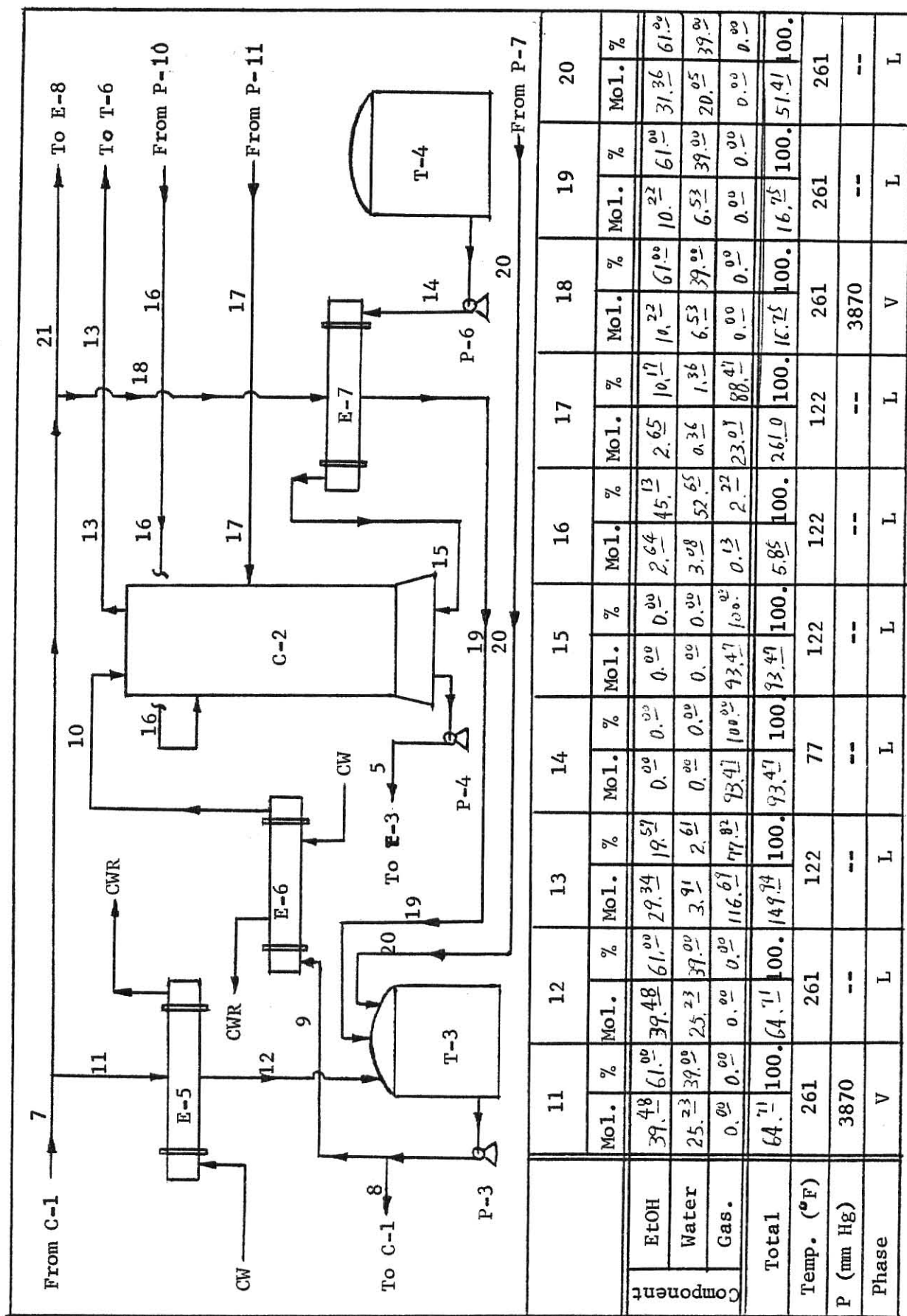


Figure 7.1b Flow sheet of KSU process with material balance (II)

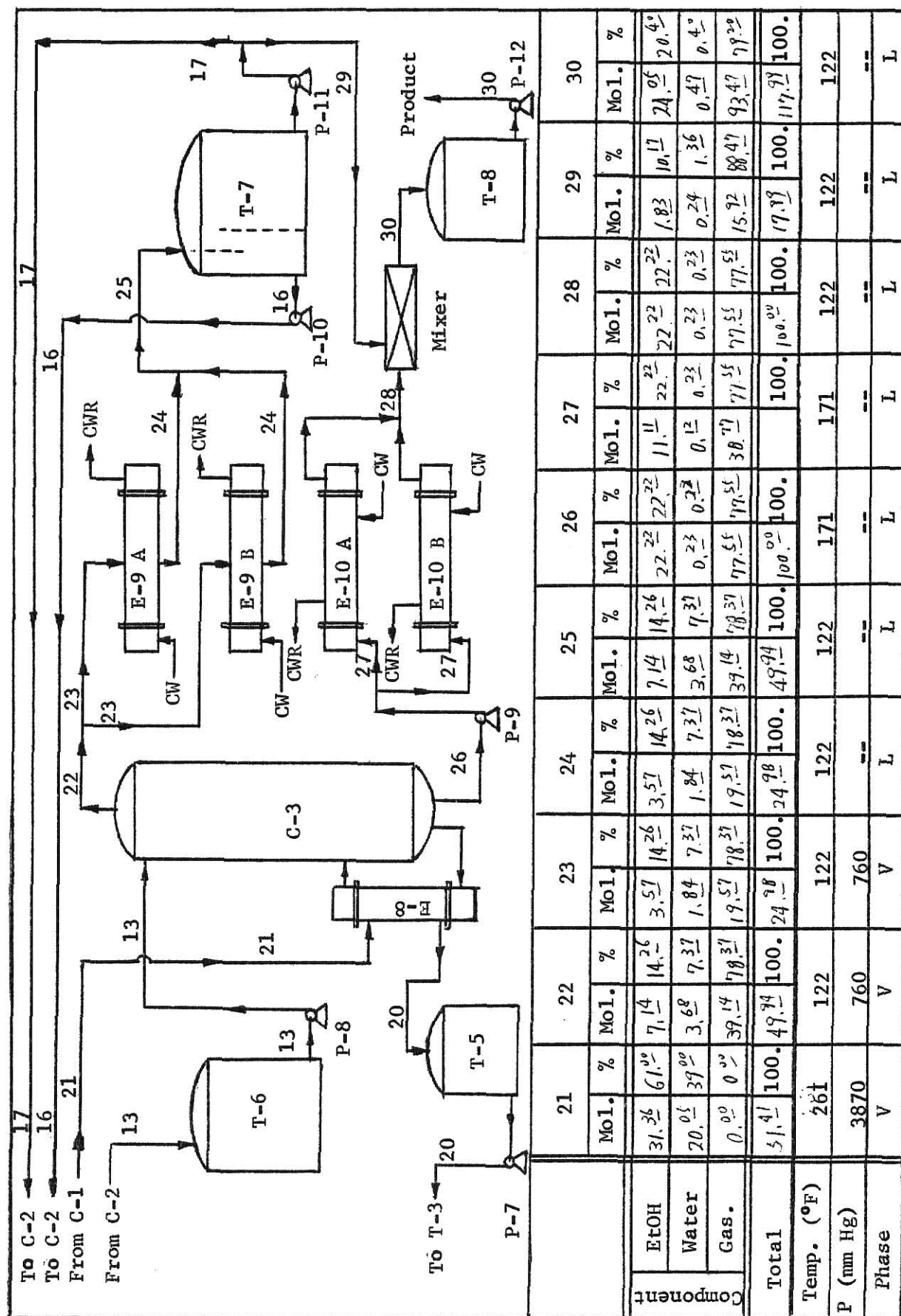


Figure 7.1c Flow sheet of KSU process with material balance (III)

