

CHROMATOGRAPHIC DISTILLATION

By

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PREFACE

Chromatographic distillation is a new technique for improving the separation of components by distillation. An experimental batch study of binary distillation and distillation with injection of a third, more volatile, component was done. The chromatographic method, on a continuous basis, was economically unfavorable when compared with vacuum distillation.

Appreciation is expressed to Dr. R. N. Maddox for his guidance of this study and to the H. L. Doherty Foundation whose financial assistance made it possible.

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CHAPTER I
INTRODUCTION

Chromatographic distillation offers a technique for improving the fractional separation of two liquids with similar vapor pressures. The word "chromatographic" refers to an operation in which a third component, more volatile than the other two, is injected into the bottom of a column during the course of conventional distillation. This chromatographic method can be used in batch or continuous distillation.

Experimental studies were conducted on a batch distillation column. A comparison of distillate compositions, with and without injection, was made. Theoretical calculations were made for comparison with results of batch experiments. An economic comparison was made between benzene chromatographic distillation and vacuum distillation, on a continuous basis, of the toluene and p-xylene system.

Chromatographic distillation differs from extractive distillation, where the added component goes out the bottom of the column. The chromatographic component is distilled through the column and must be separated from the desired distillate product. Chromatographic, as applied to distillation, should not be confused with gas chromatography, an analytical technique for quantitative analysis of liquid and gas samples.

Batch distillation results for distillate and still compositions depend on several variables: the composition of the charge; the relative volatility of the mixture; the number of plates in the column; the reflux ratio; the holdup of material in the column. Under chromatographic distillation, the relative volatility will change. For accurate comparisons, it is necessary to hold the other variables, reflux ratio, charge, the number of plates, and holdup, at constant values. Thus, any difference in distillate composition can be attributed to the injection technique.

Batch distillation is an unsteady-state process. The concentration of the more volatile component in the stillpot decreases with time. Consequently, temperature and composition profiles change with time at any point in the column. Separation by distillation results in smooth, continuous temperature and composition profiles.

The relative volatility is an important variable in a distillation system. It indicates the ease of separation of the two components by distillation. The relative volatility of a mixture is approximately the ratio of the vapor pressures of the two pure liquids at the temperature of operation. The volatility of a component is the partial vapor pressure divided by the mole fraction in the liquid phase.

After the relative volatility, the reflux ratio is the most effective variable in controlling the ease and sharpness of separation of any two components by a distillation column. The reflux ratio may vary from infinity to zero. A practical laboratory means of achieving a desired reflux ratio requires intermittent take-off of distillate. When the periods are less than a minute, the distillation results are not affected by alternate operation at total and zero reflux.

CHAPTER II
SURVEY OF BATCH
DISTILLATION THEORY

Chromatographic distillation, an unusual and new technique, is attributed to Arthur Rose. The information available to interested persons is sparse; no published material was found on this subject. However, batch distillation theory provides a means for analyzing and predicting the behavior of a given binary system in the course of separation. It forms the basis for evaluating chromatographic distillation.

It is common practice to represent the theoretical or experimental results in the form of a distillation curve by plotting the composition of the cuts, expressed in mole fraction of the more volatile component, against mole per cent of the charge distilled. The theoretical distillation curves are based on the integration of the Rayleigh equation for simple distillation (2).

$$\ln(L) = \int \frac{dx_s}{(y - x_s)} \quad (1)$$

Equation (1) is derived in the Appendix. The equilibrium relationship between the composition of the vapor, y , and the composition of the still, x_s , at any time is needed to evaluate the integral on the right of Equation (1).

E. H. Smoker and A. Rose (2) presented a graphical integration of Equation (1). Their paper develops in detail a method of computing curves for batch distillation

of binary mixtures at any reflux ratio. They used a vapor-liquid equilibrium diagram of a binary mixture to relate graphically the still and distillate liquid compositions in equilibrium for a distillation system of any given number of equilibrium steps. After the manner of McCabe-Thiele, the operating line for the rectifying section is set on the diagram by the reflux ratio. Choosing the still composition, the equilibrium contact steps are made on the graph to find the distillate composition. Thus, the integrand in Equation (1) is evaluated at the chosen point. Choosing several more points, for decreasing still composition, leads to a graphical integration of Rayleigh's equation and the distillation curve.

The graphical approach does not need to assume constant relative volatility, if the vapor-liquid equilibrium diagram of the mixture is available. It can handle a change in the reflux ratio during the course of distillation. The effect of holdup was ignored. The accuracy of the graphical results depends on the care taken in constructing the graphs. Systems with small relative volatilities and large numbers of theoretical plates are tedious by graphical methods with consequent inaccurate results. For these reasons an analytical solution to Rayleigh's equation is desired.

A. Rose and L. M. Welshans discussed such an approach for determining binary distillation curves (3). Their method gives the maximum sharpness of separation when

holdup is negligible with a given column and mixture. The theory indicates the general nature of the effect of relative volatility, reflux ratio, and plates on the sharpness of separation in batch fractionation. They assume a binary mixture, having a constant relative volatility, is being fractionated by batch distillation under substantially total reflux in a column having negligible holdup. The composition of the distillate stream is related to the still composition, under the conditions stated, by;

$$x_d = \frac{E x_s}{[1 + (E-1)x_s]} \quad (2)$$

Using Equation (2), Rayleigh's Equation (1) can be integrated. Thus, the moles remaining in the still is related to the still composition by;

$$\ln(L) = \frac{1}{(E-1)} [\ln x_s - E \ln(1-x_s)] + C \quad (3)$$

For calculational purposes, the distillate composition and moles remaining in the still can be calculated separately from the chosen still composition. Equations (2) and (3) can be combined to give;

$$L = \frac{x_d^{\frac{1}{E-1}} [E - (E-1)x_d]}{(1-x_d)^{E/(E-1)}} + C' \quad (4)$$

This expression is a relation between moles remaining in the still and composition of the liquid leaving the column as distillate. The integration constants are found from the initial conditions of charge and composition. The complete derivations of these equations are in the Appendix.

For more realistic predictions of distillation curves, reflux conditions in the column should be considered. The reflux ratio is one of the most important variables in batch fractionation because of its relation to the sharpness of separation and to the time required for distillation. A method for estimating distillation curves with the effect of reflux was introduced by A. Rose and H. H. Long (5). They considered graphical solutions of Rayleigh's equation for batch fractionation of ideal binary mixtures when holdup is negligible. The effect of reflux and the relationship between the still composition and the distillation composition under these conditions is accounted for by Smoker (1).

$$x_s = k + \frac{(mc^2)^n (x_d - k)}{\left\{ E - mc(\alpha - 1) \left[\frac{E - (mc^2)^n}{\alpha - mc^2} \right] (x_d - k) \right\}} \quad (5)$$

where k represents the intersection point of the equilibrium line and the operating line on a McCabe-Thiele diagram.

By the use of such an equation, batch distillation curves can be calculated for a given binary system. For each distillation case chosen, the reflux ratio becomes a parameter, forming a family of lines on the distillation diagram.

It is of interest to consider the effect of holdup on the sharpness of separation. A. Rose, L. M. Welshans, and H. H. Long have presented equations for holdup in

columns (4). The analysis is restricted to a binary mixture being distilled under substantially total reflux. A constant relative volatility is also assumed. The holdup will be distributed uniformly throughout the column and holdup in the condenser will be zero.

With the above assumptions, the expression for holdup is,

$$h = \frac{H}{\ln E} \ln [1 + x_S(E-1)] \quad (6)$$

For binary distillation, h will be the amount of holdup for the more volatile component of the system.

By making a material balance of the more volatile component about the column just before and after the removal of a small portion of distillate, the following equation is obtained,

$$x_S \frac{dL}{dx_S} - \frac{Ex_S}{(1+b'x_S)} \frac{dL}{dx_S} + L + \frac{Ab'}{(1+b'x_S)} = 0 \quad (7)$$

This linear differential equation is solved, in part, by making an approximate binominal expansion. Under certain conditions, the series converges rapidly. So that,

$$L = \frac{Kx_S^p}{(1-x_S)^{p+1}} - \frac{Ab'}{(1-x_S)^{p+1}} \quad (8)$$

This solution requires that E be large, and thus limits its usefulness. Equation (8) can be combined with Equation (2) to give,

$$L = \frac{Kx_d^p(E-b'x_d) - Ab'(E-b'x_d)^{p+1}}{[E(1-x_d)]^{p+1}} \quad (9)$$

For purposes of computation it is generally better to use the equations separately. These equations contain the factors relative volatility, plates, and holdup. By assuming suitable values for these and for the initial composition of the mixture, values of L and x_d may be obtained. Since L is defined as the total moles remaining in the still at any time, the total moles of product distilled over at any time will be; $L_0 - H - L = D$.

The introduction of holdup causes a complication in the calculation of the integration constant, K , for Equations (8) and (9) because the value of the still composition used in calculating the constant is not the composition of the original mixture. This arises because the value of x_s decreases somewhat even before any product is removed. The decrease is due to the passage of some of the charge into the column. The value of x_s when equilibrium has been reached but before any product is removed is given by the expression,

$$L_0 x_{s_0} = (L_0 - H)x_1 + H \left[\frac{\ln(1+x_1 b')}{\ln E} \right] \quad (10)$$

The resulting value of x_1 , when substituted in Equation (8) gives the integration constant K . These equations are discussed in the Appendix.

The results of these equations show that even a relatively large holdup of 40 per cent of charge still allows a fair separation to be accomplished. As the holdup approaches zero, the curves approach those made for maximum sharpness of separation.

Some distillation systems will not have large efficiency factors under normal operating conditions, because of low relative volatilities. In view of this, the assumptions made in deriving Equations (8) and (9) would not apply. It would be necessary to consider other means of solution to Equation (7). Numerical solutions of differential equations would be one method of solving this equation.

CHAPTER III
SPECIFIC PROPOSITION

It has been proposed by Arthur Rose that the injection of a more volatile component during the course of binary distillation improves the separation between the binary components. The improved separation can be shown on batch distillation curves.

An experimental study of conventional binary distillation of aromatic mixtures and distillation with injection of a third component, benzene, will be made. From the results, an economic comparison will be made between the chromatographic method and a vacuum distillation method.

Although the experimental study will be made with batch distillation, the economic comparison will be made on a continuous basis. The experimental study will give the amount of improved separation between the binary components and amount of added component necessary to improve the separation. This information can be applied to a continuous distillation scheme. The vacuum distillation scheme reflects the increased relative volatility between the components at lower pressures. See Figures 1 and 2 for schematic diagrams of the two methods. The feed and products are the same for both processes. The chromatographic scheme requires an additional column for separation of the chromatographic component, benzene, from the desired

