THE RECOVERY OF METHANOL

FROM THE MOTHER LIQUOR

OF A PHARMACEUTICAL ACTIVE INGREDIENT

BY

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A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

AT

NEW JERSEY INSTITUTE OF TECHNOLOGY

Newark, New Jersey

1976

ABSTRACT

The company has been sending to the sewer the filtrate from one of our chemical processes. This filtrate contains 63 vol. % methanol. The recovery of this methanol would reduce the amount of purchased methanol. The recovery would also reduce the Biological Oxygen Demand of the plant effluent. In the near future the local sewer authority will be billing the company for BOD.

The goal of the recovery process is to obtain methanol of satisfactory quality for reuse in the process from which it came. A literature search and a laboratory study verified the non-ideality of the system. Preliminary calculations indicating the separability of the system were verified by batch still demonstrations. A recovery process was developed to utilize a set of existing equipment. This process was successfully demonstrated.

The column runs with the calculated set of parameters yielding 99.5 vol. % pure methanol with an overall recovery of 99% by volume. The economic analysis indicates savings of $24,800/year in purchase of methanol and an additional saving of $34,000/year in BOD charges. The total operating expenses will be about $8,000/year. This gives an overall savings of about $50,000/year. Therefore it is recommended that this process be put into use.

APPROVAL OF THESIS

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APPROVED: _____

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NEWARK, NEW JERSEY

MAY, 1976

PREFACE

Historically, pharmaceutical companies have not fully optimized the processes for the production of their active ingredients. There are two major reasons for this. First and foremost, cost of synthetic and clinical research greatly outweigh any advantage to be gained in the optimization of a given process. Secondly, the cost of optimizing small batch processes is generally greater than any economies gained by optimizing a process.

With the current changes in the economy, pharmaceutical companies are seeking to optimize processes to reduce the contaminant level of effluent streams. They are still not optimizing reactions, but they are looking for solvent recovery systems, possible recyclable liquors, and minimum crystallization and drying times. Economics, coupled with the environmentalists' urge to reduce harmful plant effluents, have increased efforts in the recycling and solvent recovery areas. This thesis develops a process for the recovery of methanol from the mother liquor of a pharmaceutical active ingredient.

I wish to express my appreciation to the Pharmaceutical Division of CIBA-Geigy Corporation, Summit, New Jersey, for the use of its laboratories and solvent recovery units. I would like to thank my supervisor, Richard B. Margerison, Ph.D., for his assistance in obtaining company approval for this particular topic.

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Chapter 1

INTRODUCTION

The term - mother liquor - will be used throughout this paper with the following definition. The "mother liquor" is the liquid left after a solid material, usually a crystallized product, has been removed from a liquid-solid slurry.

The process which generates the material under study is a three-step synthesis. In step 1, raw materials A and B are reacted in an aqueous medium. The reaction mixture is then neutralized with ammonium hydroxide to produce the solid intermediate C which is centrifuged and placed still wet in a mixture of methanol and diethylamine. The methanol is used as a solvent. The diethylamine is a pseudo-catalyst. Hydrazine added to the mixture reacts with C to form intermediate D. The intermediate is centrifuged, and the mother liquor is normally sewered. This mother liquor forms the bulk of the material under study...that is the recovery of the methanol. Intermediate D is reacted with hydrochloric acid to form the final product which is centrifuged and washed with more methanol, which is also normally sewered. This washed methanol added to the above mother liquor is the entire source of material to be recovered.[1] Figure 1 illustrates the process sequence.

With the coming of the "oil crisis," the cost of methanol (which is 60-65% of the sewered material) increased substantially. The