NOMENCLATURE

a_i	activity of component i in the mixture
A, B, C	Antoine constants
AA, BB	constants used in equation (4.8)
A_{ij}	parameters used in the Margules, van Laar, Wilson, and UNIQUAC activity coefficient equations
f	flash ratio (equal to V/F)
f_i^L, f_i', f_i''	fugacity of component i in the liquid phase
f_i^V	fugacity of component i in the vapor phase
F	feed entering the distillation column
g_{ij}	energy of interaction between a pair of molecules (used in the NRTL activity coefficient equation)
G^E	excess free energy of mixing
G_{ij}	parameters used in the Wilson activity coefficient eq.
K_i	vapor-liquid distribution ratio of component i in the mixture, $K_i = y_i / x_i$
K_i'	ideal equilibrium ratio of component i , $K_i' = f_i^L / f_i^V$
L	liquid leaving the distillation column
L_n	liquid leaving tray n in the distillation column
$O.F.$	objective function (defined in equation 2.12)
P_i	vapor pressure of component i
P	total pressure of the system
q_i	molecular geometric external surface of component i , used in the UNIQUAC activity coefficient equation
q_i'	molecular surface of interaction of component i , used in the UNIQUAC activity coefficient equation
Q_{exp}, Q_{cal}	excess free energy of mixture divided by RT (experimental and calculated respectively)

r	molecular size parameter, used in the UNIQUAC equation
t	centigrade temperature
T	absolute temperature
u	characteristic velocity, used in the packed column
u', u''	velocities of continuous and dispersed phases respectively
V, V_t	vapor leaving the distillation column
V_i	molar volume of the pure liquid of component i
V_n	vapor leaving tray n in the distillation column
V'	allowable vapor velocity, used in the distillation column
W	product withdrawn from the bottom of the distillation column
x_i, x'_i, x''_i	mole fraction of component i in the liquid phase
x'_{is}, x''_{is}	mole fraction of component i in the saturated liquid phase
x'	mass ratio of ethanol to gasoline
$X_{n,i}$	liquid mole fraction of component i in tray n in the distillation column
y_i	mole fraction of component i in the vapor phase
$Y_{n,i}$	vapor mole fraction of component i in tray n in the distillation column
z_i	mole fraction of component i in the feed
Z or z	coordination number, UNIQUAC equation

Greek Letters

α	over-reflection factor in Box method or relative volatility
α_{ij}	nonrandomness factor in the NRTL activity coefficient equation
γ'_{is} and γ_i	activity coefficient of component i in saturated and unsaturated liquid phases respectively

δ_i	the solubility parameter of component i
ϵ	fractional voidage
θ_i and θ'_i	average area fraction of component i, UNIQUAC equation
ρ_L and ρ_V	density of liquid and vapor respectively
ϕ	dispersed-phase hold-up
ϕ_i	average segment fraction of component i, UNIQUAC eq.
$\hat{\phi}_i$	vapor phase fugacity coefficient of component i in the mixture
τ_{ij}	parameters in the NRTL and UNIQUAC activity coefficient equations

Subscripts

E	ethanol
G	gasoline
i or j	component i or j
m-1, m, m+1	plate number of the distillation column below the feed plate
n-1, n, n+1	plate number of the distillation column above the feed plate
s	saturated
W	water

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APPENDIX A

BOX METHOD

The procedure of this method is as follows:

- 1). start with a group of complex of k points, where k is at least one greater than the number of variables.
- 2). evaluate the value of the objective function, FSQ , for each point.
- 3). rank the points, so that the lowest value of the objective function is placed in position 1, the next lowest in position 2 ect. The point with the largest value is placed in the k -th position.
- 4). draw a vector of length L from the k -th point to the centroid of the remaining points.
- 5). find a new point k' by extending this vector an additional distance αL , where the over-reflection factor, α , is always greater than 1.
- 6). evaluate $FSQ(k')$, and compare with $FSQ(k)$.
- 7). if $FSQ(k') < FSQ(k)$, replace the point k by the point k' , and go back to step 3.
- 8). if $FSQ(k') > FSQ(k)$, determining a new point k'' by moving half way from the point k' to the centroid. Evaluate $FSQ(k'')$ and compare with $FSQ(k)$.
- 9). if $FSQ(k'') < FSQ(k)$, replace the point k by the point k'' , and go back to step 3.
- 10). if $FSQ(k'') > FSQ(k)$, the distance between the point k'' and the centroid is again halved to determine the point k''' , then go back to step 3. This procedure of moving toward the centroid continues until a point k^r is found where $FSQ(k^r) \leq FSQ(k)$, or until r reaches a specified value, say 6.

APPENDIX B

APPLICATION OF REGULAR SOLUTION THEORY TO

ETHANOL-WATER-GASOLINE MIXTURES

By the regular solution theory (10), for a mixture E, W, G1, G2
 ---, we may write:

$$RT \ln \gamma_k = V_k \left[\sum (\delta_k - \delta_i) \phi_i \right]^2 \quad (B.1)$$

with

$$\delta_i = (U_i^v / V_i)^{1/2} \quad (B.2)$$

$$\phi_i = x_i V_i / \left(\sum x_i V_i \right) \quad (B.3)$$

where

U_i^v is the energy of vaporization, cal/mole,

V_i is the liquid molal volume, ml/mole,

δ_i is the solubility parameter of component i,

ϕ_i is the volume fraction of component i.

For Ethanol

$$RT \ln \gamma_E = V_E \left[(\delta_E - \delta_W) \phi_W + \sum (\delta_E - \delta_{Gi}) \phi_{Gi} \right]^2 \quad (B.4A)$$

It is reasonable to assume the solubility parameters of all gasoline fractions to be identical and we replace all δ_{Gi} 's with δ_G to obtain:

$$RT \ln \gamma_E = V_E \left[(\delta_E - \delta_W) \phi_W + (\delta_E - \delta_G) \sum \phi_{Gi} \right]^2 \quad (B.4B)$$

but

$$\sum \phi_{Gi} = \phi_G$$

so

$$RT \ln \gamma_E = V_E \left[(\delta_E - \delta_W) \phi_W + (\delta_E - \delta_G) \phi_G \right]^2 \quad (B.4C)$$

For Water

$$RT \ln \gamma_W = V_W [(\delta_W - \delta_E) \phi_E + \sum (\delta_W - \delta_{Gi}) \phi_{Gi}]^2 \quad (B.5A)$$

again

$$\sum \phi_{Gi} = \phi_G$$

and

$$RT \ln \gamma_W = V_W [(\delta_W - \delta_E) \phi_E + (\delta_W - \delta_G) \phi_G]^2 \quad (B.5B)$$

From equations (B.4C) and (B.5B), we can see that γ_E and γ_W depend on ϕ_G regardless of ϕ_{Gi} 's.

For G_i

$$RT \ln \gamma_{Gi} = V_{Gi} [(\delta_{Gi} - \delta_E) \phi_E + (\delta_{Gi} - \delta_W) \phi_W]^2 \quad (B.6)$$

but

$$\phi_E + \phi_W = 1.0 - \phi_G$$

So, γ_{Gi} also depends only on ϕ_G and not on ϕ_{Gi} 's. If V_{Gi} 's are all equal, then γ_{Gi} 's are all equal.

APPENDIX C

PROGRAM FOR

DEHYDRATION AND FALSH VAPORIZATION CALCULATIONS

```

C  1      : ETHANOL
C  2      : WATER
C  3      : GASOLINE
C  A(I),B(I),C(I) : ANTOINE CONSTANTS
C  AA(I),BB(I) : CONSTANTS USED IN EQUATION (4.8)
C  FRFLM    : MOLE FRACTION OF FEED FLASHED
C  FRFLW    : WEIGHT FRACTION OF FEED FLASHED
C  GAM(I)   : ACTIVITY COEFFICIENT OF COMPONENT I
C  GAMAS3   : ASSUMED ACTIVITY COEFFICIENT OF GASOLINE
C  GAMAC3   : CALCULATED ACTIVITY COEFFICIENT OF GASOLINE
C  K180(I)  : VAPOR-LIQUID DISTRIBUTION RATIO HYPOTHETICAL COMPONENT
C            I OF GASOLINE AT 180 °C
C  K120(I)  : VAPOR-LIQUID DISTRIBUTION RATIO HYPOTHETICAL COMPONENT
C            I OF GASOLINE AT 120 °C
C  K(I)     : ACTUAL VAPOR-LIQUID DISTRIBUTION OF COMPONENT I IN
C            THE MIXTURE
C  MW(I)    : MOLECULAR WEIGHT
C  NN       : PROGRAM INDEX; 1: FOR DEHYDRATION CALCULATION, 2: FOR
C            FLASH VAPORIZATION CALCULATION
C  NP       : PLATE INDEX
C  PT       : TOTAL PRESSURE
C  RR       : MOLAR FLOW RATE RATIO OF LIQUID TO VAPOR
C  XB(I)    : BOTTOM PRODUCT COMPOSITIONS ( MOLE FRACTION )
C  XM(I)    : LIQUID COMPOSITIONS ( MOLE FRACTION )
C  YM(I)    : VAPOR COMPOSITIONS ( MOLE FEACTION )
C  ZM(I)    : FEED COMPOSITIONS ( MOLE FRACTION )
C  ZH(I)    : FEED COMPOSITIONS WHEN DIVIDED INTO 22 COMPONENTS

```

```

DIMENSION K180(20),K120(20),A(3), B(3),C(3),XM(3),ZM(3),MW(3)
@,VAPP(3),YM(22),XX(22),K(22),GAM(3),XB(22),AA(22),BB(22),ZH(
@22),XH(22),YH(22),XW(3),YW(3)