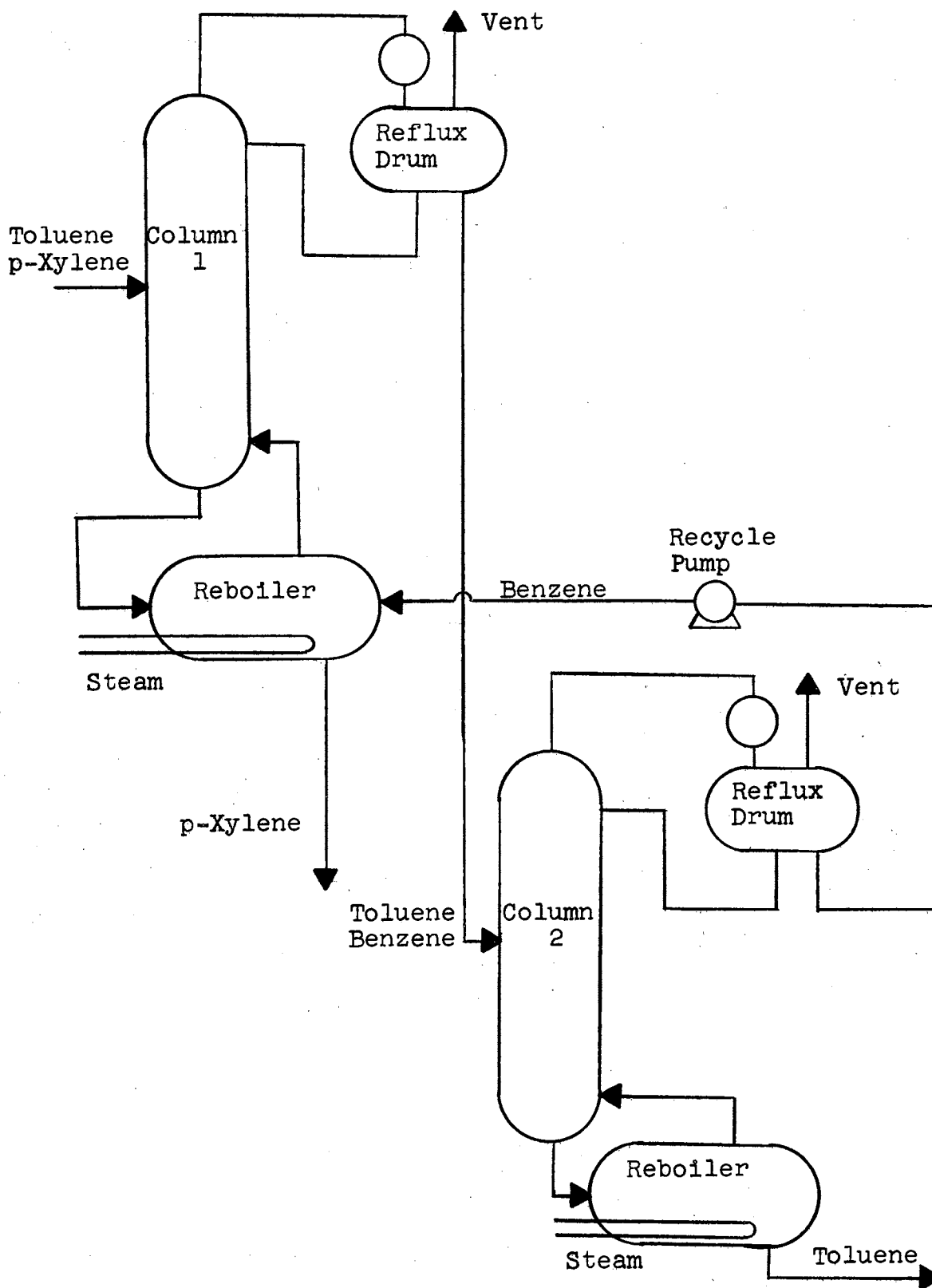


FIGURE 1

Schematic Diagram of Chromatographic Distillation System

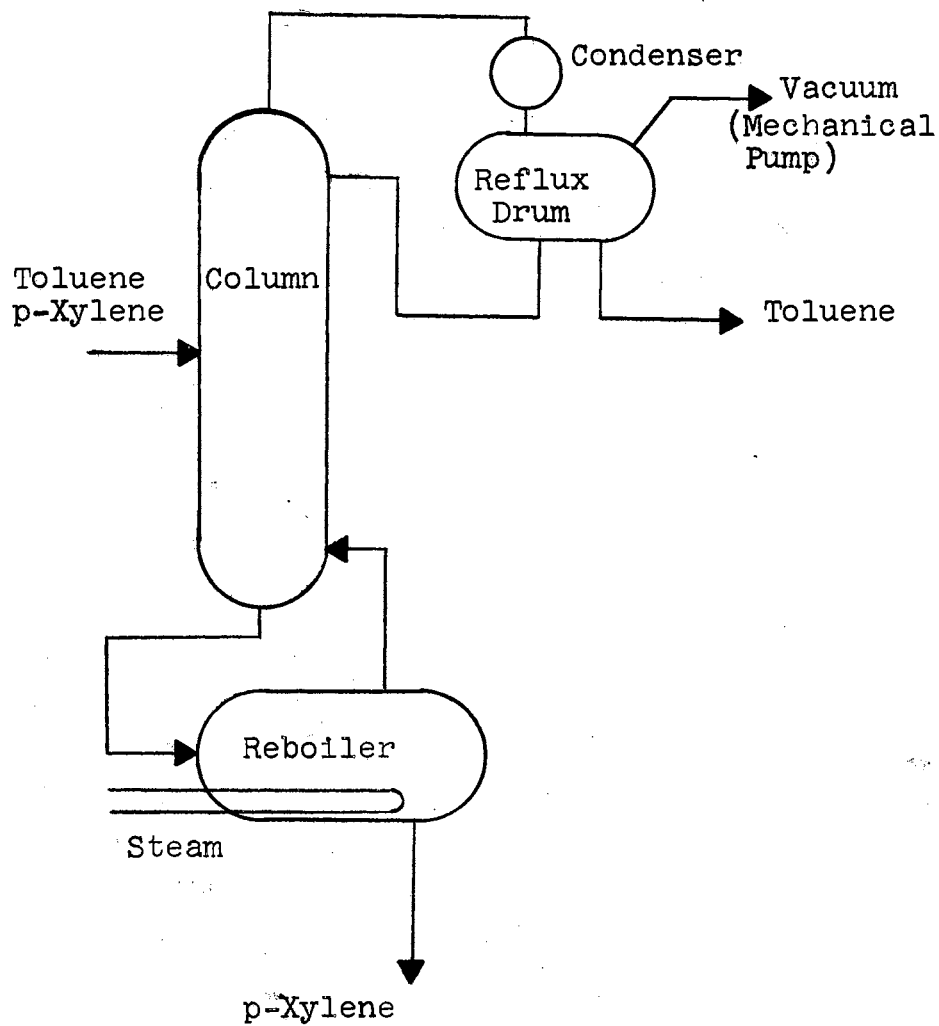


FIGURE 2

Schematic Diagram of Vacuum Distillation System

component. The vacuum scheme requires a mechanical vacuum system which has a capacity equivalent to 1 per cent of the total vapor flow rate from the column.

The column design will depend on the flow rate and the improved equilibrium relationships of the components. The matching of an experimental batch distillation curve, on a benzene-free basis, and a theoretical curve will fix the increased relative volatility. A definite amount of the injected component is associated with the new relative volatility.

The economic comparison of chromatographic and vacuum distillation is based on purchased equipment costs. The fixed-capital costs can be estimated as percentages of purchased equipment costs. This method is described by Aries & Newton (8). The operating costs for utilities, steam and cooling water, are needed to complete the economic comparison.

CHAPTER IV

EXPLANATION OF EQUIPMENT AND EXPERIMENTS

The basic experimental technique was batch distillation. Temperature, composition, and material data were collected and analyzed to prepare experimental batch distillation curves for aromatic mixtures.

An Oldershaw column was used in the laboratory study. This piece of equipment, made of glass, consists of perforated plates, arranged vertically, surrounded by a vacuum jacket. The column is available in 5, 10, 15, 20, 30, and 40 sieve-plate sections. For the Oldershaw column, plate efficiencies are approximately 63 percent (7). With ground glass joints at either end of each column, any combination of plates can be chosen for laboratory work. A diagram of an assembled column is shown in Figure 3. In use with the column are the stillpot, distillation head, and condenser.

After charging the stillpot with a binary aromatic mixture, heat was applied by an electric mantle and the column brought to equilibrium. The operating reflux was set by a Flexopulse timer and distillation was started. When making injection runs, a glass leg, filled with benzene, was attached to a neck of the stillpot. Intermittent injection of benzene was made through a stopcock into the stillpot.

The liquid dividing head on the distillation column was controlled by a Flexopulse repeat cycle timer and

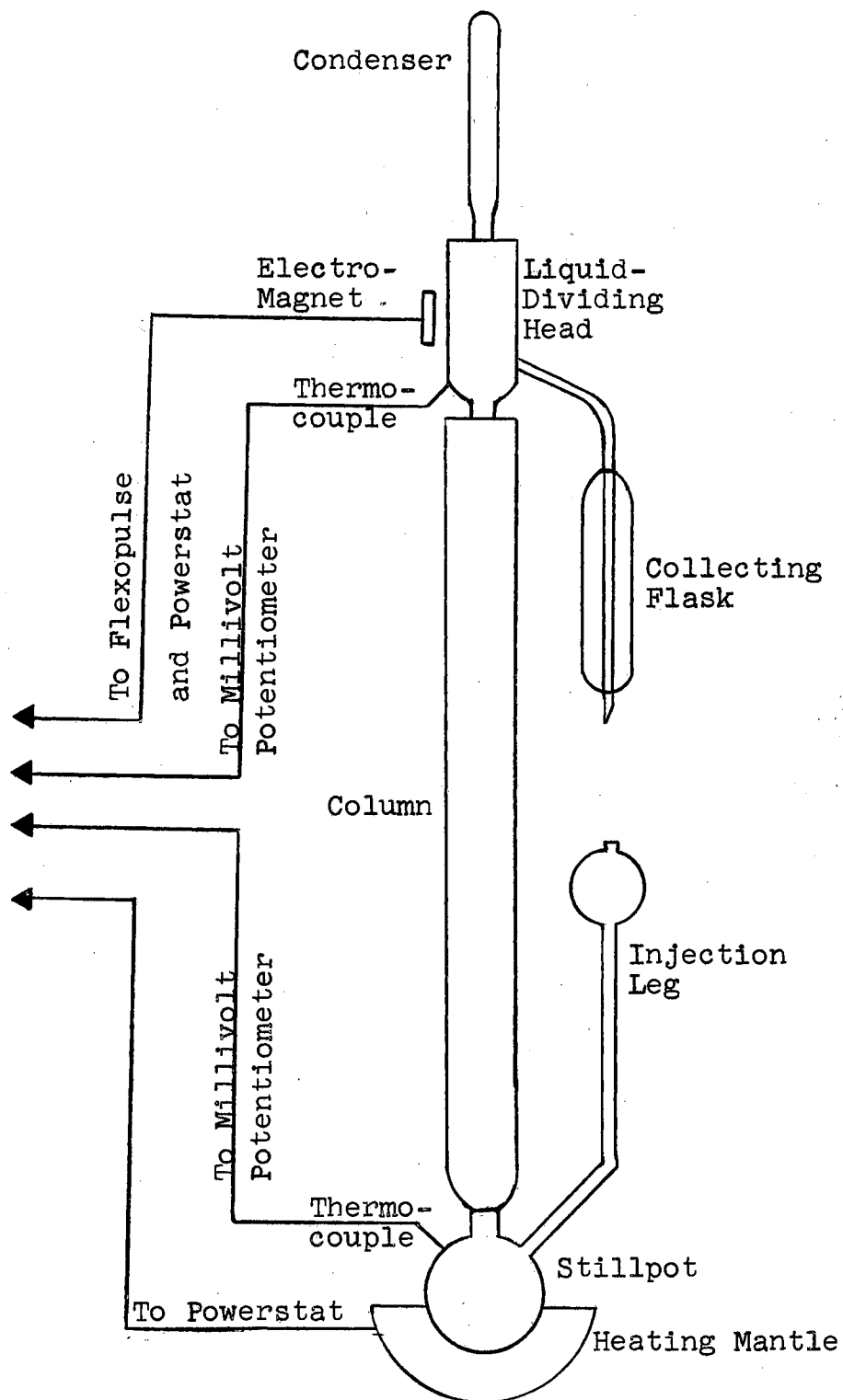


FIGURE 3

Schematic Diagram of Oldershaw Column and Chromatographic Distillation Injection Set-up

electromagnet. The timer closes and opens a contact repeatedly as long as a synchronous motor is energized.

The voltage delivered to the electromagnet on the liquid dividing head and the heating mantle surrounding the stillpot was controlled by Powerstat variable transformers, 116 series. This type supplies constant voltage from 0 to 140 volts. The cycles are 50/60 with a constant maximum load of 7.5 amps. The upper limit of the mantle temperature is 450° C.

Temperatures were determined with Chromel-Copnic thermocouples used in conjunction with a Leeds & Northrup 8690 millivolt potentiometer. The readings were converted to °F by a thermocouple table. The potentiometer is a single range, two-dial, portable potentiometer. It is primarily used for general temperature measurements, by means of thermocouples. The basic instrument consists of a millivolt selector switch, a slidewire, and a switch to select the function to be performed. Also included are a galvanometer, a standard cell, and a 1.5 volt battery. The sum of the two readings is the value of voltage set on the potentiometer. The battery rheostat is used with the 1.5 volt battery to standardize the current in the potentiometer circuit. The galvanometer key must be closed to determine circuit balance.

The compensator is used to set the reference junction voltage to the value which corresponds to the temperature of the reference junction when using the instrument for

measuring thermocouple voltages. The reference junction is at the thermocouple head when copper lead wires are used to connect the thermocouple to the instrument. The required voltage can be obtained from a conversion table for the type thermocouple being used. The millivolt switch and slidewire are used to obtain a circuit balance when measuring an unknown voltage.

Liquid samples were collected overhead and analyzed on a gas chromatography instrument (F & M model 609). The ternary samples of aromatics in the experiments were readily analyzed by this technique. However, the p-xylene and m-xylene isomer chromatographic separation proved to be difficult. A tracing of the successful separation is shown in Figure 4.

Gas chromatography should not be confused with chromatographic distillation. Gas chromatography is a simple analytical method that sharply separates components of complex mixtures. In a gas chromatography unit the compounds in a mixture migrate at differing speeds when carried along by an inert gas through a tube that has been treated in a special way. The conventional design consists of a quarter-inch diameter column several feet long, packed with a pulverized inert substance which is coated with a liquid partitioner. The role of the partitioner is to separate various components of the sample. As the sample is moved through the column by the carrier gas, the partitioner must interfere in a

selective fashion with the progress of each compound present, slowing up the progress of some and letting others travel through the column more swiftly. At the outlet of the column a detecting device signals the emergence of each different compound by activating a recording pen on a strip of chart.

To obtain sharply defined gas chromatograms, it is necessary to vary the pressure and flow rate of the carrier gas, the operating temperature of the column, the structure and particle size of the column packing, and the nature of the liquid partitioner. The areas under different peaks in a fractogram are roughly proportional to the fractional amounts of each substance in the original sample. With care the method is accurate to about 2 per cent (9). The gas chromatograph will separate not only compounds with closely similar properties but also various forms of individual compounds, such as isomers.

In the F & M 609 gas chromatograph, each sample, as it emerges from the end of the column, is swept into a hydrogen flame ionization detector which in conjunction with the electrometer generates an electrical signal proportional to the amount of component in the carrier gas. This signal is fed to a potentiometric recorder to produce chromatograms. The speed and ease of changing columns and column temperature makes the unit an ideal tool for use in developing isothermal gas chromatographic

analyses. The Model 609 provides independent temperature controls on the injection port, column, and detector block.

During analysis it was necessary to adjust the range and attenuation on the unit to obtain the proper size of peaks. The actual quantitative analysis was accomplished by measuring the areas under the peaks produced on the recorder paper. This was most easily done by means of an integrator pen trace. The pen traces zig-zag lines below the base line of the peaks on the chart. For a peak interval, the value is obtained by counting the chart graduations crossed by the integrator pen. Every division has an arbitrary value of ten. The overall accuracy of the integrator is within ± 0.10 per cent of the full scale.

The experimental data, in the Appendix, was collected and analyzed using the instruments described. A binary mixture of known composition was charged to the stillpot; the column was brought to equilibrium and distillate take-off begun. During the chromatographic runs, benzene was injected intermittently into the stillpot. Stillpot and condenser temperatures, distillate liquid samples, and amount of distillate were collected. The experimental data was used to prepare distillation curves. The comparison of chromatographic and binary batch distillation is made with these curves.

An IBM 1620 electronic computer was utilized to calculate theoretical batch distillation curves. The three Fortran programs used on the machine are given in the Appendix. Program I calculates curves for total reflux from Equations (2) and (3). Theoretical curves for reflux are done by Program II. Equation (1) is numerically integrated, using Equation (5). Newton's method of tangents is used for convergence of trial and error values of the still composition. Program III uses Euler's method to solve Equation (7). This program calculates curves with holdup at total reflux. These numerical techniques are given in Salvadori and Baron (6).

CHAPTER V

DISCUSSION OF RESULTS

Theoretical batch distillation curves were prepared by the three computer programs shown in the Appendix. The numerical accuracy of the programs, given the same distillation conditions, was checked by the results shown in Table I. Theoretical curves are compared with experimental curves for a given distillation system.

After preliminary study, both theoretical and experimental, toluene and p-xylene proved to be the most attractive distillation system. The distillation separation on a batch basis was easy and the experimental runs were relatively short. Graph 1 shows the small effect of 2 per cent holdup, present in the experimental runs.

Batch distillation runs were made on the toluene and p-xylene system with drop-wise injection of benzene, see Tables V and VI. Graph 2 compares a conventional curve with an injection curve, on a benzene-free basis.

Binary experimental results, from Tables III and IV, are compared with a calculated curve, Table XIII. The calculated curve is based on experimental values of relative volatility, reflux ratio, and actual plates. Despite experimental errors and a holdup of 2 per cent (unaccounted for in the computer program), the agreement is satisfactory. See Graph 3 which is based on molar units.

In Graph 4, the experimental injection curve is matched by a calculated curve. A relative volatility of 2.4, from Table XIV, was used.