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[1]Letters A, B, C, and D are used to protect a proprietary synthesis.
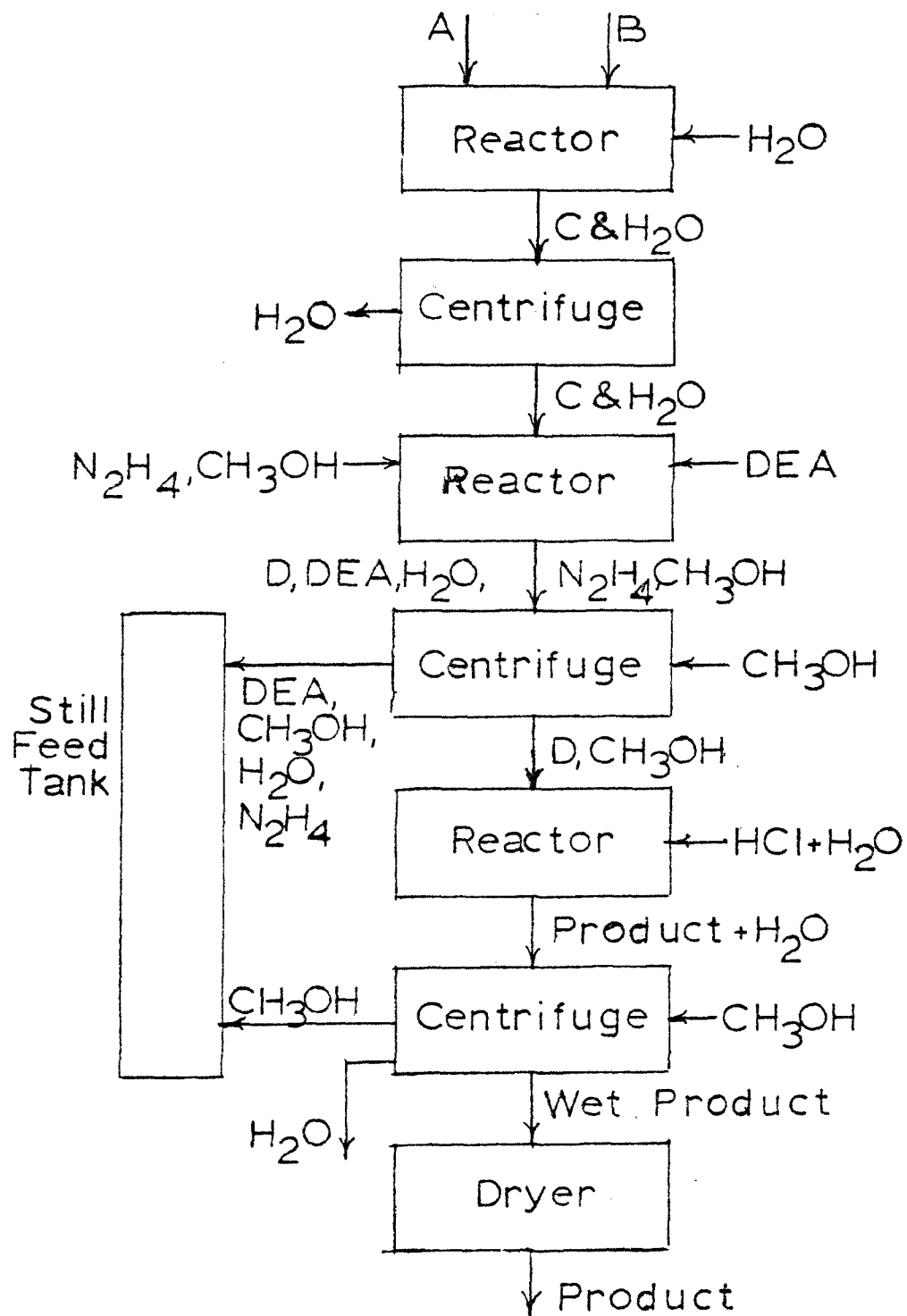
Fig.1
Process
Flow Diagram

present cost (March 1976) of methanol is $.47 per gallon. The above process consumes, as an operating expense, about fifty thousand gallons of methanol per year. To date, this methanol, used as a mother liquor, has been discarded to the sanitary sewer system. The municipal sewer authority will be charging the company for Biological Oxygen Demand, since the gross effluent will upset the normal operation of the treatment plant. With these two facts in mind, it was decided to study the possible recovery of the methanol for use in other processes, recycling to the above-mentioned process, restoration to pure methanol, or for sale as a pseudo technical-grade solvent.

To begin the study, a literature search was made to find any possible binary, ternary, or quaternary azeotropes between methanol, unused reactants, and the pseudo catalyst. The literature reports only the existence of two binary azeotropes. One azeotropic pair is methanol (40%) and diethylamine (60%), and the other pair is water (32%) and hydrazine (68%).

Since one of the restrictions placed on the recovery process was that no capital expense was to be incurred, calculations were done to determine if an existing column could perform the separation. Laboratory work was done to determine if a separation of the recovered materials would yield any of the known azeotropes upon maximization of the reclaimed methanol.

After it was determined that the separation could be made, one of the existing columns was selectively chosen for the attempted recovery. The column design parameters were determined and the appropriate calculations were accomplished so as to utilize the column. Three plant distillations were carried out. The third distillation finally gave the expected results.

Chapter 2

BACKGROUND AND THEORY

The mother liquor is made of four substances: methanol, water, diethylamine, and hydrazine. The mother liquor composition, which would be the feed composition, was determined by gas chromatography. This composition, which is given in Table 1, has negligible fluctuations. The total quantity of material generated is approximately 1300 liters/day.

A search of the literature determined that four materials formed binary azeotropes. The first azeotrope found was between diethylamine (60 vol. %) and methaonl (40 vol. %).[2] The second and only other azeotrope found was between water (32 vol. %) and hydrazine (68 vol. %).[3]

Since the preliminary calculations are based on the assumption of an ideal solution, a laboratory check was made to determine how closely the mother liquors approached ideality. This check was done by mixing volumes of analytical grades of the components equivalent to their percent composition in the feed solution. The final volume of an ideal solution should equal the sum of the component volumes. In this case, a non-ideal volume of ninety-eight percent of the expected total further demonstrated the need for laboratory work.

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[2]Horsley, Lee H., _Azeotropic Data - III_, Washington, D.C.:   American Chemical Society, 1973, p. 78.

[3]Horsley, p. 13.

Keeping the above information in mind, it was decided to do a calculation to determine if any one of the existing columns could separate the methanol from the other three materials.

Impurity levels were established predicated on a volatility ordering of the materials in question. Table 1 lists the materials in order of decreasing volatility as determined by vapor pressure data. The key components are methanol and water. The non-key components are diethylamine and hydrazine.

TABLE 1

MOTHER LIQUOR COMPOSITION

Component:	Volume fraction:	Mole fraction:
Diethylamine	.006	0.001
Methanol	.637	0.44
Water	.354	0.55
Hydrazine	.003	0.009

Thus it was assumed for minimum stage calculations that all of the diethylamine and methanol went into the distillate and the balance of the material (i.e., water and hydrazine) exited in the bottoms. The assumed distillate and bottoms compositions are given in Table 2. The quality control specifications for water content in fresh methanol (0.1 vol. %) was halved to get the distillate value for water. A recovery of 99 volume % of the methanol was assumed. This assumed recovery will be verified when actual recovery process is tried.