```

```

REAL K,MW,GAM,K180,K120,NP

```

```

READ,(A(I),B(I),C(I),MW(I),ZM(I),I=1,3)

```

```

READ,(K180(I),K120(I),I=1,20)

```

```

NN=1

```

```

PT=730.0

```

```

DO 1 I=3,22

```

```

J=I-2

```

```

BB(I)=ALOG(K180(J)/K120(J))/(1.0/640.0-1.0/580.0)

```

```

AA(I)=ALOG(K180(I))-BB(I)/640.0

```

```

1 CONTINUE

```

```

IF(NN.EQ.2) GO TO 50

```

```

*****
**                                     **
**      PROGRAM BELOW IS FOR DEHYDRATION CALCULATIONS      **
**                                     **
*****

```

```

      RR=2.0
      WRITE(6,37)
      NP=0.0
      READ,(XB(I),I=1,22)
      TF=180.0
      XM(1)=XB(1)
      XM(2)=XB(2)
      XM(3)=1.0-XM(1)-XM(2)
2  CONTINUE
      TC=(TF-32.0)/1.8
      CALL UINQUA(TC,XM,GAM)
      DO 3 I=1,2
      VAPP(I)=10.0*(A(I)-B(I)/(C(I)+TC))
      K(I)=VAPP(I)/PF*GAM(I)
3  CONTINUE
      DO 4 I=3,22
      K(I)=EXP(AA(I)+BB(I)/(TF+460.0))*GAM(3)
4  CONTINUE
      XX(1)=XB(1)
      XX(2)=XB(2)
      SUMMYM=0.0
      DO 5 I=1,22
      YM(I)=XX(I)*K(I)
      SUMMYM=SUMMYM+YM(I)
5  CONTINUE
      DSUM=ABS(SUMMYM-1.0)
      YM3=SUMMYM-YM(1)-YM(2)
      IF(DSUM.LE.0.01) GO TO 6
      IF(TF.LE.80.0) GO TO 999
      TF=TF-0.5
      GO TO 2
6  WRITE(6,100) TF,(XX(I),I=1,11)
      WRITE(6,200) (XX(I),I=12,22)
      WRITE(6,100) TF,(YM(I),I=1,11)
      WRITE(6,200) (YM(I),I=12,22)
      WRITE(6,300) NP,TC,YM(1),YM(2),YM3,XM(1),XM(2),GAM(1),
      @GAM(2),GAM(3),RR
      DO 7 I=1,22
      XX(I)=(YM(I)+XB(I)*(RR-1.0))/RR
7  CONTINUE
      XM(1)=XX(1)
      XM(2)=XX(2)
      XM(3)=1.0-XM(1)-XM(2)
      IF(NP.EQ.8) GO TO 999
      NP=NP+1.0
      GO TO 2

```

```

*****
**
** PROGRAM BELOW IS FOR FLASH VAPORIZATION CALCULATIONS **
**
*****

50 CONTINUE
  GAMAS3=1.26
  GAM(3)=GAMAS3
  FRFLM=0.04
  DO 51 I=3,22
    ZH(I)=ZM(3)/20.0
51 CONTINUE
  WRITE(6,400) ZM(1),ZM(2),ZM(3),FRFLM,PT
  TF=80.0
  TFI=0.01
52 TF=TF+TFI
  SUMMXH=0.0
  SUMMYH=0.0
  DO 53 I=3,22
    K(I)=EXP(AA(I)+BB(I)/(TF+460.0))*GAM(3)
    XH(I)=ZH(I)/(FRFLM*K(I)+1.0-FRFLM)
    YH(I)=XH(I)*K(I)
    SUMMXH=SUMMXH+XH(I)
    SUMMYH=SUMMYH+YH(I)
    IF(SUMMXH.GT.1.0) GO TO 52
    IF(SUMMYH.LE.0.0) GO TO 52
53 CONTINUE
  JJ=0
  DIFF=1.0-SUMMXH
  XXM=0.0
  XMI=0.1
54 XXM=XXM+XMI
  XM(1)=XXM
  XM(2)=DIFF-XM(1)
  XM(3)=SUMMXH
  IF(XM(2).LE.0.0) GO TO 52
  TC=TF-32.0)/1.80
55 CONTINUE
  CALL UNIQUA(TC,XM,GAM)
  GAMCA3=GAM(3)
  GAM(3)=GAMAS3
  DO 56 I=1,2
    VAPP(I)=10.0**(A(I)-B(I)/(C(I)+TC))
    K(I)=VAPP(I)/PT*GAM(I)
56 CONTINUE
  A1=XM(1)
  A2=XM(2)
  XM(1)=ZM(1)/(FRFLM*K(1)+1.0-FRFLM)
  XM(2)=ZM(2)/(FRFLM*K(2)+1.0-FRFLM)
  SUMMX=XM(1)+XM(2)+XM(3)
  XCHECK=1.0-SUMMX

```

```

XCHEK1=ABS(XCHECK)
A1D=ABS(XM(1)-A1)
A2D=ABS(XM(2)-A2)
IF(A1D.GT.0.0001.OR.A2D.GT.0.0001) GO TO 55
IF(XCHECK.LT.0.0) GO TO 54
IF(XCHEK1.LT.0.001) GO TO 57
IF(JJ.GE.10) GO TO 57
JJ=JJ+1
XXM=XXM-XMI
XMI=XMI/10.0
GO TO 54
57 IF(XM(2).LT.0.0) GO TO 52
YM(1)=XM(1)*K(1)
YM(2)=XM(2)*K(2)
YM(3)=SUMMYH
SUMMYH=YM(1)+YM(2)+YM(3)
YCHECK=1.0-SUMMYH
YCHEK1=ABS(YCHECK)
IF(SUMMYH.LT.1.0) GO TO 52
IF(YCHEK1.LT.0.001) GO TO 58
TF=TF-TFI
TFI=TFI/10.0
IF(TFI.GT.0.01) GO TO 52
58 CONTINUE
AB=46.0*XM(1)+18.0*XM(2)+96.0*XM(3)
BA=46.0*YM(1)+18.0*YM(2)+96.0*YM(3)
XW(1)=46.0*XM(1)/AB
XW(2)=18.0*XM(2)/AB
XW(3)=1.0-XW(1)-XW(2)
YW(1)=46.0*YM(1)/BA
YW(2)=18.0*YM(2)/BA
YW(3)=1.0-YW(1)-YW(2)
FRFLW=(YM(1)*46.0+YM(2)*18.0+YM(3)*96.0)*FRFLM/(ZM(1)*46.0+
@ZM(2)*18.0+ZM(3)*96.0)
WRITE(6,500)
WRITE(6,501) TF
WRITE(6,502) TC
WRITE(6,503) XM(1),XW(1)
WRITE(6,504) XM(2),XW(2)
WRITE(6,505) XM(3),XW(3)
WRITE(6,506) SUMMX
WRITE(6,507) YM(1),YW(1)
WRITE(6,508) YM(2),YW(2)
WRITE(6,509) YM(3),YW(3)
WRITE(6,510) SUMMYH
WRITE(6,511) GAM(1)
WRITE(6,512) GAM(2)
WRITE(6,513) GAMAS3,GAMAC3
WRITE(6,514) A1,XM(1),A2,XM(2),FRFLW
37 FORMAT(1H1)
100 FORMAT(/10X,F7.2,1X,11F8.5)
200 FORMAT(18X,12F8.5)
300 FORMAT(/7X,F3.0,F7.2,1X,12F8.5)
400 FORMAT(/14X,9F12.4)
500 FORMAT(/20X,'THERMODYNAMIC CRITERIA MET')

```

```

501 FORMAT(/20X,'EQUILIBRIUM TEMPERATURE (FARENHEIT) =' ,F12.4)
502 FORMAT(/20X,'EQUILIBRIUM TEMPERATURE (CENTIGRADE)=' ,F12.4)
504 FORMAT(/20X,'XM(H2O) =' ,F12.4,5X,'XW(H2O) =' ,F12.4)
503 FORMAT(/20X,'XM(ETOH)=' ,F12.4,5X,'XW(ETOH)=' ,F12.4)
505 FORMAT(/20X,'XM(GAS) =' ,F12.4,5X,'XW(GAS) =' ,F12.4)
506 FORMAT(/20X,'SUMMX =' ,F12.4)
507 FORMAT(/20X,'YM(ETOH)=' ,F12.4,5X,'YW(ETOH)=' ,F12.4)
508 FORMAT(/20X,'YM(H2O) =' ,F12.4,5X,'YW(H2O) =' ,F12.4)
509 FORMAT(/20X,'YM(GAS) =' ,F12.4,5X,'YW(GAS) =' ,F12.4)
510 FORMAT(/20X,'SUMMY =' ,F12.4)
511 FORMAT(/20X,'GAM(ETOH) =' ,F12.4)
512 FORMAT(/20X,'GAM(H2O) =' ,F12.4)
513 FORMAT(/20X,'GAM(GAS) =' ,F12.4)
514 FORMAT(/20X,12F9.4//)
999 STOP
END