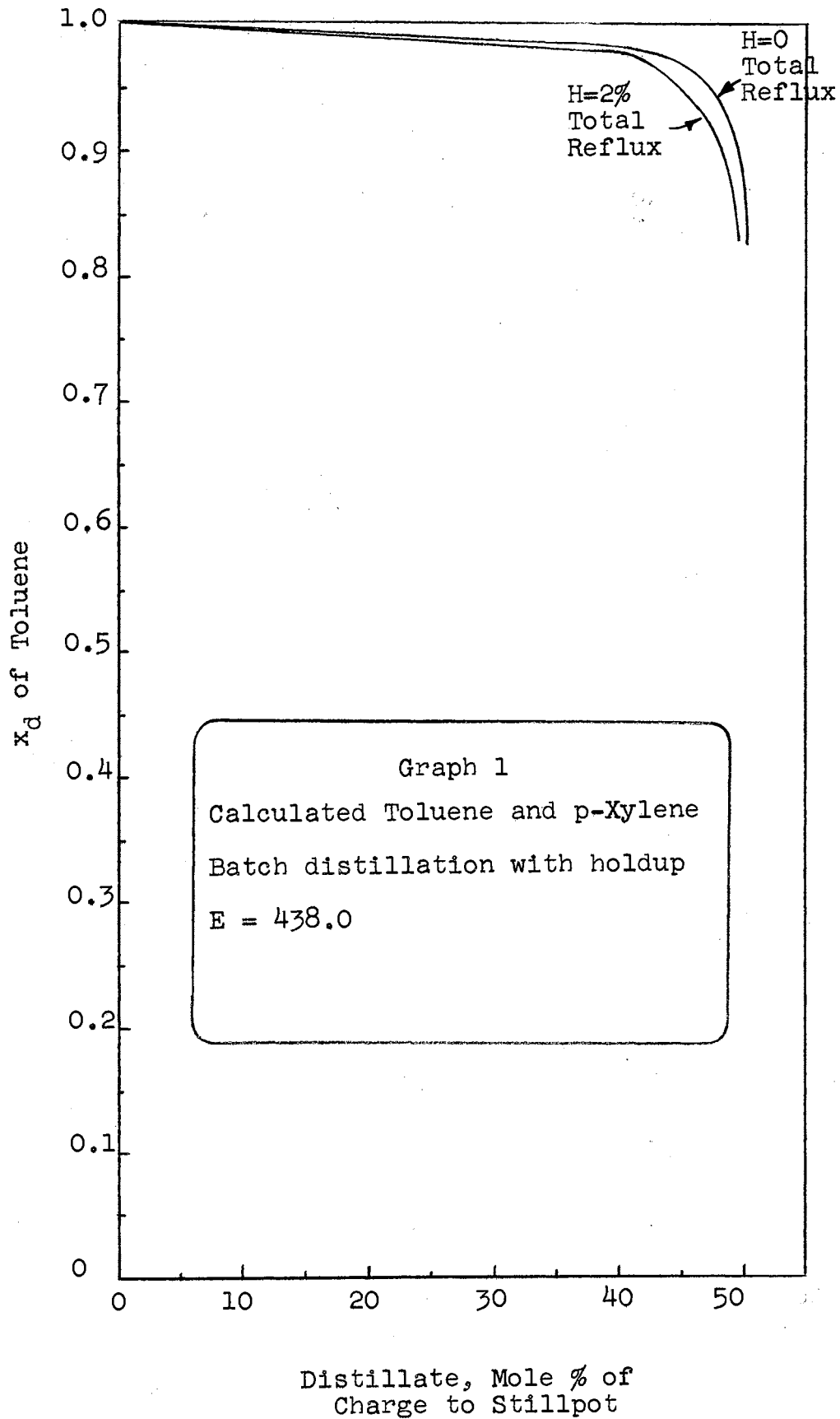
TABLE I

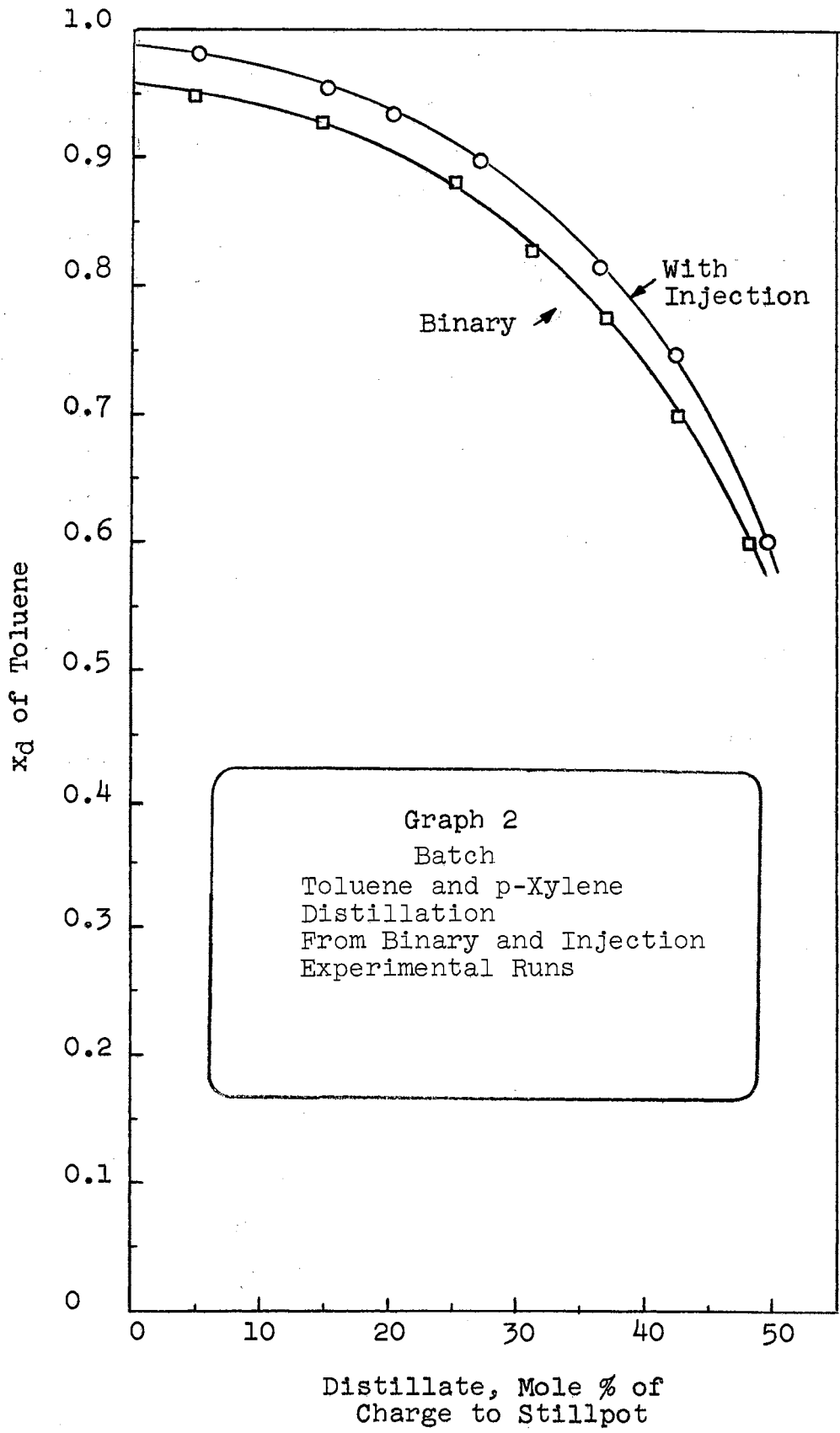
Numerical accuracy of computer programs, comparison of program results for p-xylene and meta-xylene batch distillation composition curves ($E=2.969$).

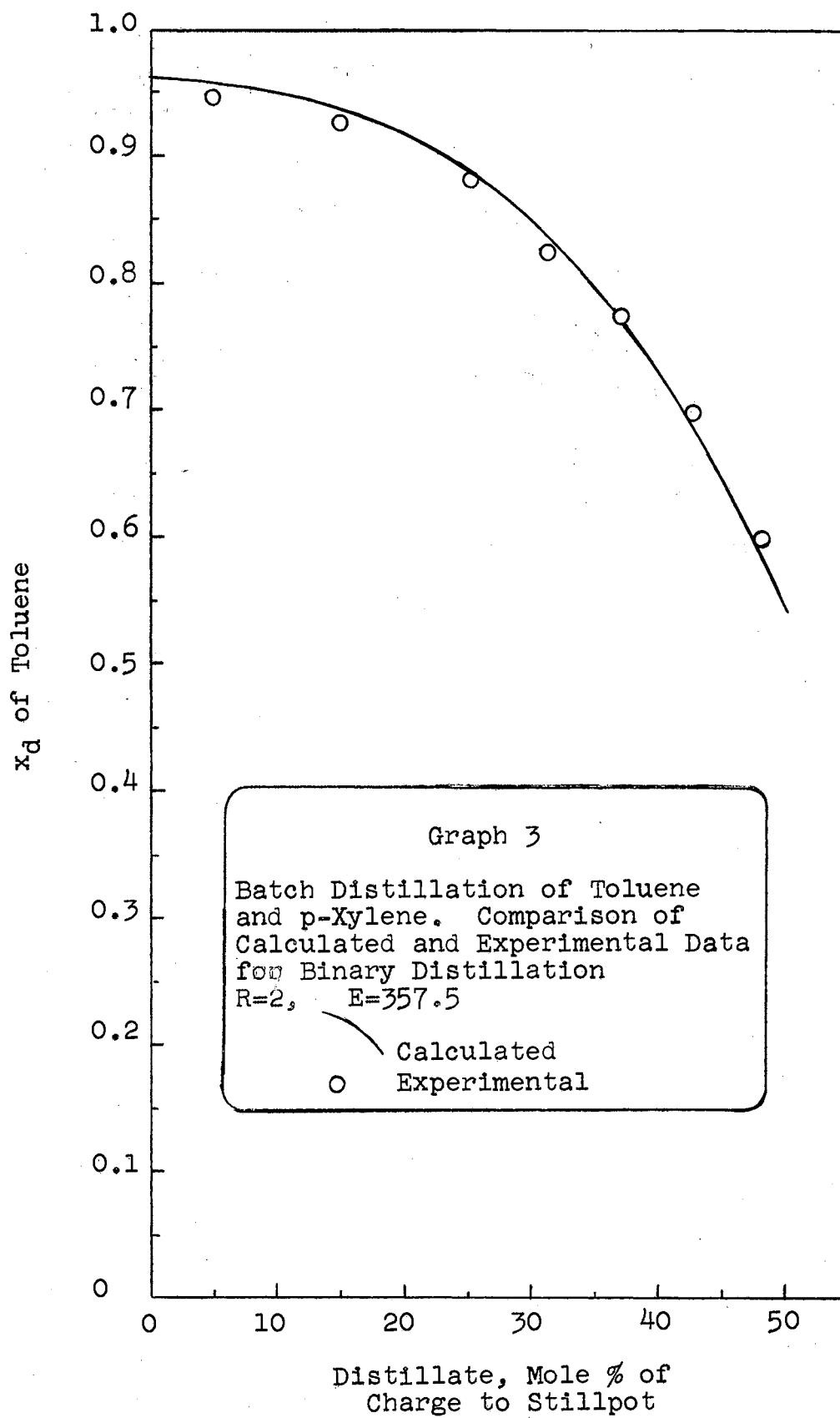
still composition = 0.50, charge = 100 moles of p-xylene

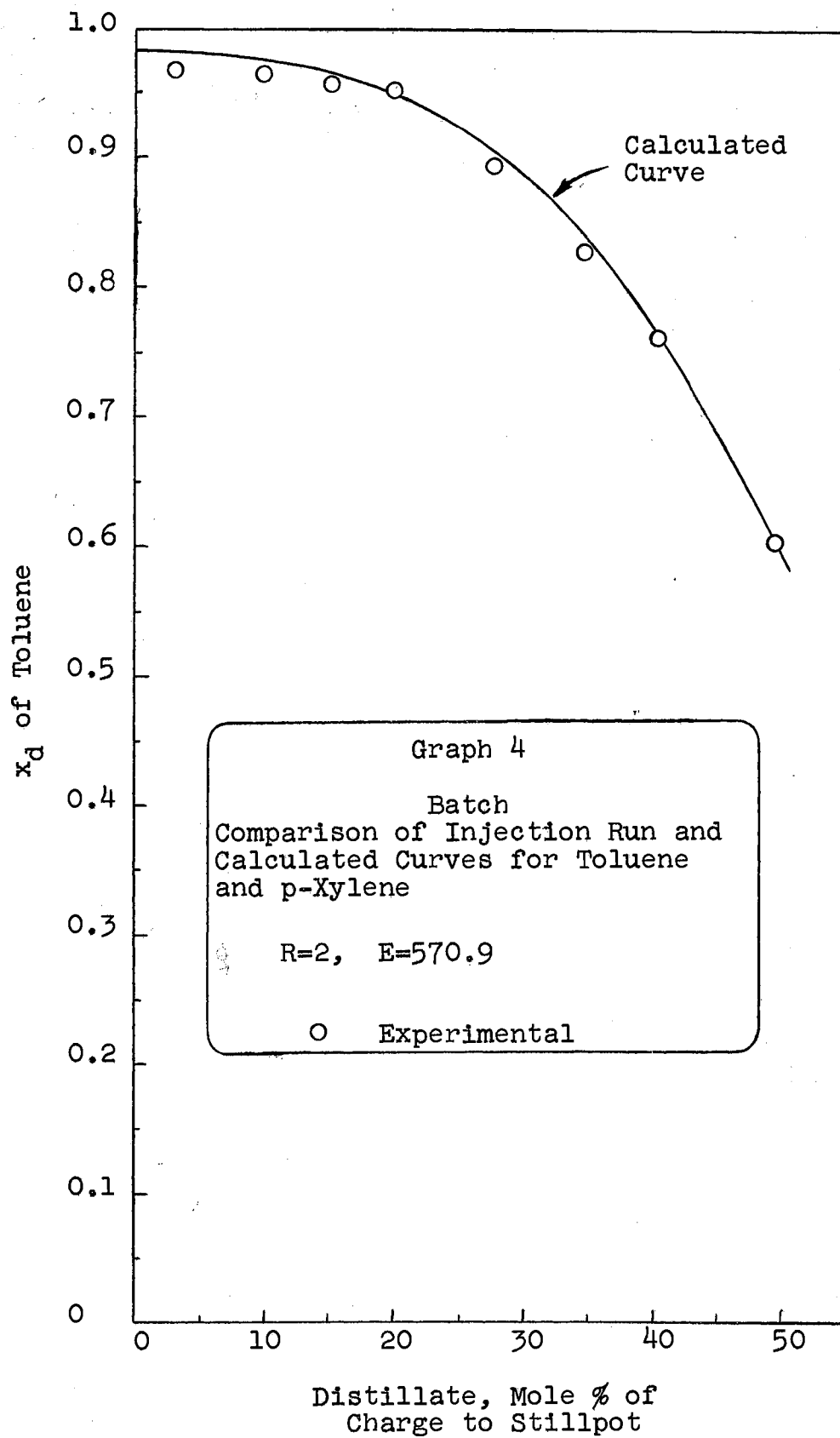
Program Number	I	II	III
Name	Batch distillation with total reflux	Batch distillation with finite reflux	Batch distillation with holdup
Conditions	constant α , total reflux $H = 0$	constant α , $H = 0$ $R = 9,999$	total reflux, constant α , $H = 0$
$E = \alpha^n$	2.97	2.97	2.97
x of still (p-xylene)	x of distillate (p-xylene)	x of distillate (p-xylene)	x of distillate (p-xylene)
0.480	0.732	0.732	0.732
0.460	0.716	0.716	0.716
0.380	0.645	0.644	0.645
0.190	0.410		0.410

Prepared from Tables VIII, IX, and X









Thus, the injection of benzene during toluene and p-xylene distillation improves the relative volatility from 2.1 to 2.4. This is consistent with vapor pressure ratios for toluene and p-xylene at lower temperatures (see Graph 5).

These results were utilized in making an economic comparison between chromatographic distillation and vacuum distillation of toluene and p-xylene. From the sample calculations (in the Appendix), the chromatographic scheme costs 43 per cent more than the vacuum setup. The costs are based on process equipment, as given in Aries and Newton, see Table II. Also, the chromatographic utilities cost for operation is nearly three times as much as vacuum distillation utilities costs.