TABLE 2

INITIAL DISTILLATE AND BOTTOMS SPECIFICATIONS

Component:	Distillate mole fraction:
Diethylamine	0.074
Methanol	0.876
Water	0.050

	Bottoms mole fraction:
Methanol	0.001
Water	0.948
Hydrazine	0.052

Vapor-liquid equilibrium data for diethylamine, water, and hydrazine were obtained using vapor pressure data calculated from Antoine coefficients obtained from the literature.[4,5,6] Methanol vapor pressures were obtained from data in Perry.[7]

The calculation of the temperature at the bottom of the column presented a temporary problem. Since the pressure drop across the column is not zero, a pressure drop was assumed, with the pressure drop functionally dependent on the number of trays (all existing columns being sieve trayed). The number of theoretical stages can be defined using the fractionation bounds as determined by a minimum

[4.] Dreisbach, Robert R., *Physical Properties of Chemical Compounds*, vol. III.   Washington, D.C.:   American Chemical Society, 1951, p. 336.

[5.] Dreisbach, p. 463.

[6.] Dreisbach, p. 474.

[7.] *Chemical Engineers Handbook*, Robert H. Perry et. al. (eds.) Fourth Edition, New York: McGraw Hill, Inc., 1963, p. 3-54, 3-60.

stage/minimum reflux set of calculations, coupled with the use of a stage reflux correlation. The number of theoretical stages, as calculated by the Fenske equation, is dependent upon the relative volatility of the light and heavy keys, and the assumed separation. The relative volatility used is a statistical average of the volatility data at the top and bottom of the column with METHANOL and WATER as the respective light and heavy keys.

The technique used to solve the iterative problem of bottoms pressure and number of trays is as follows:

1. Assume a number of theoretical stages.

2. Calculate the pressure at the column (pressure drop of 5 mm/Hg per tray).

3. Perform a bubble point calculation at the column bottom.

4. Recalculate the average component relative volatilities.

5. Use the Fenske equation to find the minimum number of stages.

6. Compare calculated number of theoretical stages with original assumption.

The sequence was repeated starting with the newly calculated number of stages until the assumed calculated trays agreed. The results of this series for the given specifications are shown in Table 3. Sample calculations are shown in Appendix 1.

TABLE 3

RESULT OF PRELIMINARY THEORETICAL STAGE CALCULATIONS

Minimum Theoretical Stages: 12.5

	Pressure (mm Hg absolute)	Temperature (°C)
Top	760	63.8
Bottom	821.8	102.8

The three available columns, A-1, A-2, A-3, have thirty, fifteen, and fifty-five actual plates respectively. Therefore, by appropriately choosing the actual reflux ratio, any of the columns could be used from a stage point of view, but realistically A-2 with 15 actual plates is a weak contender. Columns A-2, and A-3 have steam heated reboilers while column A-1 uses live steam. The condensers for all three columns are water cooled exchangers. From a pressure level point of view any of the three columns would do the job since all have a rated pressure level of 19.70 psig.

With the recovery feasibility established, it was necessary to perform laboratory verification.

The distillation was set up using a five-liter round-bottom flask fitted with a non-refluxed fourteen-inch Vigreaux column (see Fig. 2). The column has slightly more than one theoretical stage. Thermometers were placed in the still pot liquid, in the vapor space above the

liquid, and at the top of the column. Two and eight tenths liters of mother liquor were charged. The composition of this material is identical to that shown in Table 1. After three hours of distillation, 1.7 liters of distillate had been collected. The still pot liquid temperature had reached 99°C. and the top column vapor temperature had reached 85°C. The distillate was collected in 100 ml. portions. These samples were analyzed using gas chromatography. Typical results are shown in Table 4, with the full results tabulated in Appendix 5.

From the results shown in Table 4 it is clear that the residue was approaching the calculated temperature and composition. The distillate temperature did not reach the calculated temperature and composition because the fractionating capabilities of the Vigreaux column approached only 1.5 equilibrium stages. Therefore, a second distillation was tried using an 18-inch column packed with glass beads and fitted with a reflux condenser (see Fig. 3). This column has five to ten equilibrium stages. Thermometers were placed in the still pot liquid and at the top of the column. A reflux ratio of approximately 2 was set. Two liters of mother liquor were (see Table 1) charged to a 5-liter round-bottom flask. After 6 hours, 455 milliliters of distillate had been collected. The still pot liquid temperature reached 81°C and the overhead vapor temperature reached 63.5°C. Samples of the residue and distillate were analyzed using gas chromatography. Typical results are given in Table 5, with again full results tabulated in Appendix 5.
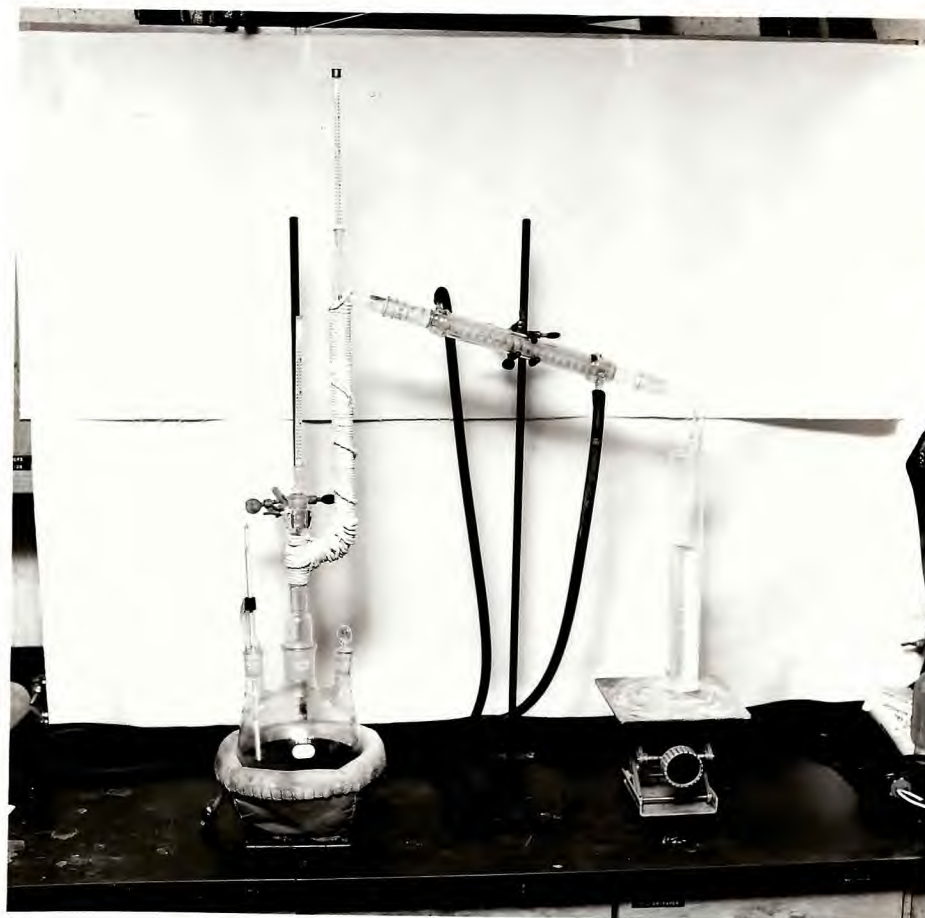
Fig. 2
Apparatus
First Laboratory
Distillation