```

```

SUBROUTINE UNIQUA(TC,XM,GAM)
  DIMENSION XM(3),GAM(3),R(3),Q(3),QP(3),PH(3),TH(3),THP(3),
  @CE(3,3),TA(3,3),BB(3),L(3)
  REAL L
  DATA R/2.11,0.92,5.17/
  DATA Q/1.97,1.40,4.40/
  DATA QP/0.92,1.0,4.40/
  DATA CE/0.0,518.2,1895.,21.35,0.00,9180,210.5,17950,0.0/
  DATA AA,A,B,C,Z/0.0,0.0,0.0,0.0,10.0/
  DATA BB/0.0,0.0,0.0/
  DO 1 I=1,3
    L(I)=Z*(R(I)-Q(I))/2.0-(R(I)-1.0)
1 CONTINUE
  DO 2 I=1,3
    A=A+XM(I)*R(I)
    B=B+XM(I)*Q(I)
    C=C+XM(I)*QP(I)
2 CONTINUE
  DO 3 I=1,3
    PH(I)=XM(I)*R(I)/A
    TH(I)=XM(I)*Q(I)/B
    THP(I)=XM(I)*QP(I)/C
3 CONTINUE
  DO 4 II=1,3
    DO 4 I=1,3
      TA(I,II)=EXP(-CE(I,II)/1.987/(TC+273.15))
      BB(II)=BB(II)+THP(I)*TA(I,II)
4 CONTINUE
  DO 5 I=1,3
    AA=AA+XM(I)*L(I)
5 CONTINUE
  DO 6 I=1,3
    GAM(I)=EXP(ALOG(PH(I)/XM(I))+Z*Q(I)*ALOG(TH(I)/PH(I)))/2.0+L
    @ (I)=-PH(I)/XM(I)*AA-QP(I)*ALOG(BB(I))+QP(I)-QP(I)*(TH(I)*TA
    @ (I,1)/BB(1)+TH(2)*TA(I,2)/BB(2)+TH(3)*TA(I,3)/BB(3)))
6 CONTINUE
  RETURN
END

```

APPENDIX D

DETAILED EXPERIMENTAL DATA FOR DEHYDRATION TEST

1. Data for the first run

Room temperature : 25 °C
 Heat input : 62.5 volts; 2.0 amps.
 Time of heat supply : 9:50
 Initial volume of wet gasohol in the
 boiling flask : 280 ml
 Distillate collected : 437 ml
 Bottom product collected : 619 ml

Time *	Temperature	Bottom product	
min.	millivolts **	ml	wt%
0	2.440	63	0.118
4	2.460		
9	2.493	110	0.070
21	2.600		
30	2.665		
45	2.795		
54	2.912		
64	3.095	95	0.029
84	3.302		
95	3.325		
105	3.367		
123	3.450	95	0.018
135	3.475		
195	---	100	0.005

* Time after feeding
 ** Copper-constantan thermocouple with room
 temperature cold junction

2. Data for the second run

Room temperature : 24.5 °C
 Heat input : 55 volts; 1.8 amps.
 Density of wet gasohol : 0.732 gram/ml
 Density of distillate : 0.676 gram/ml
 Density of bottom product : 0.806 gram/ml
 Time of heat supply : 14:50
 Time of feeding : 15:01
 Time of steady state : 16:41
 Initial volume of wet gasohol in
 the boiling flask : 150 ml

Total volume of wet gasohol fed	:	705 ml
Distillate collected	:	277 ml
Bottom product collected	:	445 ml
Hold-up of gasohol in the trays	:	30 ml
End of experiment	:	17:37

Time *	Temperature **	Distillate collected		Bottom product	
		Incremental ml	Cumulative ml	Incremental ml	Incremental-cumulative wt%
0	1.878	0	0	55	0.244
10	2.433	15	15		
20	3.041	19	34		
30	3.607	20	54		
40	3.920	18	72		
50	4.020	16	88	88	0.044
60	4.208	17	105		
70	4.210	17	122		
80	4.190	17	139	51	0.017
90	4.180	17	156		
100	4.160	16	172		
110	4.165	16	188		
120	4.165	16	204	65	0.018
130	4.165	16	220		
140	4.165	16	236		
150	4.165	16	252		
157	4.165	9	261	57	0.016

* Time after feeding

** Copper-constantan thermocouple with room temperature cold junction

APPENDIX E

MATERIAL BALANCE FOR THE KSU PROCESS

1. Data for the Process Design

Density of ethanol:	49.3 lb/cu.ft
Density of water:	62.4 lb/cu.ft
Density of gasoline:	45.2 lb/cu.ft
Density of gasohol:	45.7 lb/cu.ft
Specific heat of ethanol:	0.505
Specific heat of water:	1.0
Specific heat of gasoline:	0.52
Latent heat of ethanol:	204 Btu/lb
Latent heat of water:	970 Btu/lb
Latent heat of gasoline:	139 Btu/lb
Molecular weight of ethanol:	46 lb/lb-mole
Molecular weight of water:	18 lb/lb-mole
Estimated molecular weight of gasoline:	96 lb/lb-mole
Pseudo-molecular weight of gasohol:	85.9 lb/lb-mole
Size of the plant:	200 mil gal gasohol/year
Operating hours:	8,000 hrs/year

Composition of the feed to
the distillation column :

ethanol	7.3 wt.% (3.0 mol.%)
water	97.7 wt.% (97.0 mol.%)

Composition of the bottoms
of the distillation column :

ethanol	less than 0.1 mol.%
water	about 99.9 mol.%

Reflux ratio of the
distillation column :

2.0

Composition of the raffinate
of the extraction column :

ethanol	15.0 mol.%
water	85.0 mol.%

Composition of the feed
to the dehydration column :

ethanol	19.57 mol.%
water	2.61 mol.%
gasoline	77.82 mol.%

Composition of gasohol :

ethanol	about 11.0 wt.%
	(or) 20.4 mol.%
water	less than 0.1 wt.%
	(or) 0.5 mol.%

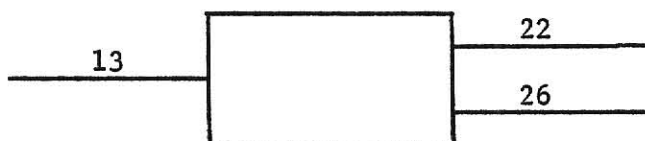
2. Calculation

The flow rate of the gasohol product:

$$\begin{aligned}
 200,000,000(\text{gal/year})/8,000(\text{hr/year}) &= 25,000(\text{gal/hr}) \\
 25,000(\text{gal/hr})/7.48(\text{gal/cu.ft}) &= 3,342(\text{cu.ft}) \\
 3,342(\text{cu.ft}) \times 45.3(\text{lb/cu.ft})/25.9(\text{lb/lb-mole}) \\
 &= 1,770.6(\text{lb-mole}) = 118(\text{lb-mole/4 min})
 \end{aligned}$$

The composition of stream 13 is:

ethanol	19.57 mol.%
water	2.61 mol.%
gasoline	77.82 mol.%



Using 100 moles of the bottom product as a basis, and by plate-to-plate calculation as shown in Chapter V, we obtain:

Stream 13:

ethanol	29.34 moles,	19.57 mol.%
water	3.91 moles,	2.61 mol.%
gasoline	116.69 moles,	77.82 mol.%

Stream 22 and 25:

ethanol	7.14 moles,	14.26 mol.%
water	3.68 moles,	7.37 mol.%
gasoline	39.14 moles,	78.37 mol.%

Stream 26 and 28:

ethanol	22.22 moles,	22.22 mol.%
water	0.23 moles,	0.23 mol.%
gasoline	77.55 moles,	77.55 mol.%

also we obtain:

Stream 23 and 24:

ethanol	3.57 moles,	14.26 mol.%
water	1.84 moles,	7.37 mol.%
gasoline	19.57 moles,	78.37 mol.%

Stream 27:

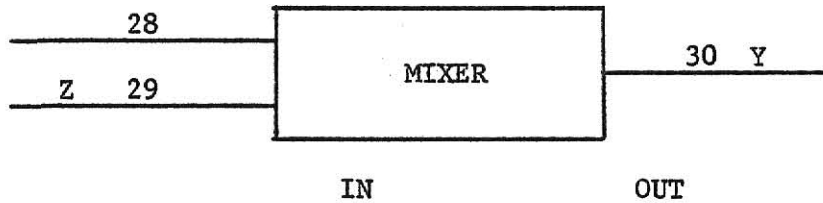
ethanol	11.11 moles,	22.22 mol.%
water	0.12 moles,	0.23 mol.%
gasoline	38.77 moles,	77.55 mol.%