The improved separation observed for a binary system with benzene injection is explained by an increased relative volatility, resulting from a lower effective temperature over the range of distillation. However, the technique is economically unattractive when compared with vacuum distillation.

TABLE II

(FROM TABLE XIX)

SUMMATION AND COMPARISON OF COSTS
FOR THE DISTILLATION SCHEMES

Chromatographic Distillation with Benzene Injection		Vacuum Distillation	
2 Towers	\$17,500	Tower	\$ 9,900
2 Condensers	3,800	Mechanical Vacuum System	2,000
2 Reboilers	6,800	Condenser	2,000
2 Reflux drums	1,400	Reflux drum	450
Pump	200	Reboiler	2,000
Benzene	<u>700</u>		<u> </u>
Purchased Equipment Cost	30,400		16,350
Equipment Installation	9,100		4,900
Utilities Installation	12,200		6,500
Instrumentation	<u>7,600</u>		<u>4,100</u>
Physical Plant Cost	59,300		31,850
Engineering and Construction	<u>17,800</u>		<u>9,600</u>
Fixed Capital	77,100		41,450
Utilities Cost for Operation	\$/hr		\$/hr
Water	3.08		1.08
Steam	<u>6.66</u>		<u>2.31</u>
	9.74		3.39

CHAPTER VI

CONCLUSIONS

The improved separation of binary aromatic systems by the technique of chromatographic distillation with benzene has been observed. The presence of a lower boiling, separation-promoting component lowers the average temperature of the distillation run. The net result of this addition of low-boiler is a greater relative volatility between the two components being separated.

Vacuum distillation also increases the relative volatility. An economic comparison of the methods for distillation indicates that chromatographic distillation fixed-capital costs are 43 per cent more than vacuum distillation. The costs are based on purchased process equipment. The other components of fixed capital are considered as percentage values of equipment costs.

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APPENDIX

EXPERIMENTAL DATA

TABLE III

DATA FROM RUN NO. B-12

Experimental binary batch distillation of toluene and p-xylene

Reflux Ratio = 2

Holdup = 2%

Plates = 11

<u>Time, Hours</u>	<u>Condenser Temperature, °F</u>	<u>x_d of Toluene</u>	<u>Distillate, Mol % of Charge</u>
0	228.5		
0.083	231.4	0.954	10.0
0.250	233.76	0.917	20.2
0.367	237.17	0.862	30.1
0.450	241.09	0.807	35.14
0.517	243.71	0.755	40.44
0.600	249.17	0.707	45.44
0.667	254.62	0.606	50.44
0.733	258.51	0.521	55.64

TABLE IV

DATA FROM RUN NO. B-15

Experimental binary batch distillation of toluene and p-xylene

Reflux ratio = 2

Holdup = 2%

Plates = 11

<u>Time, Hours</u>	<u>Still Temperature, °F</u>	<u>Condenser Temperature, °F</u>	<u>x_d of Toluene</u>	<u>Distillate, Mol % of Charge</u>
0	253.59	230.08		
0.133	256.95		0.950	9.8
0.200	257.21	234.29	0.925	20.0
0.417	262.89	238.48	0.868	30.4
		247.87	0.775	40.0

TABLE V

DATA FROM RUN NO. I-13

Experimental batch distillation of toluene and p-xylene
with benzene injection

Reflux ratio = 2

Holdup = 2%

Plates = 11

<u>Time, Hours</u>	<u>Still Temperature, °F</u>	<u>Condenser Temperature, °F</u>	<u>x_d of Toluene</u>	<u>(benzene-free basis) Distillate, Mol % of Charge</u>
0	249.69			
0.150	232.97		0.961	6.2
0.317	226.92		0.976	8.0
0.433	235.07	186.82	0.981	9.5
0.533		194.12	0.973	12.5
0.717		209.68	0.956	17.3
0.867	256.12	220.58	0.948	24.6
1.000	258.25	223.75	0.892	31.8
1.167		219.52	0.847	38.0
1.300	264.37	224.28	0.764	44.4
1.433	269.07	232.71	0.605	50.4

TABLE VI

DATA FROM RUN NO. I-16

Experimental batch distillation of toluene and p-xylene
with benzene injection

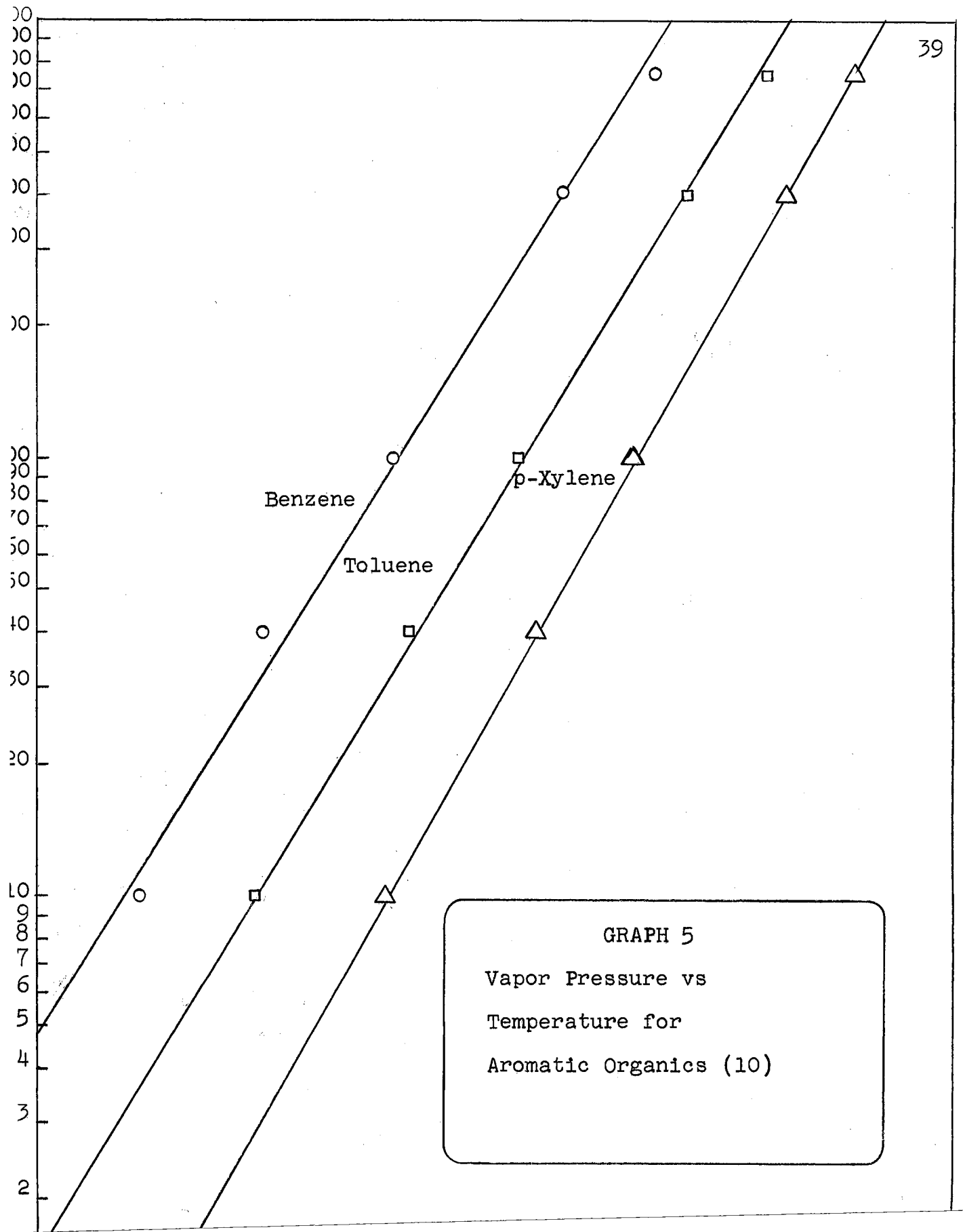
Reflux Ratio = 2

Holdup = 2%

Plates = 11

<u>Time, Hours</u>	<u>Still Temperature, °F</u>	<u>Condenser Temperature, °F</u>	<u>x_d of Toluene</u>	<u>(benzene-free basis) Distillate, Mol % of Charge</u>
0	250.47	219.52		
0.250	249.95	214.74	0.957	12.64
0.500		204.87	0.951	23.2
0.800		200.31	0.943	30.7
0.983	250.73	204.60	0.903	38.8
1.350	263.92	220.31	0.817	45.9

CALCULATED DATA



GRAPH 5
Vapor Pressure vs
Temperature for
Aromatic Organics (10)

TABLE VII
VAPOR PRESSURE DATA

from

Chemistry & Physics Handbook (10)

Pressure mm of Hg	1	10	40	100	400	760
<u>BENZENE</u>						
Temp., °C	-36.7	-11.5	+ 7.6	26.1	60.6	80.1
(1/T)x100	.4229	.3822	.3562	.3342	.2997	.2831
<u>TOLUENE</u>						
Temp., °C	-26.7	+ 6.4	31.8	51.9	89.5	110.6
(1/T)x100	.4057	.3577	.3279	.3076	.2757	.2606
<u>ETHYLBENZENE</u>						
Temp., °C	- 9.8	+25.9	52.8	74.1	113.8	136.2
(1/T)x100	.3797	.3344	.3068	.2880	.2584	.2443
<u>para-XYLENE</u>						
Temp., °C	- 8.1	27.3	54.4	75.9	115.9	138.3
(1/T)x100	.3773	.3328	.3053	.2865	.2570	.2430
<u>meta-XYLENE</u>						
Temp., °C	- 6.9	28.3	55.3	76.8	116.7	139.1
(1/T)x100	.3756	.3317	.3045	.2857	.2565	.2426
<u>ortho-XYLENE</u>						
Temp., °C	- 3.8	+32.1	59.5	81.3	121.7	144.4
(1/T)x100	.3713	.3276	.3006	.2821	.2532	.2395

TABLE VIII

DATA FOR TABLE I CALCULATED BY PROGRAM I

E = 2.97

<u>x_s</u>	<u>Still</u>	<u>x_d</u>	<u>Distillate</u>
.500	99.999	.748	.000
.498	99.197	.746	.802
.488	95.304	.738	4.695
.487	94.925	.738	5.074
.460	85.687	.716	14.312
.435	77.495	.695	22.504
.431	76.316	.692	23.683
.404	68.865	.668	31.134
.400	67.831	.664	32.168
.380	60.575	.645	39.424
.352	56.605	.617	43.394
.287	44.184	.544	55.815
.259	39.574	.509	60.425
.253	38.633	.501	61.366
.215	33.006	.448	66.993
.190	26.935	.410	73.064

TABLE IX

DATA FOR TABLE I CALCULATED BY PROGRAM II

REFLUX RATIO = 9,999 E = 2.97

<u>x_s</u>	<u>Still</u>	<u>x_d</u>	<u>Distillate</u>
.496	98.399	.744	1.600
.492	96.831	.741	3.168
.488	95.293	.738	4.706
.480	92.306	.732	7.693
.476	90.855	.728	9.144
.460	85.320	.716	14.679
.456	83.999	.712	16.000
.440	78.949	.699	21.050
.428	75.390	.688	24.609
.424	74.244	.685	25.755
.408	69.850	.671	30.149
.384	63.777	.648	36.222
.380	62.820	.644	37.179
.376	61.878	.640	38.121
.372	60.950	.636	39.049
.356	57.375	.620	42.624
.336	53.192	.599	46.807
.320	50.051	.582	49.948
.312	48.543	.572	51.456
.308	47.804	.568	52.195

TABLE X

DATA FOR TABLE I CALCULATED BY PROGRAM III

HOLDUP = 0

E = 2.97

<u>x_s</u>	<u>Still</u>	<u>x_d</u>	<u>Distillate</u>
.49	96.068	.740	3.931
.48	92.325	.732	7.674
.47	88.757	.724	11.242
.46	85.354	.716	14.645
.45	82.103	.708	17.896
.44	78.997	.699	21.002
.42	73.177	.682	26.822
.41	70.448	.673	29.551
.40	67.829	.664	32.170
.39	65.315	.654	34.684
.37	60.573	.635	39.426
.36	58.335	.625	41.664
.34	54.097	.604	45.902
.33	52.089	.593	47.910
.32	50.148	.582	49.851
.31	48.272	.571	51.727
.29	44.697	.548	55.302
.27	41.336	.523	58.663
.26	39.728	.510	60.271
.24	36.643	.483	63.356
.23	35.159	.470	64.840

TABLE XI

DATA FOR GRAPH 1 CALCULATED BY PROGRAM I

$$E = 437.97$$

<u>x_s</u>	<u>Still</u>	<u>x_d</u>	<u>Distillate</u>
.500	99.999	.997	.000
.492	98.417	.997	1.582
.490	98.029	.997	1.970
.479	95.950	.997	4.049
.464	93.252	.997	6.747
.441	89.396	.997	10.603
.420	86.142	.996	13.857
.392	82.154	.996	17.845
.362	78.268	.995	21.731
.334	74.956	.995	25.043
.296	70.881	.994	29.118
.268	68.148	.993	31.851
.241	65.703	.992	34.296
.218	63.751	.991	36.248
.185	61.141	.990	38.858
.184	61.065	.989	38.934
.169	59.949	.988	40.050
.152	58.730	.987	41.269
.109	55.847	.981	44.152
.072	53.564	.971	46.435
.057	52.682	.963	47.317
.031	51.194	.933	48.805
.024	50.796	.915	49.203
.008	49.850	.779	50.149
.003	49.488	.568	50.511
.000	49.203	.226	50.796
.000	48.949	.037	51.050

TABLE XII

DATA FOR GRAPH 1 CALCULATED BY PROGRAM III

HOLDUP = 2.00

E = 437.97

<u>x_s</u>	<u>Still</u>	<u>x_d</u>	<u>Distillate</u>
.48	96.110	.997	1.889
.47	94.275	.997	3.724
.46	92.507	.997	5.492
.45	90.804	.997	7.195
.44	89.161	.997	8.838
.43	87.575	.996	10.424
.42	86.044	.996	11.955
.40	83.133	.996	14.866
.39	81.749	.996	16.250
.37	79.111	.996	18.888
.36	77.853	.995	20.146
.35	76.633	.995	21.366
.29	70.026	.994	27.973
.27	68.060	.993	29.939
.26	67.115	.993	30.884
.25	66.195	.993	31.804
.23	64.424	.992	33.575
.22	63.571	.991	34.428
.16	58.852	.988	39.147
.13	56.713	.984	41.286
.10	54.689	.979	43.310
.08	53.390	.974	44.609
.06	52.116	.965	45.883
.05	51.482	.958	46.517
.04	50.841	.948	47.158
.01	48.649	.815	49.350

TABLE XIII

CALCULATED DATA FOR GRAPH 3 FROM PROGRAM II

REFLUX RATIO = 2.00

E = 357.53

<u>x_s</u>	<u>Still</u>	<u>x_d</u>	<u>Distillate</u>
.48	95.848	.959	4.151
.46	91.986	.953	8.013
.44	88.381	.946	11.618
.42	85.001	.938	14.998
.40	81.819	.929	18.180
.38	78.809	.917	21.190
.36	75.948	.903	24.051
.34	73.216	.887	26.783
.32	70.591	.867	29.408
.30	68.055	.844	31.944
.28	65.589	.818	34.410
.26	63.175	.787	36.824
.24	60.796	.753	39.203
.22	58.435	.715	41.564
.20	56.072	.673	43.927
.18	53.688	.627	46.311
.16	51.259	.576	48.740
.14	48.755	.521	51.244
.12	46.137	.462	53.862
.10	43.349	.398	56.650

TABLE XIV

CALCULATED DATA FOR GRAPH 4 FROM PROGRAM II

REFLUX RATIO = 2.00

E = 570.86

<u>x_s</u>	<u>Still</u>	<u>x_d</u>	<u>Distillate</u>
.48	95.959	.973	4.040
.46	92.208	.969	7.791
.44	88.711	.965	11.288
.42	85.441	.959	14.558
.40	82.369	.952	17.630
.38	79.473	.944	20.526
.36	76.731	.934	23.268
.34	74.120	.921	25.879
.32	71.622	.904	28.377
.30	69.215	.884	30.784
.28	66.882	.860	33.117
.26	64.602	.831	35.397
.24	62.357	.798	37.642
.22	60.129	.760	39.870
.20	57.900	.717	42.099
.18	55.647	.669	44.352
.16	53.348	.617	46.651
.14	50.973	.560	49.026
.12	48.484	.498	51.515
.10	45.823	.430	54.176

SAMPLE CALCULATIONS

Economic comparison of chromatographic and vacuum distillation:

Neglecting operating labor, the utilities are a major manufacturing cost. The feed and products are the same for both schemes. The benzene can be recycled and its cost is small. The fixed capital, installation costs, and auxiliaries costs can be estimated as percentages of purchased process equipment. For these reasons, a comparison is made on purchased cost and utilities cost of operation basis. The following table gives the outline of cost estimation.