TABLE 4

LABORATORY DISTILLATION 1

Component	Vol. % Charge	Vol. % Distillate	Vol. % Residue
Diethylamine	0.6	1.5	4.61
Methanol	63.7	88.4	7.08
Water	35.4	8.6	54.90*
Hydrazine	0.3	1.5	26.50*
Unknown	trace	----	6.91**

TABLE 5

LABORATORY DISTILLATION 2

Component	Vol. of Charge	Vol. % Distillate	Vol. % Residue
Ammonia	trace	0.03***	----
Diethylamine	0.6	trace	9.92
Methanol	63.7	99.76	27.33
Water	35.4	0.17	59.80*
Hydrazine	0.3	----	---- *
Unknown	trace	0.04	2.95**

NOTES:

*The particular gas chromatographic column used was unable to separate hydrazine and water. Water was determined by Karl Fischer titration and the hydrazine figure obtained by subtraction from the chromatographic data.

**Some solid particles were observed in the residue, probably process by-products. Laboratory workup determined material to be an amine hydrochloride.

***An ammoniacal odor (not amine) was detected in the distillate. Therefore, Technical Services was requested to check for the presence of ammonia. A possible source is residual NH_4OH from step 1 of the synthetic process.

The distillate temperature and composition were very encouraging because the laboratory data had essentially the same values as obtained by the preliminary calculations. A sample of the distillate was sent to Quality Control to see if the material met the specifications for restored grade methanol. There are thirteen specifications for restored grade methanol (see Appendix 6). The distillate failed three tests. They were:

		Specification	Distillate value
1.	Water	0. 1%	0.5%
2.	Alkalinity	0.2 ml of 0.02N H_2SO_4	2.16 ml of 2.0N H_2SO_4
3.	Substances darkening sulfuric acid:	To Pass Test	Fails Test

None of the failures are felt to be serious. First the methanol is to be recycled to the process from which it came, thus it does not have to meet the restored grade specifications. Secondly the process liquors contain about 30 vol. % water and it is desirable to have them highly alkaline. The acid darkening substances were discovered to be due to dirty distillation equipment, (the still had been used to purify benzyl alcohol). Therefore, a pilot run should be made using existing plant equipment.
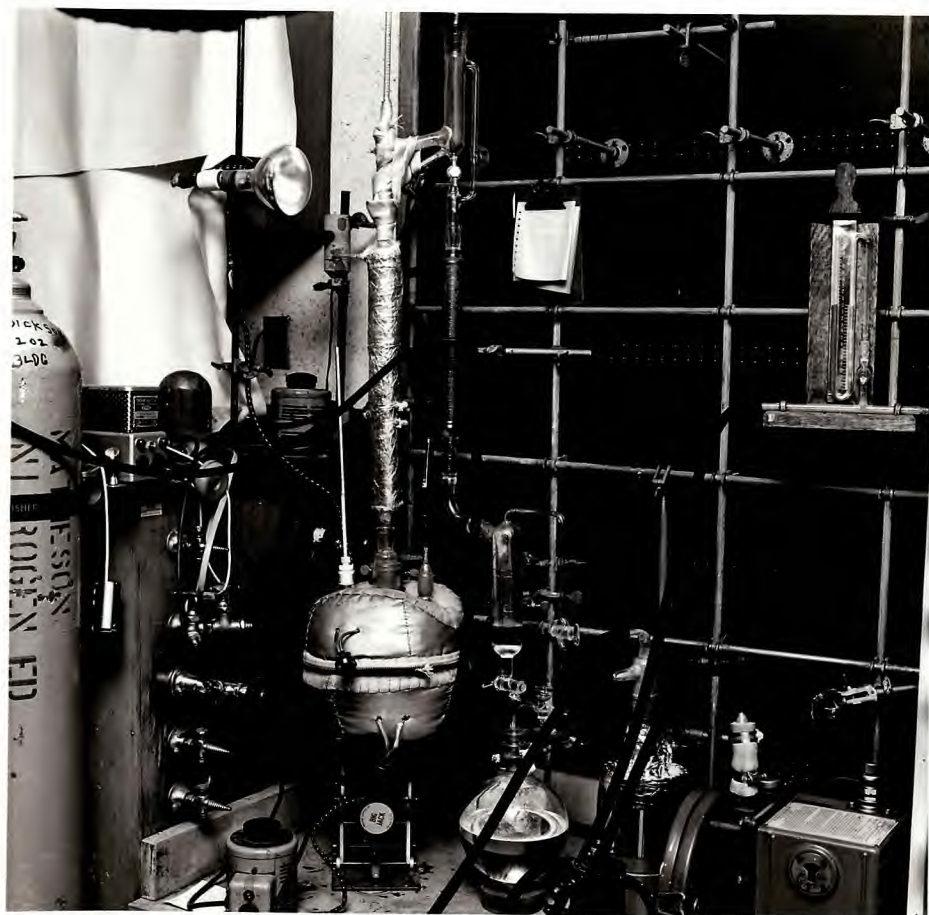
Fig. 3
Apparatus
Second Laboratory
Distillation