From the E-W-G phase diagram (Figure 1.2), we obtain:

Stream 16:

ethanol	2.64 moles,	45.13 mol.%
water	3.08 moles,	52.65 mol.%
gasoline	0.13 moles,	2.22 mol.%

By material balance over the mixer we obtain:



ethanol	$22.22 + 0.1017 Z$	$= Y \text{ XM(E)}$
water	$0.23 + 0.0136 Z$	$= Y \text{ XM(W)}$
gasoline	$77.55 + 0.8847 Z$	$= Y \text{ XM(G)}$

Also $\text{XM(E)} + \text{XM(W)} + \text{XM(G)} = 1.0$, and $\text{XM(E)} = 0.204$

Solving these equations, we obtain:

Stream 29:

ethanol	1.83 moles,	10.17 mol.%
water	0.24 moles,	1.36 mol.%
gasoline	15.92 moles,	88.47 mol.%

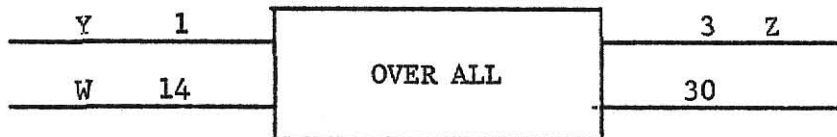
Stream 30:

ethanol	24.05 moles,	20.40 mol.%
water	0.47 moles,	0.40 mol.%
gasoline	93.47 moles,	79.20 mol.%

But stream 25 = stream 17 + stream 29, so

Stream 17:

ethanol	2.65 moles,	10.17 mol.%
water	0.36 moles,	1.36 mol.%
gasoline	23.09 moles,	88.47 mol.%



	IN	OUT
ethanol	$0.03 Y$	$= 0.001 Z + 24.05$
water	$0.97 Y$	$= 0.999 Z + 0.47$
gasoline	W	$= 93.47$

Solving these equations, we obtain:

Stream 14:

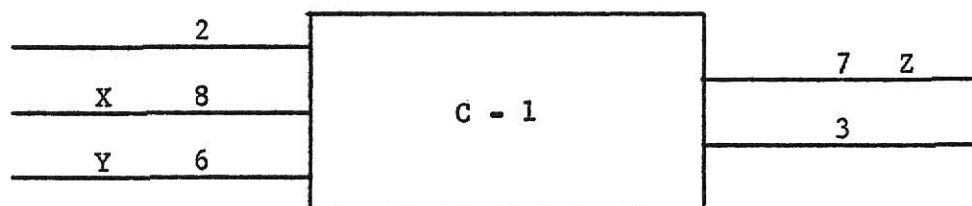
ethanol	0 moles,	0 mol.%
water	0 moles,	0 mol.%
gasoline	93.47 moles,	100 mol.%

Stream 1 and 2:

ethanol	24.85 moles,	3 mol.%
water	803.61 moles,	97 mol.%
gasoline	0.00 moles,	0 mol.%

Stream 3 and 4:

ethanol	0.80 moles,	0.1 mol.%
water	803.14 moles,	99.9 mol.%
gasoline	0.00 moles,	0.0 mol.%



IN

OUT

ethanol	$24.85 + 0.61 X + 0.15 Y$	$= 0.61 Z + 0.80$
water	$803.61 + 0.39 X + 0.85 Y$	$= 0.39 Z + 803.14$
gasoline	0	$= 0$

Also, $Y = 2/3 Z$

Solving these equations, we obtain:

Stream 5 and 6:

ethanol	2.97 moles,	15 mol.%
water	16.80 moles,	85 mol.%
gasoline	0.00 moles,	0 mol.%

Stream 7:

ethanol	81.06 moles,	61 mol.%
water	51.81 moles,	39 mol.%
gasoline	0 moles,	0 mol.%

Stream 8:

ethanol	54.04 moles,	61 mol.%
water	34.54 moles,	39 mol.%
gasoline	0.00 moles,	0 mol.%

The heat load of the condenser (E-9) is:

$$Q = 204 \times 7.14 \times 46 + 970 \times 3.68 \times 18 + 139 \times 39.14 \times 96$$

$$= 653,539 \text{ Btu}$$

Assume 10% heat loss from the surface of the dehydration column,

then the heat load of the reboiler (E - 8) is:

$$Q = 653,539 \times 1.10 = 718,893 \text{ Btu}$$

But the latent heat of the vapor (61 mol.% ethanol, 39 mol.% water) is:

$$L = 204 \times 0.61 \times 49 + 970 \times 0.39 \times 18 = 12,534 \text{ Btu/lb-mole}$$

So the quantity of stream 21 is:

$$W = 718,893 / 12,534 = 57.36 \text{ lb-mole, i.e.,}$$

Stream 20 and 21:

ethanol	34.99 moles,	61 mol.%
water	22.37 moles,	39 mol.%
gasoline	0 moles,	0 mol.%

The heat load of E-7 is:

$$Q = 0.52 \times (122 - 77) \times 93.47 \times 96 = 209,971 \text{ Btu}$$

So the quantity of stream 18 is:

$$W = 209,971 / 12,534 = 16.75 \text{ lb-mole, i.e.,}$$

Stream 18:

ethanol	10.22 moles,	61 mol.%
water	6.53 moles,	39 mol.%
gasoline	0 moles,	0 mol.%

Finally, stream 7 = stream 11 + stream 18 + stream 21, so we obtain:

Stream 11 and 12:

ethanol	39.48 moles,	61 mol.%
water	25.23 moles,	39 mol.%
gasoline	0 moles,	0 mol.%

From the calculations above, we see that with 100 moles of bottom product of the dehydration column as a basis, the gasohol product is 117.99 moles, which is equivalent to the flow rate of the gasohol of this designed process (118 lb-mole/4 min).

APPENDIX F

EQUIPMENT DESIGN FOR THE KSU PROCESS

1. Distillation Column (C-1):

1.1 Number of Plates of Distillation Column

The numbers of ideal plates of the distillation under three different operating pressures determined by the McCabe-Thiele method are shown in Table A.1 and on Figure A.1. The overall plate efficiency is estimated at 0.75 (20), then for 75 psia operating pressure, the number of the actual plates in the column is:

$$N = 17 / 0.75 = 23$$

1.2 Diameter of the Distillation Column

Mass flow rate of the vapor is:

$$\begin{aligned} V &= 81.06 \times 46 \times 15 + 51.81 \times 18 \times 15 \\ &= 69,920 \text{ lb/hr} = 19.4 \text{ lb/sec.} \end{aligned}$$

Allowable vapor velocity (V') (22) is:

$$\rho_V = 0.392 \text{ lb/cu.ft}$$

$$\rho_L = 51.80 \text{ lb/cu.ft}$$

For 24" plate spacing and 1" seal,

$$V' (\rho_V / (\rho_L - \rho_V))^{\frac{1}{2}} = 0.21 \text{ so,}$$

$$V' = 2.4 \text{ ft/sec.}$$

$$A = (19.4 / 0.392) / 2.4 = 20.6 \text{ sq.ft}$$

$$D = 5.1 \text{ ft}$$

For safety of operation, the diameter of the distillation column is designed to be 6 ft.

1.3 Height of the Distillation Column

The plate spacing is designed to be 24" (or 2 ft). There are 23

plates for this column, the height of this column is 52 ft (including the base).

2. Extraction Column (C-2)

2.1 Determination of NTU for the Extraction Column

Determination of NTU for the extraction column is shown in Figures A.2 and A.3, and is as follows:

Leaving streams were assumed saturated and in equilibrium with each other. Then:

For part I:

Stage I:

From the equilibrium curve (as shown in Figure A.2), we obtain x^1 (the mass fraction of ethanol to gasoline in the aqueous phase) to be 2.86, and compositions of C (obtained from Figure 1.2) are 62 wt% ethanol, 21.68 wt% water, and 16.32 wt% gasoline.