TABLE XV

COST ESTIMATION OUTLINE FOR DISTILLATION SCHEMES

TOTAL CAPITAL

I. Fixed Capital

A. Physical Plant Cost

1. Purchased equipment cost (calculated from graphs)
2. Equipment installation cost (30 per cent of purchased equipment cost)
3. Utilities total installed cost, average services (40 per cent of purchased equipment cost)
4. Instrumentation, extensive controls (25 per cent of purchased equipment cost)

B. Engineering and Construction Costs (30 per cent of Physical Plant Cost)

The proposed toluene production from toluene and p-xylene mixture is:

5×10^8 lb/yr of toluene production

$5 \times 10^8 / 92 \text{ lb/mol} \times 360 \text{ day/yr} \times 24 \text{ hr/day} = 63 \text{ mol/hr}$
toluene

rate of p-xylene = 63 mol/hr

rate of feed = 126 mol/hr to both schemes

The data on benzene, toluene, and p-xylene is*:

TABLE XVI

	Benzene	Toluene	p-xylene
Molecular Wt	78.1	92.1	106.2
Boiling Point, °F	176	231	281
Specific Gravity	0.885	0.872	0.866
Gallon/Lb Mol	10.6	12.7	14.7
Ft ³ Gas/Lb	4.86	4.12	3.57
Heat of Vaporization, (Btu/lb)	169	156	146

I. Cost estimate for the chromatographic distillation scheme

Chromatographic distillation with benzene injection is shown in Figure 1. It was found from a computer study that a relative volatility of 2.40 best fits the chromatographic distillation curve of toluene and p-xylene (on a benzene-free basis). The normal relative volatility is

* From NGSMA Data Book.

about 2.1. See Graph 4. This estimate requires the sizing of plate towers, condensers, reboilers, reflux drums or receiving tanks, instruments, utilities costs, and a pump from the material flow rate and operation conditions of pressure and temperature.

A relative volatility of 2.4 corresponds to a benzene flow rate equal to the toluene rate. Therefore, 63 mol/hr of benzene is injected into the reboiler of the first column.

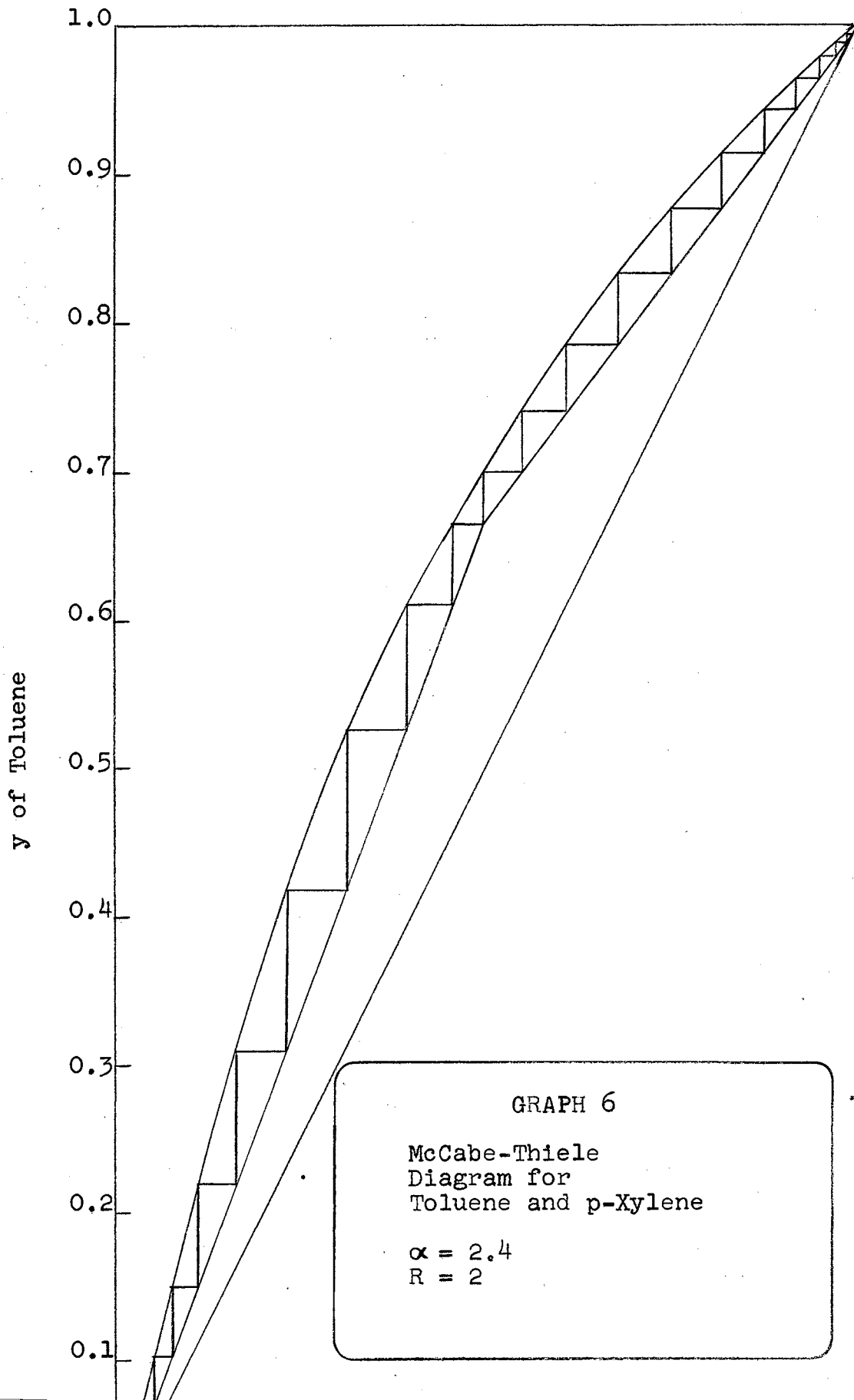
Data for McCabe-Thiele diagram of toluene and p-xylene chromatographic distillation:

$$\alpha = 2.40 \quad M = \alpha x/(1-x) \quad y = M/(M+1)$$

TABLE XVII

Vapor-Liquid Equilibrium Data For Graph 6

<u>x</u>	<u>1-x</u>	<u>M</u>	<u>y</u>
0	1	0	0
0.2	0.8	0.6	0.375
0.4	0.6	1.6	0.616
0.6	0.4	3.61	0.784
0.8	0.2	9.61	0.906
1.0	0	∞	1



The number of plates = 23 (see Graph 6)

For sizing the tower:

the average temperature = 229° F

the average molecular weight = 92

the average liquid density = 51.3 lb/ft³

the average gas density = 0.183 lb/ft³

The maximum allowable superficial vapor velocity =

$$0.152 \sqrt{\frac{51.3 - 0.183}{0.183}} = 2.54 \text{ ft/sec}$$

the tray spacing = 20", the liquid slot seal = 1",

coefficient = 0.152

weight flow rate = 378 mol/hr x 92 = 34,800 lb/hr

by nomograph (11), the tower diameter = 39"

The tower purchased cost = \$400 x 23 trays = \$9,200

Condenser design and cost

The heat duty = 378 mol/hr x 85 x 162.5 Btu/lb

$$= 5,230,000 \text{ Btu/hr}$$

The mean temperature driving force =

$$\frac{(204-70)-(204-100)}{\ln(134/104)} = 118 \text{ °F}$$

Coefficient = 150 Btu/hr ft² °F

$$\text{Area} = 5,230,000/150 \times 118 = 296 \text{ ft}^2$$

Condenser purchased cost = \$2,300

shell and tube (steel), floating head

Utility cost of cooling water

$$\text{Flow rate} = \frac{5,230,000 \text{ Btu/hr}}{(1 \text{ Btu/lb}^\circ\text{F} \times 30^\circ\text{F})} = 174,000 \text{ lb/hr}$$

$$= 20,800 \text{ gal/hr}$$

$$\text{Cost} = 20,800 \text{ gal/hr} \times \frac{\$0.1}{1000 \text{ gal}} = \$2.08/\text{hr}$$

Design and cost of reflux drum

$$378 \text{ mol/hr} \times 11.65 \text{ gal/mol} = 4,400 \text{ gal/hr}$$

$$10\% = 440 \text{ gal}$$

$$\text{Cost} = \$800 \text{ for steel tank}$$

Benzene injection reboiler design and cost

$$\text{Heat duty} = 315 \text{ mol/hr} \times 106.2 \times 146 \text{ Btu/lb} + 63$$

$$\text{mol/hr} \times 78.1 \times 169 \text{ Btu/lb}$$

$$= 4,880,000 + 830,000 = 5,710,000 \text{ Btu/hr}$$

$$\text{Mean temperature driving force} = 330 - 266$$

$$= 64 \text{ }^\circ\text{F}$$

$$\text{Coefficient} = 200 \text{ Btu/hr ft}^2 \text{ }^\circ\text{F}$$

$$\text{Area} = 5,710,000 / (200 \times 64) = 446 \text{ ft}^2$$

$$\text{Reboiler cost} = \$4,800 \text{ steel reboiler, steel pipe}$$

Utility steam cost

$$100 \text{ psi steam at } \$0.7/1000 \text{ lb}$$

$$330 \text{ }^\circ\text{F, saturated, with heat of vaporization of}$$

$$887 \text{ Btu/lb}$$

$$\text{Flow rate} = (5,710,000 \text{ Btu/hr}) / (887 \text{ Btu/lb}) = 6,450 \text{ lb/hr}$$

$$\text{Cost of steam} = 6,450 \times \$0.7/1000 = \$4.52/\text{hr}$$

Benzene recycle pump design and cost

$$63 \text{ mol/hr} \times 10.6 \text{ gal/mol} \times \text{hr}/60 \text{ min} = 11 \text{ gal/min}$$

$$\text{Pump cost} = \$200, \text{ centrifugal, iron}$$

Benzene raw material cost

$$158 \text{ mol} \times 10.6 \text{ gal/mol} \times \$0.42/\text{gal} = \$700$$

Second tower of benzene injection system for separation of benzene and toluene

For benzene and toluene separation at 760 mmHg, the average $\alpha = 2.48$

$$M = \alpha x / (1-x)$$

$$y = M / (M+1)$$

TABLE XVIII

Vapor-Liquid Equilibrium Data for Graph 7

<u>x</u>	<u>1-x</u>	<u>M</u>	<u>y</u>
0	1	0	0
0.2	0.8	0.62	0.383
0.4	0.6	1.65	0.623
0.6	0.4	3.73	0.790
0.8	0.2	9.93	0.907
1.0	0	∞	1

The reflux ratio = 2

The product rate = 63 mol/hr of benzene

2 x 63 = 126 mol/hr, liquid

126 + 63 = 189 mol/hr, vapor

From Graph 7,

$$n = 12$$

$$\frac{11}{23}$$

plates

Number of plates in second column

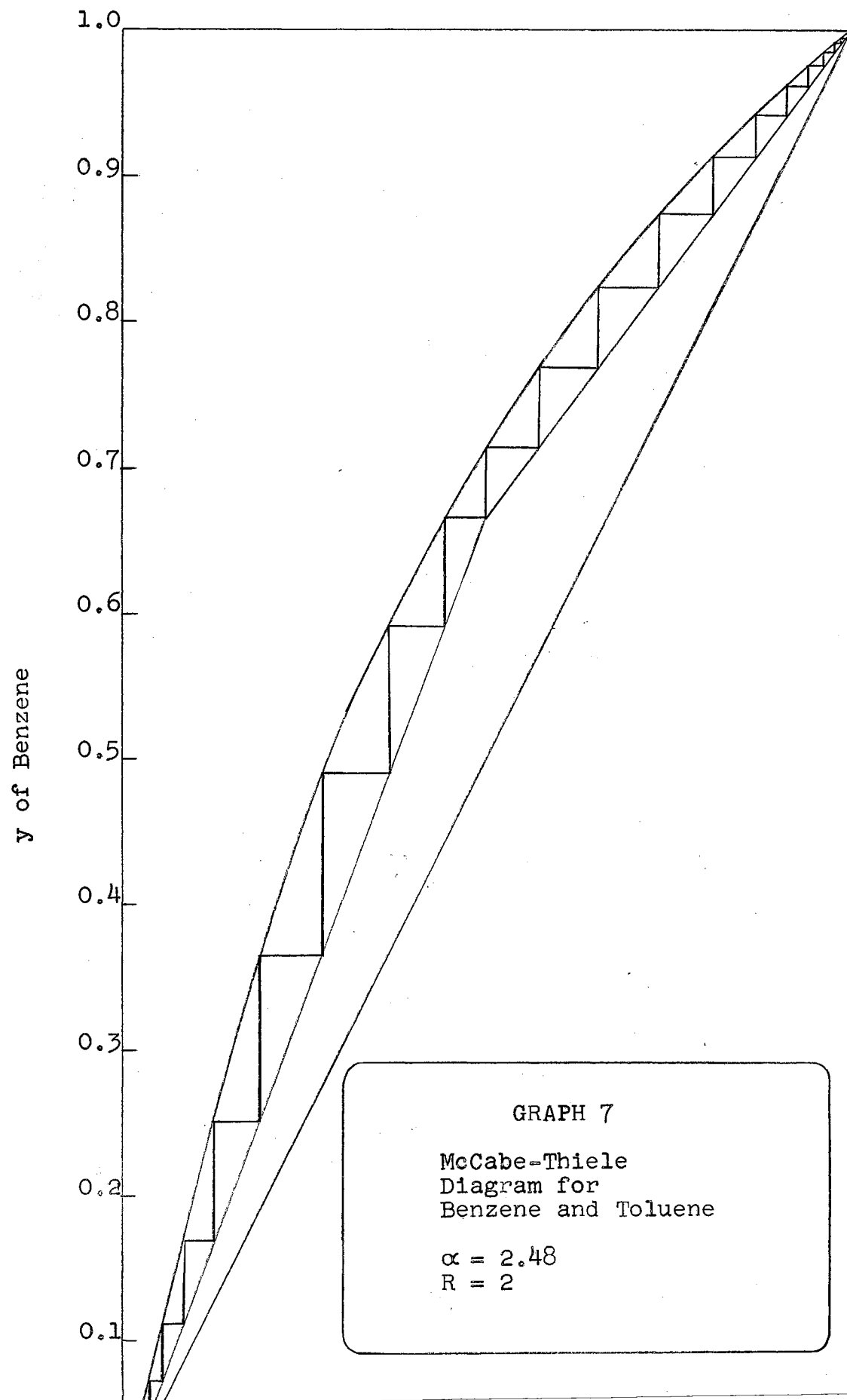
For Sizing the Column:

Average temperature = 203 °F

Average molecular weight = 85

Average liquid density = 52.6 lb/ft³

Average gas density = 0.1755 lb/ft³



The maximum allowable

$$\text{vapor velocity} = 0.52 \sqrt{\frac{52.6 - 0.176}{0.1755}} = 2.63 \text{ ft/sec}$$

The flow rate = $189 \times 85 = 16,050$ lb/hr, weight flow
rate

From a nomograph (11),

diam. = 36" Diameter of second column

Benzene and toluene tower cost = $\$360 \times 23 = \$8,300$

Benzene and toluene condenser design and cost

Heat duty = $189 \text{ mol/hr} \times 78 \times 169 \text{ Btu/lb} = 2,490,000$
Btu/hr

Coefficient = $150 \text{ Btu/hr ft}^2 \text{ }^\circ\text{F}$

Mean temperature driving force =

$$\frac{(176 - 70) - (176 - 100)}{\ln(106/76)} = 89.3 \text{ }^\circ\text{F}$$

Condenser area = $2,490,000 / (150 \times 89.3) = 186 \text{ ft}^2$

Condenser cost = $\$1,500$ steel shell and tube,
fixed tube

Reflux drum size and cost

$189 \text{ mol} \times 12.7 \text{ gal/mol} \times 10\% = 240 \text{ gal};$

cost = $\$600$

Utility water cost:

Flow rate = $2,490,000 / (1 \times 30) = 830,000 \text{ lb/hr} =$
 $9,900 \text{ gal/hr}$

Water cost = $9,900 \times \$0.1/1000 = \$1.00/\text{hr}$

Benzene and toluene reboiler design and cost

$$\text{Heat duty} = 189 \text{ mol/hr} \times 92 \times 156 \text{ Btu/lb} = \\ 2,710,000 \text{ Btu/hr}$$

$$\text{Mean temperature driving force} = 330 - 231 = 99 \text{ }^\circ\text{F}$$

$$\text{Coefficient} = 200$$

$$\text{Reboiler area} = 2,710,000 / (200 \times 99) = 137 \text{ ft}^2$$

$$\text{Reboiler cost} = \$2,000$$

Utility steam cost for reboiler

Steam 100 psi 330 °F saturated

$$\text{Heat of vaporization} = 887 \text{ Btu/lb} \quad \text{Cost} = \$0.7/1000 \text{ lb}$$

$$\text{Flow rate} = 2,710,000 / 887 = 3,060 \text{ lb/hr}$$

$$\text{Steam cost} = 3060 \times \$0.7/1000 = \$2.14/\text{hr}$$

II. Cost estimate for the vacuum distillation scheme

To achieve a relative volatility of 2.40 in the toluene and p-xylene system;

$$\text{Average pressure} = 250 \text{ mmHg} = 4.84 \text{ psia}$$

$$\text{Average temperature} = (170+215)/2 = 192^\circ \text{ F}$$

The distillation steps for separation of toluene and p-xylene are the same as in Graph 6.

$$\text{The reflux ratio} = 2$$

$$\text{The number of plates} = 23 \text{ plates}$$

For determining the vapor velocity through the column;

$$\text{Average molecular weight} = 99$$

$$\text{Average density of liquid} = 52.5 \text{ lb/ft}^3$$

$$\text{Average pressure} = 4.84 \text{ psia}$$

$$\text{Average density of gas} = 0.0686 \text{ lb/ft}^3$$

$$\text{Tray spacing} = 20", \text{ slot liquid seal} = 1"$$

Coefficient = 0.152

$$\begin{aligned} \text{The maximum allowable vapor velocity} &= 0.152 \sqrt{\frac{52.2 - 0.0686}{0.0686}} \\ &= 4.16 \text{ ft/sec} \end{aligned}$$

Weight flow rate = $189 \times 99 = 18,700$ lb/hr

From a nomograph, diam. = 43" Diameter of vacuum column

\$430 x 23 = \$9,900 Purchased cost of tower

Mechanical vacuum system capacity is 1% of total volume flow rate

$$\begin{aligned} \frac{18,700 \text{ lb/hr}}{60 \text{ min/hr} \times 0.0686 \text{ lb/ft}^3} &= 4,540 \text{ ft}^3/\text{min}, \\ 1\% &= 45.4 \text{ ft}^3/\text{min} \end{aligned}$$

Cost = \$2,000

Vacuum tower condenser design and cost

$$\begin{aligned} \text{Heat duty} &= 189 \text{ mol/hr} \times 92 \times 156 \text{ Btu/lb} = \\ &2,720,000 \text{ Btu/hr} \end{aligned}$$

Coefficient = 100 Btu/hr ft² °F

$$\begin{aligned} \text{Mean temperature driving force} &= \frac{(170-70) - (170-100)}{\ln(100/70)} = \\ &84^\circ \text{ F} \end{aligned}$$

$$\text{Condenser area} = \frac{2,720,000}{100 \times 84} = 324 \text{ ft}^2$$

Condenser cost = \$2,000 Shell and tube heat exchanger,
fixed-tube sheet and tube, steel

Utility water cost:

$$\text{Flow rate} = 2,720,000/1 \times 30 = 90,700 \text{ lb/hr}$$

$$\text{Cost} = 90,700 \times 0.119 \times \$0.1/1000 = \$1.08/\text{hr}$$

Reflux drum design and cost

$$\text{Rate} = 189 \text{ mol/hr} \times 12.7 \text{ gal/mol} = 2,400 \text{ gal/hr}$$

$$\text{Tank size} = 10\% (2400) = 240 \text{ gal}$$

Cost = \$450 steel vacuum receiver

Reboiler design and cost

$$\text{Heat duty} = 189 \text{ mol/hr} \times 106.2 \times 146 \text{ Btu/lb} = \\ 2,930,000 \text{ Btu/hr}$$

$$\text{Coefficient} = 150 \text{ Btu/hr ft}^2 \text{ } ^\circ\text{F}$$

$$\text{Mean temperature driving force} = 330 - 215 = 115^\circ \text{ F}$$

$$\text{Reboiler area} = \frac{2,930,000}{150 \times 115} = 170 \text{ ft}^2$$

$$\text{Reboiler cost} = \$2,000$$

Utility steam cost:

$$\text{Steam 100 psi, } 330^\circ \text{ F, heat of vaporization} = \\ 887 \text{ Btu/lb}$$

$$\text{Steam cost} = \frac{2,930,000}{887} \text{ lb/hr} \times \$0.7/1000 \text{ lb} = \$2.31/\text{hr}$$

TABLE XIX

Summation of Design and Costs for Distillation Schemes

Chromatographic Scheme		
Equipment	Description	Cost
First Tower	23 bubble trays, 39" diameter, 20" tray spacing	\$ 9,200
Condenser	Shell and tube exchanger	2,300
Reflux drum	440 gal steel tank	800
Reboiler	Steel and tube exchanger	4,800
Pump	Iron, centrifugal, benzene recycle, 11 gal/min	200
Benzene	Recycled material	700
Second tower	23 bubble trays, 36" diameter, 20" tray spacing	8,300
Condenser	Steel and tube exchanger	1,500
Reflux drum	240 gal tank	600
Reboiler	Shell and tube exchanger	2,000
<u>Purchased Equipment Cost</u>		<u>30,400</u>
<u>Utilities (steam and cooling water)</u>		<u>9.74 \$/hr</u>
Vacuum Scheme		
Equipment	Description	Cost
Tower	23 bubble trays, 43" diameter, 20" tray spacing	\$ 9,900
Vacuum System	Mechanical pump, 45 ft ³ /min	2,000
Condenser	Shell and tube exchanger	2,000
Reflux drum	240 gal tank	450
Reboiler	Shell and tube exchanger	2,000
<u>Purchased Equipment Cost</u>		<u>16,350</u>
<u>Utilities (steam and cooling water)</u>		<u>3.39 \$/hr</u>

NOMENCLATURE

- C = constant of integration in Equation (3)
- C' = constant of integration in Equation (24)
- C'' = constant of integration in Equation (4)
- D = distillate product, moles
- E = α^n , efficiency factor in batch distillation
- H = total holdup in a column, moles
- A = $H / \ln(E)$
- L = liquid in stillpot of a column, moles
- K = integration constant in Equation (8)
- M = $\alpha x / (1-x)$
- P = total pressure of a vapor-liquid system
- P_A = vapor pressure of a more volatile component
- P_B = vapor pressure of a less volatile component
- P̄ = partial pressure of a component
- R = reflux ratio
- T = temperature, °K
- a = $x_s / (1-x_s)$
- α = relative volatility of two components
- b = $x_d / (R+1)$, in operating line Equation (27)
- b' = E - 1, in holdup differential Equation (7)
- b'' = 1/a
- k = root of Equation (28) between 0 and 1
- c = $1 + (\alpha - 1)k$
- h = holdup of a more volatile component in a column, moles

- $m = R/(R+1)$, slope of operating line
 n = number of theoretical plates in a column
 $p = 1/b'$, in holdup Equation (8)
 $t = \ln(1 + b'x_s)$
 v = volatility of a substance
 $u = b'' + \alpha^z$
 x = mole fraction of a more volatile component
in the liquid phase
 y_z = vapor composition at any point in a column
 y = mole fraction of a more volatile component
in the vapor phase
 $z \equiv n$
 Δ = increment value of a variable

SUBSCRIPTS

- A = a more volatile component in a mixture
 B = a less volatile component in a mixture
 d = a component in the distillate
 $'$ = intersection point on a vapor-liquid composition
graph
 s = a component in the stillpot
 $0, 1, n$ = initial and final conditions of variables

DERIVATION OF EQUATIONS

DERIVATION OF RELATIVE VOLATILITY EQUATION, BASIS OF EQUATION (2)

The volatility of any substance is defined as its partial pressure divided by its mole fraction in the liquid phase.

$$v_A = \frac{\bar{P}_A}{x_A} \quad (11)$$

In an ideal mixture the volatility of each substance is equal to the vapor pressure of the pure substance. Hence, the relative volatility expression,

$$\alpha_{AB} = \frac{v_A}{v_B} \quad (12)$$

in terms of ideal substances, is;

$$\alpha_{AB} = \frac{P_A}{P_B} \quad (13)$$

From ideal gas laws, the partial pressure of a component is the product of the total pressure on the vapor system and the mole fraction of that component in the vapor phase. Or,

$$y_A = \frac{\bar{P}_A}{P} \quad (14)$$

Combining Equation (12) with Equations (11) and (14) gives

$$\alpha_{AB} = \left(\frac{y_A}{y_B} \right) \left(\frac{x_B}{x_A} \right) \quad (15)$$

For a binary mixture of liquid and vapor, $y_B = 1 - y_A$ and $x_B = 1 - x_A$. This gives a familiar form for the

relative volatility expression,

$$\alpha_{AB} = \left(\frac{y_A}{1-y_A} \right) \left(\frac{1-x_A}{x_A} \right) \quad (16)$$

DERIVATION OF RAYLEIGH'S EQUATION (1)

A component balance gives, for a differential change in moles in the stillpot,

$$Lx_S = (x_S - dx_S)(L - dL) + ydL \quad (17)$$

Combining products and ignoring second order differentials Equation (17) becomes,

$$Lx_S = Lx_S - Ldx_S - x_S dL + ydL \quad (18)$$

Rearranging Equation (18) and integrating gives,

$$\ln(L) = \int \frac{dx_S}{[y-x_S]} \quad (19)$$

DERIVATION WITH RAYLEIGH'S EQUATION (1) UNDER CONDITIONS OF TOTAL REFLUX AND CONSTANT RELATIVE VOLATILITY, EQUATION (2), GIVING EQUATIONS (3) AND (4)

Under total reflux, in the manner of Fenske,
Equation (16) becomes,

$$x_d = \frac{Ex_S}{[1+(E-1)x_S]} \quad (20)$$

This expression, when substituted into Equation (19) gives,

$$\ln(L) = \int \frac{dx_S}{\left[\frac{Ex_S}{1+(E-1)x_S} - x_S \right]} \quad (21)$$

Clearing fractions and collecting terms gives,

$$\ln(L) = \left[\frac{1}{E-1} \right] \int \frac{dx_S}{(1-x_S)x_S} + \int \frac{dx_S}{(1-x_S)} \quad (22)$$

By partial fractions, Equation (22) becomes,

$$\ln(L) = \left[\frac{1}{E-1} \right] \left[\int \frac{dx_S}{(1-x_S)} + \int \frac{dx_S}{x_S} \right] + \int \frac{dx_S}{(1-x_S)} \quad (23)$$

Integrating Equation (23) gives,

$$\ln(L) = \frac{1}{(E-1)} [\ln x_S - E \ln(1-x_S)] + C \quad (24)$$

From Equation (20), the expression for the distillate composition at total reflux can be substituted for x_S ,

$$\ln L = \frac{1}{(E-1)} \{ \ln x_d - E \ln(1-x_d) + (E-1) \ln [E - (E-1)x_d] \} + C' \quad (25)$$

$$\text{where } C' = C - \frac{E \ln E}{(E-1)}$$

or in exponential form,

$$L = \left\{ \frac{x_d^{\left(\frac{1}{E-1}\right)} [E - (E-1)x_d]}{(1-x_d)^{\left(\frac{E}{E-1}\right)}} \right\} + C'' \quad (26)$$

DERIVATION OF SMOKER'S EQUATION (5)

Any operating line, for constant molal overflow, is a straight line on a vapor-liquid equilibrium graph,

$$y = mx + b \quad (27)$$

Eliminating y between Equations (16) and (27) results in,

$$m(\alpha - 1)x^2 + [m + b(\alpha - 1)]x + b = 0 \quad (28)$$

The root of Equation (28) of interest in distillation is between 0 and 1. Let k represent the intersection of the operating line and the equilibrium line on the graph.