Chapter 3

DESIRED SEPARATION VS. EXISTING PLANT EQUIPMENT

Since the preliminary calculations and laboratory workups indicated that two (A-1, and A-3) existing columns could handle the separation, three extraneous criteria determined the specific column selection. These three criteria were availability, ability to handle precipitated solids, and corrosion.

The first criterion was availability. Column A-3 is in constant use. Column A-1 is used to restore ethanol and is used on the average of one to three days a week. The second problem was that large particles had been noticed in the laboratory distillation residues. These particles might clog the sieve trays in the columns. Via a separate study it was found that these solids dissolve in about two volumes of boiling water. Thus column A-1, which has live steam injection at the column bottom, is favored. The third problem faced was one of corrosion. The mother liquors presumably contain amine hydrochlorides in small percentages. However, the laboratory distillation indicated that these were concentrated in the bottoms at about three per cent (the unknown in Table 5). It appeared that the steam injection into Column A-1 gave it another advantage, namely - dilution of the amine hydrochlorides. Predicated on these arguments column A-1 was chosen for use.

To aid in the process analysis of column A-1's utilization, the drawings - details etc. were obtained from the equipment files.

TABLE 6

COLUMN SPECIFICATIONS

Actual Number of Plates:	30
Type of Plate:	Sieve tray
Column Diameter:	26 in.
Tray Spacing:	12 in.
Active Area:	1.83 ft^2

Using the Souders-Brown equation for maximum vapor velocity with the active area, vapor density and finally liquid density, the napor rate was determined to be 387 Kg/hour. Since the Souders-Brown equation is felt to give velocities twenty to fifty percent below the actual maximum, 387 Kg/hour will be the operating vapor rate at a reflux ratio of 1.4. The distillate rate is thus 490 liters/hour, and is equivalent to a feed rate of 768 liters/hour. The batch still laboratory work indicated that the possible separation was better than originally expected. The existing Quality Control requirements for restored grade methanol could be used as a guide in establishing the distillate specifications. There are two Quality Control specifications directly related to the amount of allowable impurities in restored methanol: percent water with a limit of 0.1% vol., and volatile impurities other than water with a limit of 1% vol. These numbers were halved and converted to molar fractions to give the distillate requirements shown in Table 7. The bottoms composition was then calculated from the

distillate and feed compositions. Hydrazine, the least volatile
of the components, was not shown to come over in the distillate
in the laboratory trials, and was thus not included in the distil-
late composition.

TABLE 7

FINAL DESIGN SPECIFICATIONS

Component:	Mole fraction Bottoms	Mole fraction Distillate
Diethylamine	0.001	0.002
Methanol	0.001	0.997
Water	0.994	0.001
Hydrazine	0.005	0.0

These revised specifications required new calculations for the
minimum number of theoretical plates. This was done in the same manner
as described in Chapter 2, the results being tabulated in Table 8.

TABLE 8

FINAL THEORETICAL STAGE CALCULATIONS

Minimum Number of Equilibrium Stages: 13.5

	Pressure (mm Hg)	Temperature (°C)
Top	760	64.76
Bottom	827.3	102.32

The minimum reflux ratio of 0.814 was determined using Underwood's theta method. The actual number of theoretical plates as determined using an efficiency of 78% is 23. The Gilliland correlation[8] was used to determine the reflux ratio of 1.4:1.

The next step was to determine the optimum feed point. Column A-1 has two feed points, one at plate eleven and one at plate fifteen, as counted from the bottom. Since methanol and water are the light and heavy keys respectively, the methanol-water binary is a logical representation of the system. The McCabe-Thiele diagram was drawn using methanol-water vapor-liquid data found in the literature[9] (see Fig. 4). Figure 5 gives the flow diagram for the distillation process. Using a distillate concentration of 99% methanol and a bottoms composition of 0.001% methanol, the operating lines were drawn and twenty-three theoretical stages were determined. Stage seven (from bottom) was determined as the optimal feedplate. The efficiency of the actual column using Fig. 18-36 in Perry[9] was determined to be about 78%. Since 23 theoretical plates are needed the number of real plates becomes 29.5. Thus column A-1 should be able to do the separation because it has 30 plates. Multiplying 7 by the ratio 30/23 (actual/ theoretical stages) gave an actual feed plate of 9.13. Thus the feedplate to be used in practice is 11.