By material balance, we obtain:

$$\begin{array}{rclcl}
 & A & + & D & = & B & + & C \\
 \text{Ethanol} & 1,242.9 & + & D X(E) & = & 1,349.6 & + & 0.6200 C \\
 \text{Water} & 310.9 & + & D X(W) & = & 70.4 & + & 0.2186 C \\
 \text{Gasoline} & 0 & + & D X(G) & = & 11,202.5 & + & 0.1632 C
 \end{array}$$

Solving these equations, we obtain:

$$\begin{array}{rcl}
 \text{For C:} & \text{Ethanol} & = 1,020.5 \text{ lb (62.00 wt\%)} \\
 & \text{Water} & = 356.8 \text{ lb (21.68 wt\%)} \\
 & \text{Gasoline} & = 268.6 \text{ lb (16.32 wt\%)} \\
 \\
 \text{For D:} & \text{Ethanol} & = 1,127.2 \text{ lb (8.87 wt\%)} \\
 & \text{Water} & = 116.3 \text{ lb (0.91 wt\%)} \\
 & \text{Gasoline} & = 11,471.1 \text{ lb (90.32 wt\%)}
 \end{array}$$

Stage II:

From the equilibrium curve (as shown in Figure A.2), we obtain x' to be 2.25, and compositions of C (obtained from Figure 1.2) are 61.23 wt% ethanol, 27.21 wt% water, and 11.56 wt% gasoline.

By the material balance, we obtain:

$$\begin{array}{rcl}
 & A & + \quad D & = & B & + & C \\
 \text{Ethanol} & 1,242.9 & + D X(E) & = & 1,349.6 & + 0.6123 C \\
 \text{Water} & 310.9 & + D X(W) & = & 70.4 & + 0.2721 C \\
 & 0 & + D X(G) & = & 11,202.5 & + 0.1156 C
 \end{array}$$

Solving these equations, we obtain:

$$\begin{array}{rcl}
 \text{For C:} & \text{Ethanol} & = & 793.8 \text{ lb (61.23 wt\%)} \\
 & \text{Water} & = & 352.8 \text{ lb (27.21 wt\%)} \\
 & \text{Gasoline} & = & 149.9 \text{ lb (16.56 wt\%)}
 \end{array}$$

$$\begin{array}{rcl}
 \text{For D:} & \text{Ethanol} & = & 900.5 \text{ lb (7.28 wt\%)} \\
 & \text{Water} & = & 112.3 \text{ lb (0.91 wt\%)} \\
 & \text{Gasoline} & = & 11,352.4 \text{ lb (91.81 wt\%)}
 \end{array}$$

For part II:

Stage III:

From the equilibrium curve (as shown in Figure A.2), we obtain x' to be 1.79, and compositions of F (obtained from Figure 1.2) are 57.08 wt% ethanol, 31.89 wt% water, and 11.03 wt% gasoline.

By material balance, we obtain:

$$\begin{array}{rcl}
 & A & + \quad E & + \quad G & = & B & + & F \\
 \text{Ethanol} & 1,242.9 & + 121.4 & + G X(E) & = & 1,349.6 & + 0.5708 F \\
 \text{Water} & 310.9 & + 55.4 & + G X(W) & = & 70.4 & + 0.3189 F \\
 \text{Gasoline} & 0 & + 12.5 & + G X(G) & = & 11,202.5 & + 0.1156 F
 \end{array}$$

Solving these equations, we obtain:

$$\begin{array}{rcl}
 \text{For F:} & \text{Ethanol} & = & 651.2 \text{ lb (57.08 wt\%)} \\
 & \text{Water} & = & 363.8 \text{ lb (31.89 wt\%)} \\
 & \text{Gasoline} & = & 125.8 \text{ lb (11.56 wt\%)}
 \end{array}$$

For G: Ethanol = 636.5 lb (5.30 wt%)
 Water = 67.9 lb (0.56 wt%)
 Gasoline = 11,315.8 lb (94.14 wt%)

For part III:

Stage IV:

From the equilibrium curve (as shown in Figure A.2), we obtain x' to be 1.25, and compositions of H (obtained from Figure 1.2) to be 53.15 wt% ethanol, 42.52 wt% water, and 4.33 wt% gasoline.

By material balance, we obtain:

$$\begin{array}{rcl}
 & A & + \quad E \quad + \quad L \quad + \quad I \quad = \quad B \quad + \quad H \\
 \text{Ethanol} & 1,242.9 + 121.4 + 122.0 + I X(E) & = \quad 1,349.6 + 0.5708 H \\
 \text{Water} & 310.9 + 55.4 + 6.5 + I X(W) & = \quad 70.4 + 0.3189 H \\
 \text{Gasoline} & 0 + 12.5 + 2,217 + I X(G) & = \quad 11,202.5 + 0.1156 H
 \end{array}$$

Solving these equations, we obtain:

For H: Ethanol = 423.3 lb (53.15 wt%)
 Water = 338.6 lb (42.52 wt%)
 Gasoline = 34.5 lb (4.33 wt%)

For I: Ethanol = 286.6 lb (3.07 wt%)
 Water = 36.2 lb (0.39 wt%)
 Gasoline = 9,007.5 lb (96.54 wt%)

Stage V:

From the equilibrium curve (as shown in Figure A.2) we obtain x' to be 0.62, and the compositions of H (obtained from Figure 1.2) to be 37.88 wt% ethanol, 61.09 wt% water, and 1.03 wt% gasoline.

By material balance, we obtain:

$$\begin{array}{rcl}
 & A & + \quad E \quad + \quad L \quad + \quad I \quad = \quad B \quad + \quad H \\
 \text{Ethanol} & 1,242.9 + 121.4 + 122.0 + I X(E) & = \quad 1,349.6 + 0.3788 H \\
 \text{Water} & 310.9 + 55.4 + 6.5 + I X(W) & = \quad 70.4 + 0.6109 H \\
 \text{Gasoline} & 0 + 12.5 + 2,217 + I X(G) & = \quad 11,202.5 + 0.0103 H
 \end{array}$$

Solving these equations, we obtain:

For H:	Ethanol	=	204.9 lb (37.88 wt%)
	Water	=	330.4 lb (61.09 wt%)
	Gasoline	=	5.6 lb (1.03 wt%)
For I:	Ethanol	=	68.2 lb (0.75 wt%)
	Water	=	28.0 lb (0.30 wt%)
	Gasoline	=	8,978.6 lb (98.95 wt%)

Stage VI:

From the equilibrium curve (as shown in Figure A.2), we obtain x' to be 0.17, and this value is less than what we want (0.452), so the number of ideal stages for the extraction column is between 5 and 6.

2.2 Determination of HTU for the Extraction Column

Determination of HTU for the extraction column was by using procedure developed by Treybal (19) for packed column. The calculated results are summarized as follows:

Gasoline phase dispersed:

A. using 1.5" metal pall rings ($\epsilon = 0.94$)

$$\begin{array}{llll} u' & = & 6.5 \text{ ft/hr} & u'' = 57.6 \text{ ft/hr} & a & = & 25 \text{ sq.ft/cu.ft} \\ \phi & = & 0.1 & d & = & 0.0225 \text{ ft} & u/u'' = 12 \end{array}$$

$$\text{HTU (based on continuous phase)} = 39.5 \text{ ft}$$

where

- d : diameter of a sphere of volume equal to that of a drop, ft
- ϵ : volume fraction
- ϕ : dispersed-phase hold-up
- u : characteristic velocity, ft/hr
- u' : velocity of continuous phase, ft/hr
- u'' : velocity of dispersed phase, ft/hr
- a : contact surface, sq.ft/cu.ft packing

B. using 1.5" stoneware rashing rings ($\epsilon = 0.71$)

$$\begin{array}{llll} u' & = & 4.9 \text{ ft/hr} & u'' = 44.0 \text{ ft/hr} & a & = & 18 \text{ sq.ft/cu.ft} \\ \phi & = & 0.1 & d & = & 0.0225 \text{ ft} & u/u'' = 15.8 \end{array}$$

$$\text{HTU (based on continuous phase)} = 43.5 \text{ ft}$$

C. using 1.5" metal pall rings ($\epsilon = 0.94$)

$$\begin{array}{llll} u' & = & 11.7 \text{ ft/hr} & u'' = 104 \text{ ft/hr} & a = 42 \text{ sq.ft/cu.ft} \\ \phi & = & 0.2 & d = 0.0269 \text{ ft} & u/u'' = 6.84 \end{array}$$

$$\text{HTU (based on continuous phase) } = 44.5 \text{ ft}$$

D. using 1.5" metal pall rings ($\epsilon = 0.94$)

$$\begin{array}{llll} u' & = & 3.3 \text{ ft/hr} & u'' = 29.2 \text{ ft/hr} & a = 13 \text{ sq.ft/cu.ft} \\ \phi & = & 0.05 & d = 0.022 & u/u'' = 22.53 \end{array}$$

$$\text{HTU (based on continuous phase) } = 38.7 \text{ ft/hr}$$

Aqueous phase dispersed:

A. using 1.5" metal pall rings ($\epsilon = 0.94$)

$$\begin{array}{llll} u' & = & 245 \text{ ft/hr} & u'' = 27.6 \text{ ft/hr} & a = 12.2 \text{ sq.ft/cu.ft} \\ \phi & = & 0.1 & d = 0.0442 \text{ ft} & u/u'' = 23.5 \end{array}$$

$$\text{HTU (based on continuous phase) } = 27.6 \text{ ft}$$

B. using 1.5" metal pall rings ($\epsilon = 0.94$)

$$\begin{array}{llll} u' & = & 178 \text{ ft/hr} & u'' = 20.0 \text{ ft/hr} & a = 9.1 \text{ sq.ft/cu.ft} \\ \phi & = & 0.05 & d = 0.031 \text{ ft} & u/u'' = 32.9 \end{array}$$

$$\text{HTU (based on continuous phase) } = 21.1 \text{ ft}$$

C. using 1.5" metal pall rings ($\epsilon = 0.94$)

$$\begin{array}{llll} u' & = & 88.1 \text{ ft/hr} & u'' = 9.9 \text{ ft/hr} & a = 4.68 \text{ sq.ft/cu.ft} \\ \phi & = & 0.02 & d = 0.0241 \text{ ft} & u/u'' = 64.2 \end{array}$$

$$\text{HTU (based on continuous phase) } = 17.8 \text{ ft}$$

D. using 1.5" metal pall rings ($\epsilon = 0.94$)

$$\begin{array}{llll} u' & = & 49.6 \text{ ft/hr} & u'' = 5.57 \text{ ft/hr} & a = 2.6 \text{ sq.ft/cu.ft} \\ \phi & = & 0.01 & d = 0.022 \text{ ft} & u/u'' = 117 \end{array}$$

$$\text{HTU (based on continuous phase) } = 17.1 \text{ ft}$$

So, we use a packed column with the aqueous phase dispersed, and estimate the dispersed-phase hold-up, ϕ , be 0.02.

2.3 Determination of Diameter of the Extraction Column

Density of gasoline = 45.2 lb/cu.ft

Mass flow rate of gasoline to the column = 13,622 lb/hr

so,

$$\begin{aligned} A &= (13,622 / 45.2) / 88.1 = 33.8 \text{ sq.ft} \\ D &= 6.6 \text{ ft} \end{aligned}$$

So, we use a 7 ft diameter column. Also we use two extractors in series. Each extractor has height of 51 ft.

3. Dehydration Column (C-3)

3.1 Number of Plates of Dehydration Column

The number of ideal plates of the dehydration column as shown in Chapter V is 6. The overall plate efficiency of this column is estimated at 0.6 (20), then the number of the actual plates of this column is:

$$N = 6 / 0.6 = 10$$

3.2 Diameter of the Dehydration Column

Mass flow rate of the vapor is:

$$V = (7.14 \times 46 + 3.68 \times 18 + 39.14 \times 96) \times 15 = 62,282 \text{ lb/hr}$$

Allowable vapor velocity (V') (22)

$$\rho_V = 0.196 \text{ lb/cu.ft}$$

$$\rho_L = 45.8 \text{ lb/cu.ft}$$

For 36" plate spacing and 1" seal,

$$V' (\rho_V / (\rho_L - \rho_V))^{\frac{1}{2}} = 0.28, \quad \text{So,}$$

$$V' = 4.28 \text{ ft/sec.}$$

$$A = 20.6 \text{ sq.ft}$$

$$D = 5.1 \text{ ft}$$

For safety of operation, the diameter of the dehydration column is designed to be 6 ft. And the height of the column is 36 ft.

TABLE A.1 COMPARISON OF NUMBERS OF IDEAL PLATES REQUIRED FOR
ETHANOL DISTILLATION UNDER DIFFERENT OPERATING
PRESSURES

P. psia	Cond. Temp.	Reflux Ratio	No. of Plates N	B.P. of the liquid °F	Reboiler	
	°F	R			Pressure of Steam ($\Delta T=54^{\circ}\text{F}^*$) psia	Pressure of Steam ($\Delta T=90^{\circ}\text{F}^*$) psia
14.7	172	2.0	14	212	39.2	64.1
41.5	228	2.0	16	270	94.5	152.8
75.0	261	2.0	17	307	155.8	240.0

* ΔT : the temperature difference between shell side and
tube side of the reboiler

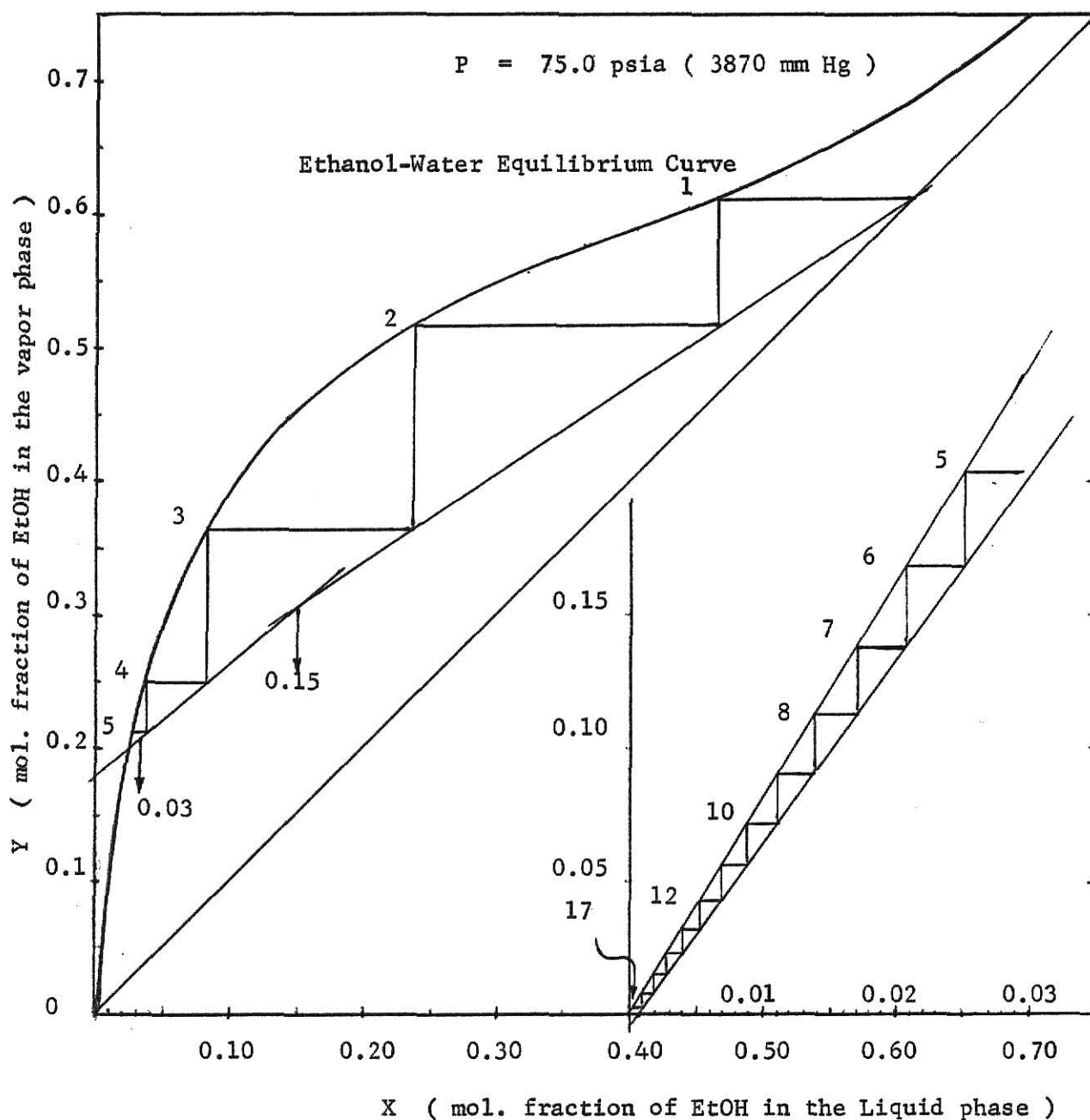


Figure A.1 Determination of ideal plates for the distillation column (operating pressure is 75 psia)