The origin is shifted to this intersection point,

$$x' = x - k \quad (29)$$

$$y' = y - (mk + b) \quad (30)$$

The operating line is,

$$y' = mx' \quad (31)$$

The equilibrium curve is,

$$y' + mk + b = \frac{\alpha (x' + k)}{1 + (\alpha - 1)(x' + k)} \quad (32)$$

When $x' = 0$, $y' = 0$

$$mk + b = \frac{\alpha k}{1 + (\alpha - 1)k} \quad (33)$$

Eliminating b ,

$$y' = \frac{\alpha x'}{[1 + (\alpha - 1)k]^2 + (\alpha - 1)[1 + (\alpha - 1)k]x'} \quad (34)$$

Let

$$c = 1 + (\alpha - 1)k \quad (35)$$

Equation (34) becomes,

$$y' = \frac{\alpha x'}{c^2 + c(\alpha - 1)x'} \quad (36)$$

or

$$x' = \frac{c^2 y'}{\alpha - c(\alpha - 1)y'} \quad (37)$$

Following a step-wise procedure, for n steps and generalizing,

$$x'_s = \frac{(mc^2)^n x'_d}{\left[E - mc(\alpha - 1) \left(\frac{E - m^2 c^2 n}{\alpha - mc^2} \right) x'_d \right]} \quad (38)$$

where $x'_s = x_s - k$, $x'_d = x_d - k$

For batch rectifying,

$$m = \frac{R}{(R+1)} \quad (39)$$

$$b = \frac{x_d}{(R+1)} \quad (40)$$

DERIVATION OF HOLDUP
EQUATIONS (6), (7), (8), (9), AND (10)

Let y_z = vapor composition at any point in a column, where z = variable equivalent to the theoretical plates. From a material balance on the more volatile component through the column;

$$h = \frac{H}{n} \int_{z=0}^{z=n} y_z dz = \frac{H}{n} \int_0^n \left[\frac{\alpha^z \left(\frac{x_s}{1-x_s} \right)}{1 + \alpha^z \left(\frac{x_s}{1-x_s} \right)} \right] dz \quad (41)$$

let $a = x_s/(1-x_s)$, $b'' = 1/a$

where $y_z/(1-y_z) = \alpha^z [x_s/(1-x_s)]$

and let $u = b'' + \alpha^z$

where $du = \alpha^z \ln \alpha dz$

Equation (41) becomes,

$$h = \frac{H}{n} \int_0^n \frac{\alpha^z}{(b' + \alpha^z)} dz = \frac{H}{n} \frac{1}{\ln \alpha} \int_0^n \frac{du}{u} \quad (42)$$

By integrating over the range of n , Equation (42) becomes,

$$h = \frac{H}{n \ln \alpha} \ln [1 + (\alpha^n - 1)x_s] \quad (43)$$

A complete expression for the holdup in a column is derived by making a material balance of the more volatile component about the column just before and after the removal of a small portion of distillate, dL . In the manner of Rayleigh, this equation is obtained,

$$x_s L + \frac{H}{n \ln \alpha} \ln [1 + x_s (\alpha^n - 1)] = (x_s - dx_s)(L - dL) + \frac{H}{n \ln \alpha} \ln [1 + (x_s - dx_s)(\alpha^n - 1)] + x_d dL \quad (44)$$

$$\text{Let } E = \alpha^n, A = \frac{H}{n \ln \alpha}, b' = \alpha^n - 1, \frac{1}{b'} = P$$

Eliminating x_d from Equation (44) by Equation (20),

$$x_s \frac{dL}{dx_s} + L - \frac{Ex_s}{1 + b'x_s} \frac{dL}{dx_s} - A \frac{\ln [1 + b'(x_s - dx_s)] - \ln (1 + b'x_s)}{dx_s} = 0 \quad (45)$$

This may be further simplified by recalling that from the definition of a derivative, if $t = \ln(1 + b'x_s)$, then

$$\frac{dt}{dx_s} = - \frac{b'}{1 + b'x_s} \quad (46)$$

x_s decreases during distillation and its derivatives are negative.

This can be compared directly with

$$\frac{dt}{dx_S} = \frac{\ln[1+b'(x_S-dx_S)] - \ln(1+b'x_S)}{dx_S} = - \frac{b'}{1+b'x_S} \quad (47)$$

The $-dx_S$ in Equation (47) gives a negative derivative.

Equation (45) becomes

$$x_S \frac{dL}{dx_S} + L - \frac{Ex_S}{(1+b'x_S)} \frac{dL}{dx_S} + \frac{Ab'}{(1+b'x_S)} = 0 \quad (48)$$

This is a linear differential equation.

By integrating part of Equation (48) and using an approximation by binomial expansion,

$$L = \frac{Kx_S^p}{(1-x_S)^{p+1}} - \frac{Ab'}{(1-x_S)^{p+1}} \quad (49)$$

under the condition that E is large.

Combining Equation (49) with Equation (20) gives;

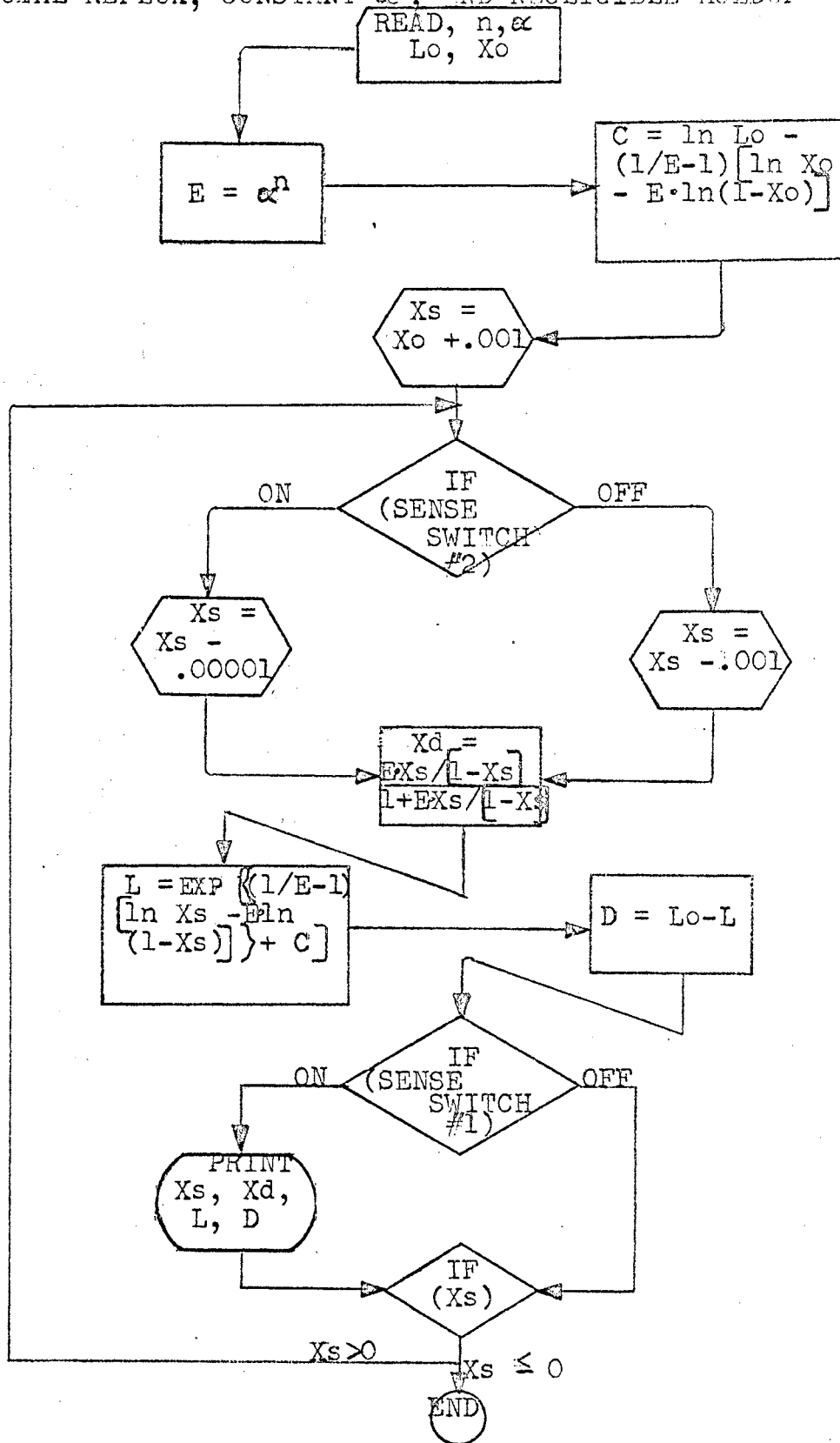
$$L = \frac{K x_d^p (E-b'x_d) - Ab'(E-b'x_d)^{p+1}}{E(1-x_d)^{p+1}} \quad (50)$$

Calculation of the integration constant is from initial composition;

$$L_0 x_{S_0} = (L_0 - H)x_1 + H \ln \left[\frac{(1+x_1 b')}{\ln E} \right] \quad (51)$$

IBM 1620 FORTRAN PROGRAMS

PROGRAM I
 FLOW DIAGRAM IBM 1620 FORTRAN
 BINARY BATCH DISTILLATION CURVES CALCULATED FROM EQUATIONS (2) AND (3)
 FOR TOTAL REFLUX, CONSTANT α , AND NEGLIGIBLE HOLDUP



PROGRAM I

```
C      BATCH DISTILLATION WITH RAYLEIGH EQUATION
1  FORMAT (F10.5,F10.5,F10.5,F10.5)
2  FORMAT (10X1HX,20X1HY,15X5HSTILL, 13X4HDIST)
3  FORMAT (F15.5,F20.5,F17.5,F19.5)
4  FORMAT (10X4H E = , F10.5)

  READ 1,P,ALPHA,SO,XO

  E = ALPHA**P

  PRINT 4,E

  PRINT 2

  C = LOG(SO) - (1./(E-1.))*(LOG(XO)-E*LOG(1.-XO))

  EL = 2.71828

  X = XO + .001

10 IF(SENSE SWITCH 2)12,15

15 X = X - .001

   GO TO 20

12 X = X -.00001

20 A = E*X/(1.-X)

   Y = A/(1.+A)

   GOLL = (1./(E-1.))*(LOG(X)-E*LOG(1.-X)) + C

   S = EL**GOLL

   D = SO - S

   IF(SENSE SWITCH 1)30,40

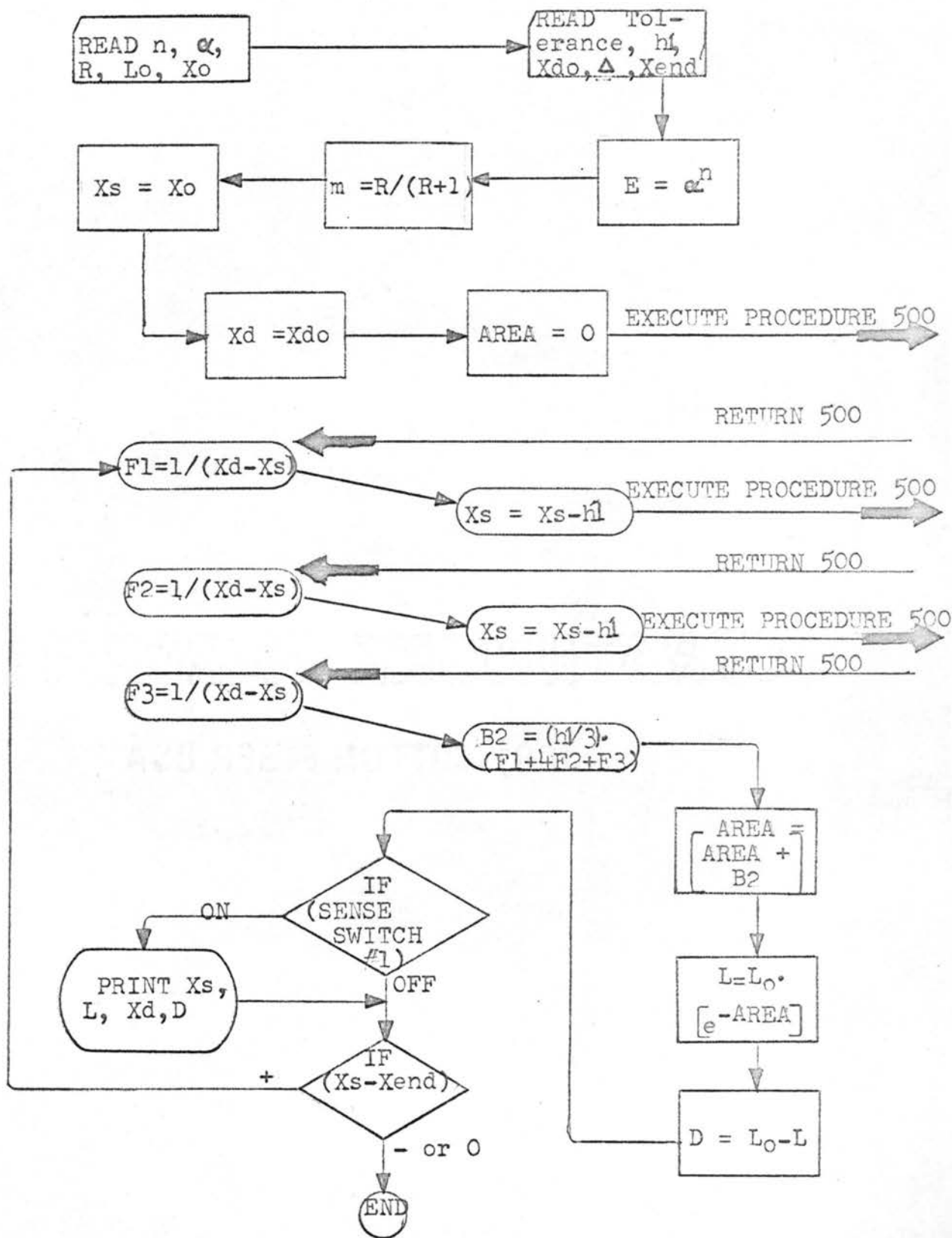
30 PRINT 3,X,Y,S,D

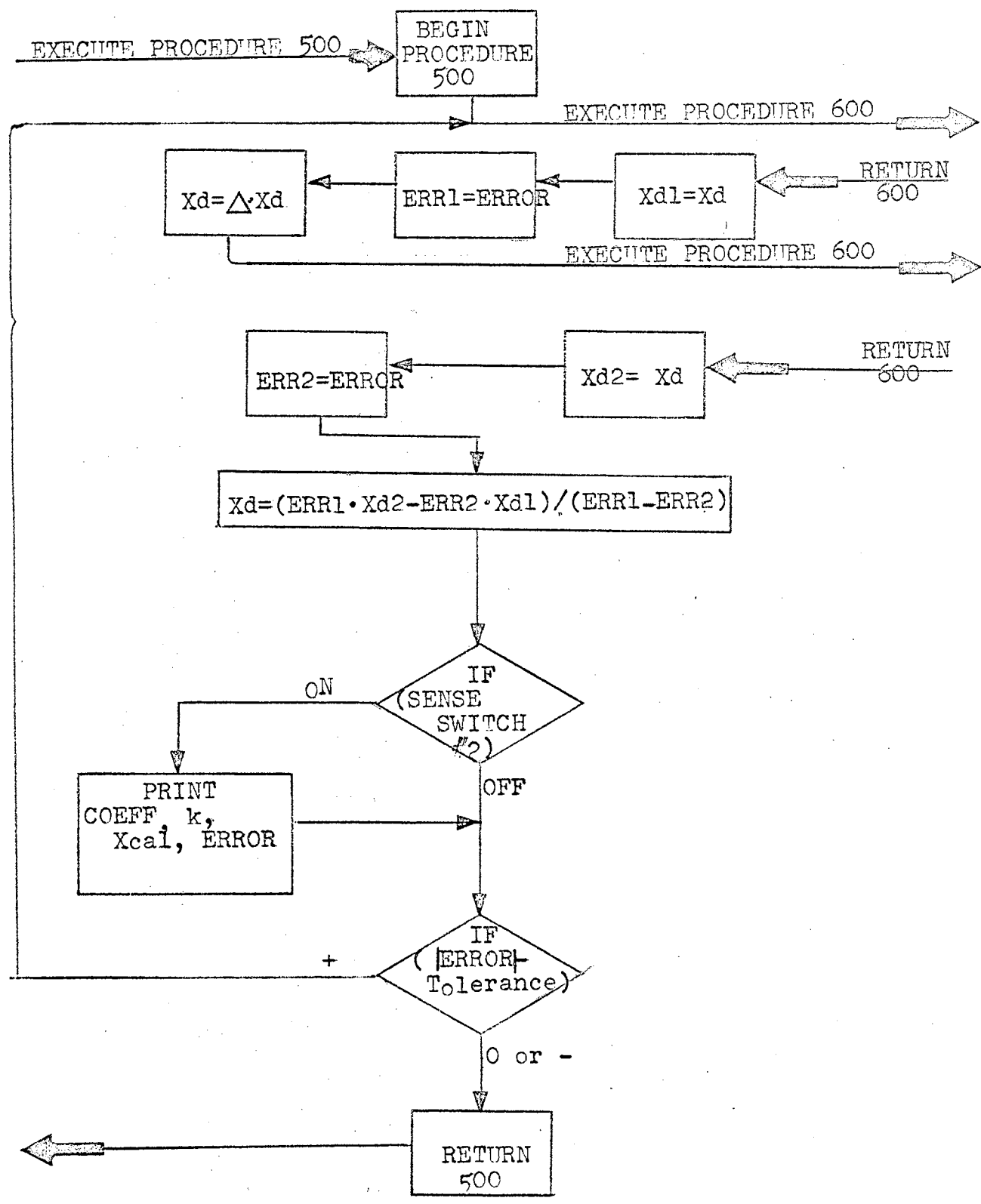
40 IF(X)50,50,10

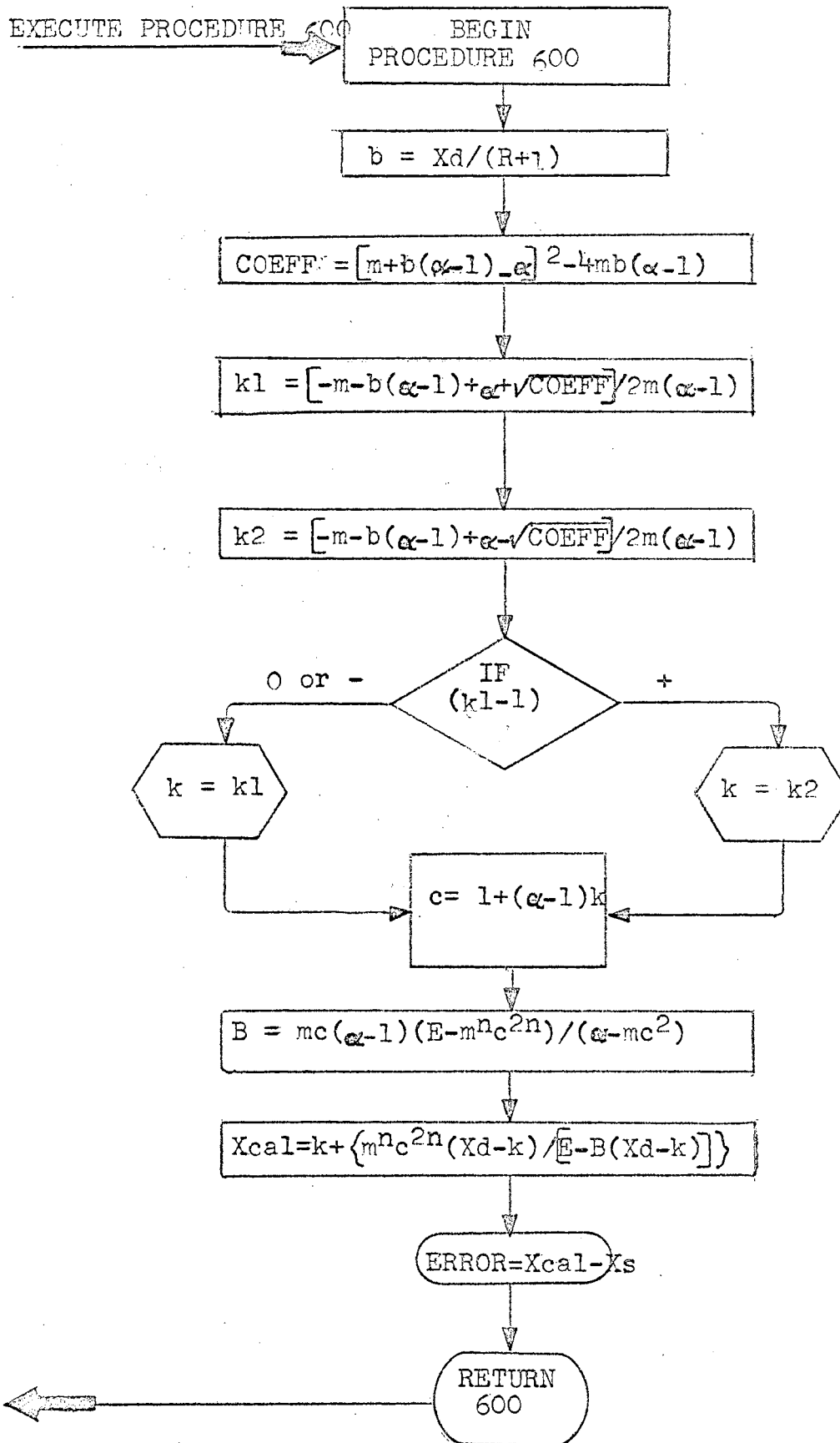
50 CONTINUE

  END
```