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[8]King, C. Judson, Separation Processes. New York: McGraw-Hill, Inc., 1971, p. 460.

[9]Chemical Engineers' Handbook, Fourth Ed. p. 13-5.

MOL FRACTION IN LIQUID Xa

MOL FRACTION IN VAPOR Ya (%)

MOL FRACTION IN LIQUID Xa (%)
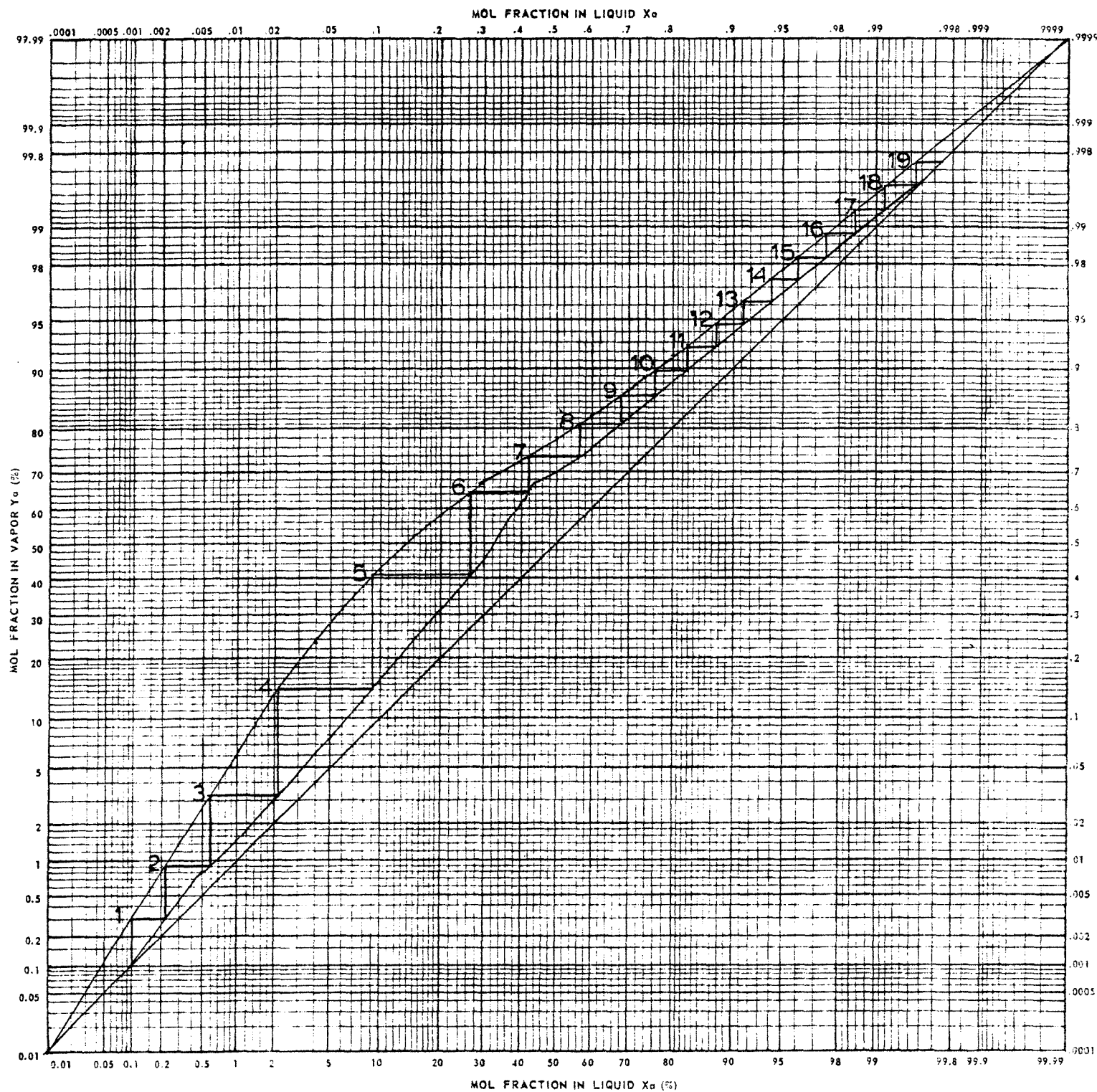
DIAGRAM FOR McCABE-THIELE GRAPHICAL METHOD FOR DETERMINING
THEORETICAL PLATES IN DISTILLATION COLUMNS