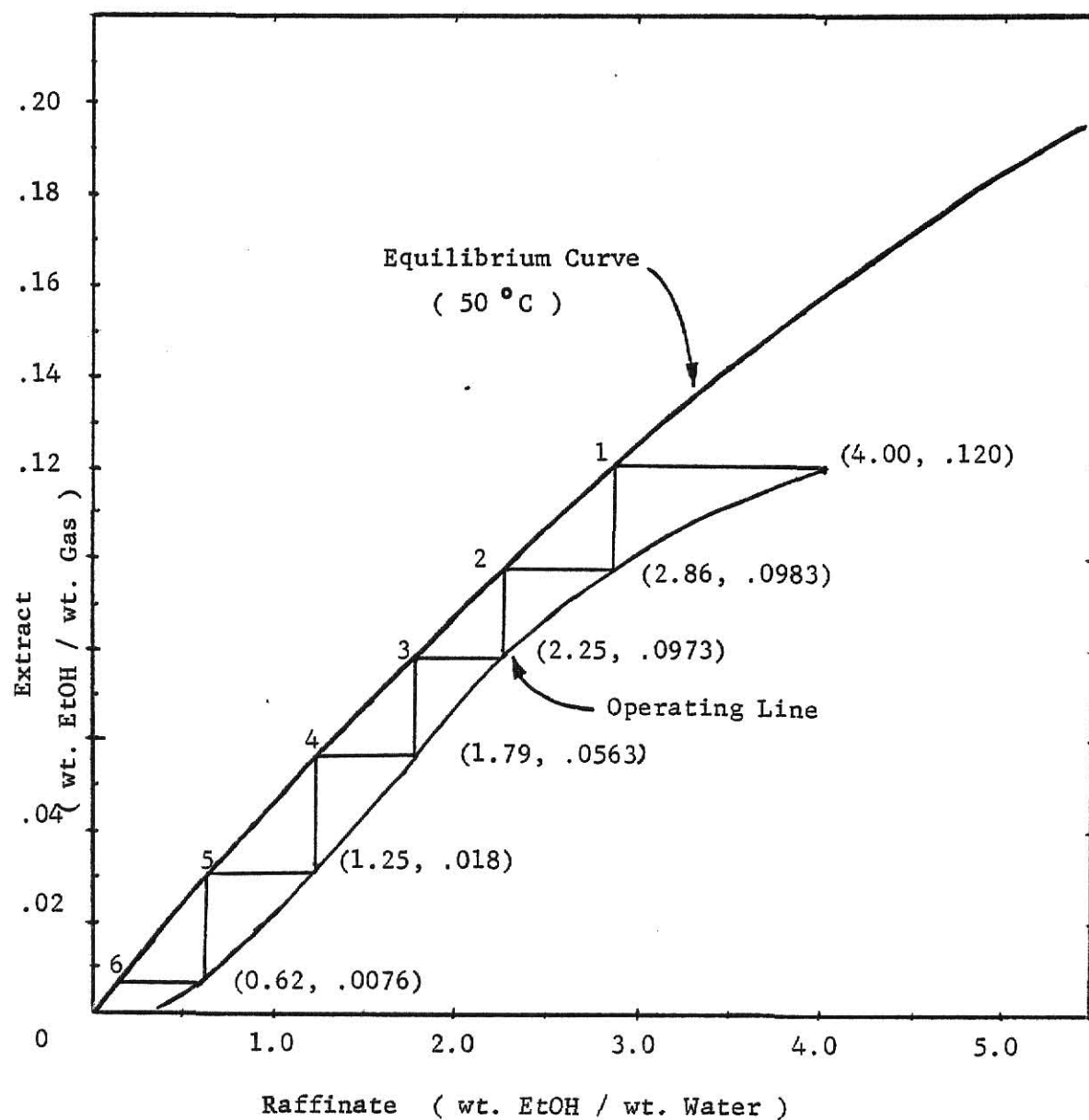


Figure A.2 Determination of ideal stages for the extraction column

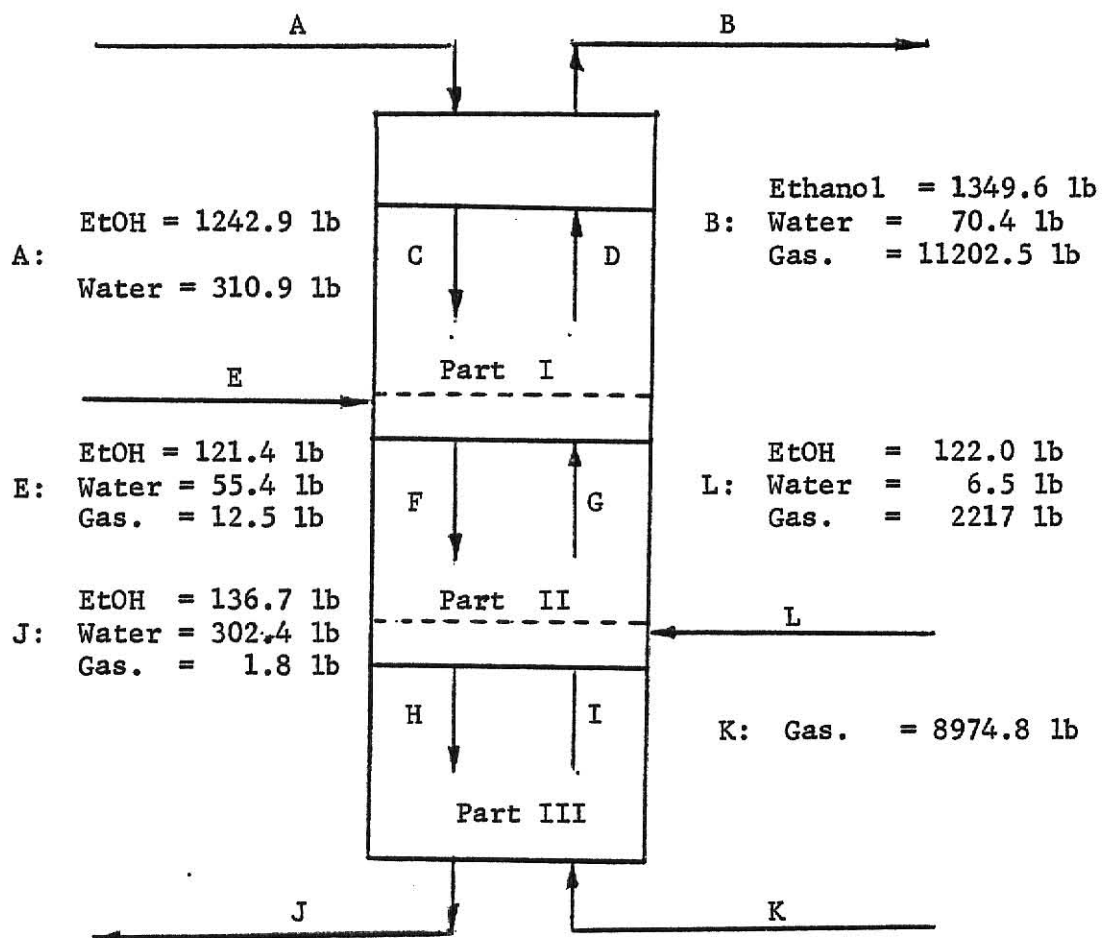


Figure A.3 Material Balance for the Extraction Column

PHASE EQUILIBRIA IN THE ETHANOL-WATER-GASOLINE SYSTEM

by

SONG-TIEN CHOU

B. S., National Taiwan University, 1974

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

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ABSTRACT

The ultimate role of gasohol in the energy future of the nation depends on whether its production can be made both energetically and economically appealing. However, to date all published energy and economic analyses have been predicated on the assumption that anhydrous ethanol would be produced and subsequently blended with gasoline. Because of the difficulty in obtaining anhydrous ethanol, the separational energy requirement plays a major role in determining the total processing energy and thus the economic outlook for gasohol production. At Kansas State University an energy-efficient process for gasohol production has been proposed. In this process, instead of producing pure ethanol for blending with gasoline, the gasoline is used as an extracting solvent to extract ethanol from aqueous solution and the product of the process is wet gasohol which is subsequently distilled to remove the undesired water.

In the first part of this study, several of more commonly used and also some of the recently developed activity coefficient equations were used to estimate the activity coefficients for the ethanol-water binary system from available data. Then the activity coefficient parameters of the UNIQUAC equation were estimated from the ethanol-water-gasoline ternary tie line data. In order to check the possibility of removal of water from the wet gasohol by equilibrium flash vaporization and distillation, theoretic calculations were made by use of the UNIQUAC equation. In these calculations, gasoline was divided into 20 hypothetical components and each hypothetical component was assumed to have

the same activity coefficient in the mixture. From the calculated results, we observe that it is impossible to remove the water of the wet gasohol by equilibrium flash vaporization, however, we can remove the water of the wet gasohol by distillation. Gasohol dehydration test also proves that. An energy analysis of this KSU process shows that the energy required to produce one pound of gasohol by the KSU process is significantly less (about 3,691 Btu per pound gasohol) than the conventional distillation process. With a unit fuel cost of \$1.43 per million Btu, the KSU process would save \$1,060,000 for 200 million gallons per year gasohol production.