BINARY BATCH DISTILLATION CURVES CALCULATED FOR ANY REFLUX.
 FROM EQUATIONS (1) AND (5), NUMERICAL INTEGRATION OF EQUA.
 (1) BY SIMPSON'S 1/3 RULE WITH TRIAL AND ERROR SOLU-
 TIONS BY NEWTON'S METHOD OF TANGENTS







PROGRAM II

```

C   BATCH DISTILLATION WITH FINITE REFLUX
C   NUMERICAL INTEGRATION BY SIMPSONS 1/3 RULE
1  FORMAT (F10.5,F10.5,F10.5,F10.5,F10.5)
2  FORMAT (F10.7,F10.7,F10.7,F10.7,F10.7)
3  FORMAT (9X14HREFLUX RATIO =,F10.5,10X3HE =,F10.5)
4  FORMAT (9X2HXS13X5HSTILL13X2HXD14X4HDIST)
5  FORMAT (F14.5,F17.5,F16.5,F17.5)

READ 1,P,AL,R,SO,XSO
READ 2,TOL,H,XD,DELTA,XEND

E = AL**P

PRINT 3,R,E
PRINT 4

SLOPE = R/(R + 1.0)
XS = XSO
AREA = 0.0

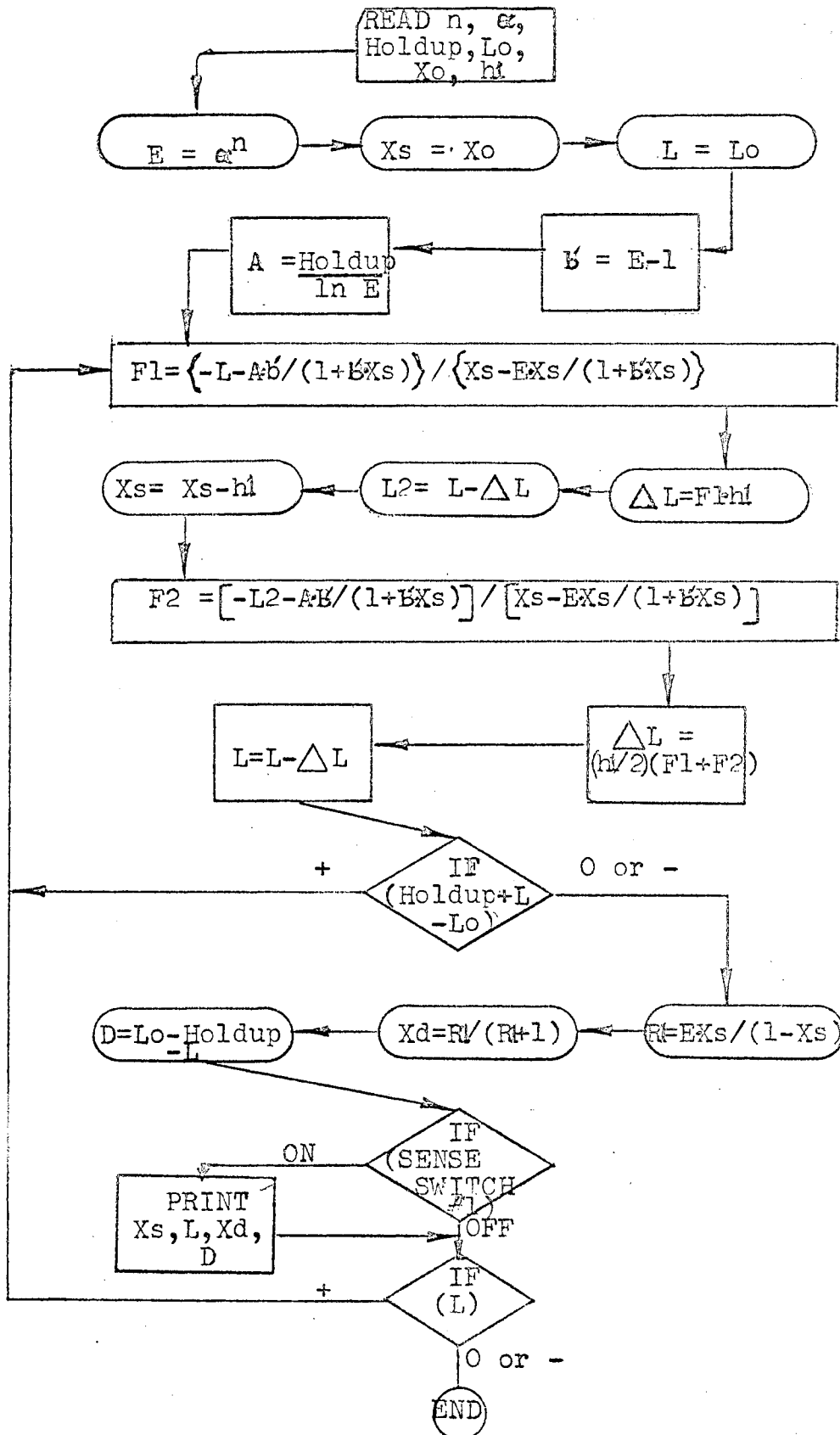
EXECUTE PROCEDURE 500
25 F1 = 1./((XD -XS)
XS = XS - H
EXECUTE PROCEDURE 500
F2 = 1./((XD -XS)
XS = XS - H
EXECUTE PROCEDURE 500
F3 = 1./((XD - XS)
B2 = (H/3.)*(F1 + 4.*F2+ F3)
AREA = AREA + B2

```

```
FRAC = EXP(-AREA)
S = SO*FRAC
D = SO - S
IF(SENSE SWITCH)1)40,50
40 PRINT 5,XS,S,XD,D
50 IF(XS-XEND)70,70,25
    BEGIN PROCEDURE 500
501 EXECUTE PROCEDURE 600
    XD1 = XD
    ERR1 = ERROR
    XD = XD*DELTA
    EXECUTE PROCEDURE 600
    XD2 = XD
    ERR2 = ERROR
    XD = (ERR1*XD2 - ERR2*XD1)/(ERR1 - ERR2)
    IF(SENSE SWITCH 2)505,510
505 PRINT 5,COEFF, ROOT,XSC,ERROR
510 IF(ABS(ERROR)-TOL)530,530,501
    BEGIN PROCEDURE 600
601 AX = XD/(R+1.0)
    COEFF=(SLOPE+AX*(AL-1.0)-AL)**2-4.0*SLOPE*(AL-1.0)*AX
    R1=(-SLOPE-AX*(AL-1.0)+AL+SQR(COEFF))/(2.0*SLOPE*(AL-1.0))
    R2=(-SLOPE-AX*(AL-1.0)+AL-SQR(COEFF))/(2.0*SLOPE*(AL-1.0))
    IF(R1 - 1.0)602,602,603
602 ROOT = RI
    GO TO 604
```

```
603 ROOT = R2
604 C = 1. + (AL-1.)*ROOT
    A = SLOPE*(C**2)
    AP = A**P
    B = SLOPE*C*(AL-1.0)*(E-AP)/(AL-A)
    XSC = ROOT + (AP*(XD - ROOT))/(E-B*(XD - ROOT))
    ERROR = XSC - XS
    RETURN 600
530 RETURN 500
70 CONTINUE
END
```

PROGRAM III
 FLOW DIAGRAM IBM 1620 FORTRAN
 BINARY BATCH DISTILLATION CURVES WITH HOLDUP, TOTAL REFLUX, AND CONSTANT
 FROM EQUATION (7), EULER'S NUMERICAL SOLUTION OF A FIRST ORDER
 DIFFERENTIAL EQUATION



PROGRAM III

```

C   BATCH DISTILLATION WITH HOLDUP
C   NUMERICAL INTEGRATION OF A FIRST ORDER DIFFERENTIAL
    EQUATION
C   BY EULERS EQUATION
1  FORMAT (F10.5,F10.5,F10.5,F10.5,F10.5,F10.5)
3  FORMAT (9X8HHOLDUP =,F10.5,10X3HE =,F10.5)
4  FORMAT (9X2HXS13X5HSTILL13X2HXD14X4HDIST)
5  FORMAT (F14.5,F17.5,F16.5,F17.5)
    READ 1,P,AL,HOLD,SO,XSO,H
    E = AL**P
    PRINT 3,HOLD,E
    PRINT 4
    XS = XSO
    S = SO
    B = E - 1.
    A = HOLD/(P*LOG(AL))
40  FUN1 = (-S-A*B/(1.+B*XS))/(XS-E*XS/(1.+B*XS))
    DELS = FUN1*H
    S2 = S - DELS
    XS = XS-H
    FUN2 = (-S2-A*B/(1.+B*XS))/(XS-E*XS/(1.+B*XS))
    DELS = (H/2.)*(FUN1+FUN2)
    S = S - DELS
    IF(HOLD+S-SO)50,50,40
50  R = E*XS/(1.-XS)

```

```
XD = R/(R+1.)  
D = SO - HOLD - S  
IF(SENSE SWITCH 1)60,70  
60 PRINT 5,XS,S,XD,D  
70 IF(S)80,80,40  
80 CONTINUE  
END
```

VITA

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Master of Science

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