SYSTEM $CH_3OH - H_2O$

Fig. 4
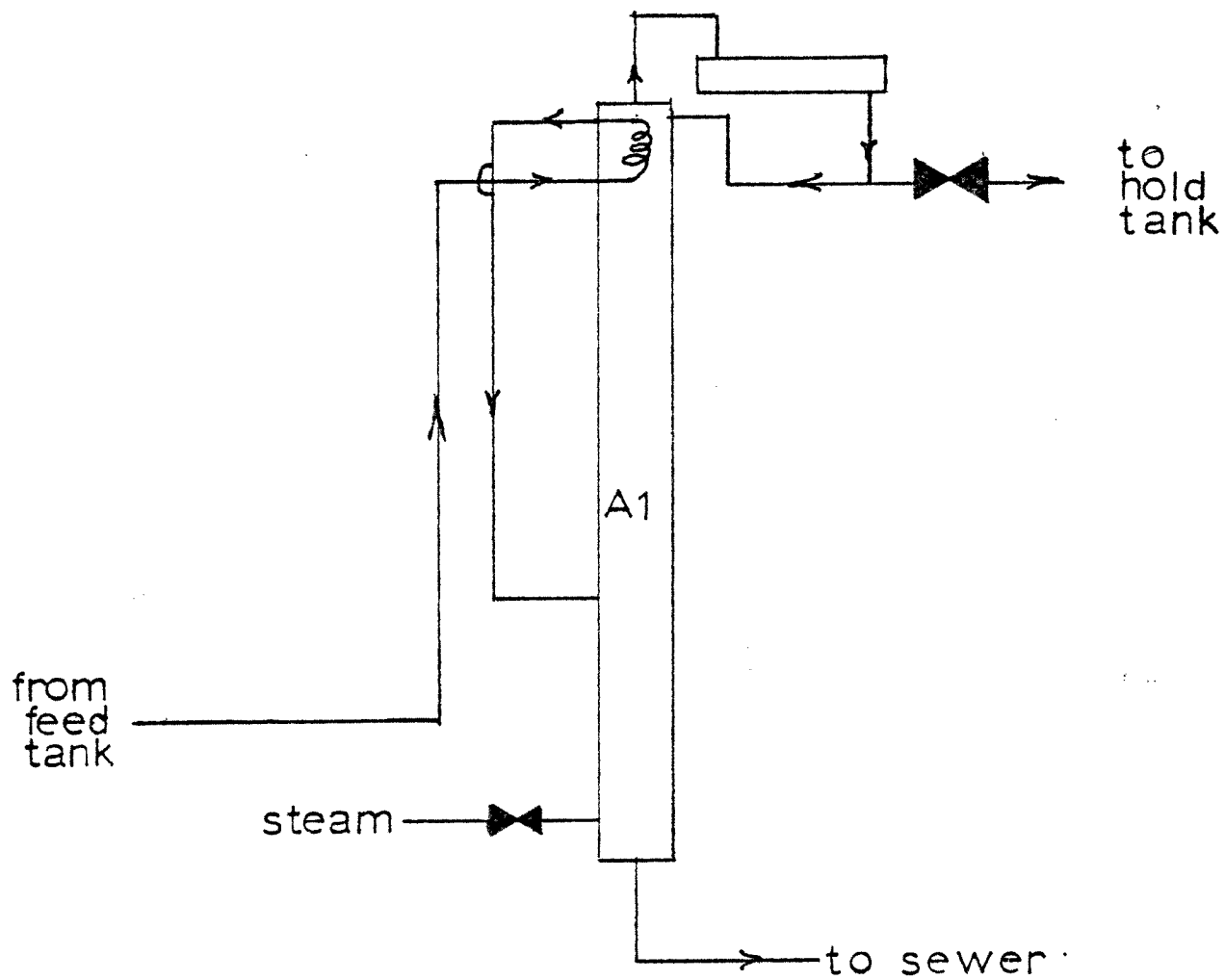
fig.5

Distillation
Flow Diagram

The feed rate chosen was 768 lt/hr, and it allows a one week accumulation of mother liquor to be run in two shifts, start-up time included.

The next step was to calculate the stripping steam rate. The stripping steam rate of 626 lb/hr was calculated via an energy balance. It was also determined that full flow through the condensers would handle the cooling requirements.

Since the flowmeters are calibrated in percent of full flow, all the necessary column control numbers were converted to the units used at the still and the plant trials were begun to verify the calculations and improve upon the laboratory data.

Chapter 4

EXPERIMENTAL RESULTS

This chapter will discuss the actual running of the plant trials, the problems encountered, and the associated results. One experimental run was anticipated to prove the recovery process giving distillate matching the design specifications.

The column is started up by feeding into it 150 liters of mother liquor as an initial charge. The feed valve is shut, the bottoms valve is closed, and the column is set for total reflux. The steam pressure is set and the steam rate is manually brought up to the required value. Once reflux is obtained, the bottoms and feed valves are opened. A sample of the reflux is continuously passed through a hydrometer to give a rough idea of the quality of the distillate. The column is operated at total reflux until the specific gravity of the reflux reaches 0.79, the specific gravity of methanol at 20°C being 0.7917.[10] The product valve is then opened and the reflux ratio is set. The distillate and the reflux rates are controlled manually.

The feed rate is set manually and is monitored by a rotameter. This proved to be of some inconvenience, as the mother liquor is very dark red and almost obscures the rotameter float.

The bottoms level is automatically controlled by an air operated valve. The volume held was arbitrarily set at fifty percent (about 150 liters). The valve is placed in a 1.5-inch line reduced from a

[10] Chemical Engineers' Handbook, Fourth Ed. p. 3-82.

3-inch line. The bottoms effluent worked its way into the valve and thickened on cooling, thus the valve occasionally stuck. Controlling the flow with a manual bypass valve alleviated the problem.

The first plant trial was run at half the calculated values of feed and product. Approximately 1800 liters of methanol were recovered from about 4000 liters of feed. If all of the methanol in the feed were recovered, this would have meant that the feed was only about 47% methanol, not 63%. It was discovered that the methanol in the sample of mother liquor previously sent for analysis was not entirely from the mother liquor but also from the washes of the product centrifuge cake. These washes had not been sent to the feed tank. An analysis of the actual feed showed 47% methanol. A sample of the distillate was sent to Quality Control, where tests showed the distillate to be 99.47% methanol. Thus about 99% of the methanol in the feed was recovered.

Of the product tests performed on the distillate by Quality Control, three failed. One of the three was water content, with a maximum limit of 0.1%. The distillate obtained on the test trial was 0.5% water. Since the calculations, which were verified by laboratory results, indicated that a lower percent water was obtainable, a second plant trial was made. The trial did not go well because the column pressure rose too high. The pressure in the column exceeded the design limits and blew the water from a liquid seal, allowing material to exit through a vent line to the roof. Once the seal had been refilled and the column restarted, the feed rate was lowered and the pressure remained

within limits. After the run it was discovered that the operator had inadvertently set a reflux to product rate ratio of 10 to 1. This allowed too much methanol to build up in the column causing the excess pressure. Only 400 liters of methanol were recovered. This amounted to only 20 percent of the methanol feed, but the water content dropped to the desired level of 0.05 percent. The material still failed the other two tests, but by smaller margins.

Since the water and the other two problems are not considered detrimental if the methanol is recycled to the process from which it came, a third plant trial was made. The proper reflux to product rate ratio was maintained for this trial. Material from this trial was laboratory- and pilot plant-tested, and found satisfactory, and reused in the plant process. Ninety-nine percent of the methanol was recovered.

Chapter 5

OVERALL DISCUSSION OF THE RESULTS

The final experimental run, which used the proper operating condition (as calculated), recovered 99 vol. % of the methanol with 99.5% purity. The recovery and purity matched the design specifications.

The major savings involved in this solvent recovery are the approximately 200,000 liters of methanol per year that can be recovered. With the present purchase price of methanol at $0.47 per gallon, the savings would be $24,800 per year.

There will be no capital costs incurred. However, there will be operating costs for utilities and labor. The rate charged for labor is $11.73 per hour, (this includes benefits). An operator would spend about six hours per week for fifty-two weeks recovering the methanol, which would cost about $3,700. The second cost to be calculated is the cost of the steam. The present charge for steam is about $3.00 per thousand pounds. The steam would be used at 1500 pounds per hour for twelve hours a week for fifty-two weeks. This would cost about $2,800 per year. The cost of pumping the cooling water is about $800/year.

At present costs, this would give a total savings of about $17,500 per year. However, this will change appreciably when the cost of Biological Oxygen Demand (BOD) is included. The local sewer authority

is planning to charge for BOD in the sanitary sewer discharge, the actual cost will be about 10 cents/lb. BOD. The BOD charges are high enough to make the recovery of this methanol almost mandatory (about $34,000/yr.). This gives a total saving of about $50,000/yr. Therefore, I recommend that this process be installed as part of the normal operation of the plant.

APPENDICES

Appendix 1

CALCULATIONS OF DISTILLATE AND BOTTOMS

COMPOSITIONS AND THEORETICAL PLATES

The sample calculation shown is for the final feed composition.

TABLE 9

FINAL FEED COMPOSITION

Basis: 1500 liters/hour feed

Component:	Vol.%	Vol. (liters)	Specific Gravity	Wt. (kg.)	MW	Kg mole	Mole fraction
Diethylamine	0.6	9.00	0.7108	6.4	73	0.09	0.008
Methanol:	63.7	955.5	0.7914	756.18	32	23.63	0.44
Water:	35.4	531.0	1.000	531.0	18	29.50	0.55
Hydrazine:	0.3	4.5	1.03	4.64	32	0.14	0.002
Total:	100.0	1500.0					1.000

TABLE 10

DISTILLATE SPECIFICATIONS

Component:	Vol.%	Vol. (liters)	Specific Gravity	Wt. (kg.)	MW	Kg mole	Mole fraction
Diethylamine:	0.5	4.80	0.7108	3.65	73	0.05	0.002
Methanol:	99.45	955.5	0.7914	756.18	32	23.63	0.996
Water:	0.05	0.48	1.00	0.48	18	0.03	0.002
Hydrazine:	0.00	0.00					0.00
Total:		960.78					1.000

TABLE 11

BOTTOMS SPECIFICATIONS

Component:	Kg mole (by difference)	Mole fraction
Diethylamine:	0.04	0.00135
Methanol:	0.0	0.0010
Water:	29.47	0.99393
Hydrazine:	0.14	0.00472
Total:	29.65	1.00000

Fenske's equation was used to determine the number of theoretical stages.

Eq. 1   Fenske's Equation

$$N = \ln\ [(x_L/x_H)_D (x_H/x_L)_B]/\ln(\alpha_{LHavg})$$

Where: N = number of theoretical plates

   X_L = mole fraction of light key

   X_H = mole fraction of heavy key

   D = refers to distillate

   B = refers to bottoms

   α_{LHavg} = average relative volatility of light to heavy key

The mole fractions are known. The relative volatilities are not known. The bottoms and distillate temperatures are required to calculate the relative volatilities. They are calculated in the following manner. The pressure at the top of the column is assumed to equal 760 mm Hg. A dew-point calculation with known pressure is made to arrive at the distillate temperature.

Eq.2 $\sum y_i/K_i = 1.0$ $y_i = x_i$ because of total condenser

Eq. 3 $K_{r(new)} = \sum y_i/\alpha_i$

Eq. 4 $K_i = P_i^\circ(T)/P_T$

Where: K_i = vapor-liquid equilibrium constant for component i

   y_i = mole fraction in vapor of component i

   $P_i^\circ(T)$ = vapor pressure at temperature T

   P_T = total pressure at point of interest - 760 mm Hg

The vapor pressure was calculated from Antoine's equation using empirical constants found in Dreisbach.[12,13,14] Methanol vapor pressure was interpolated from data in Perry's.[15]

Eq. 5   Antoine's Equation

$$\log P^\circ_i = A - B/(C + T)$$

Where: A, B, and C are empirical constants.

A temperature was assumed. In this case, 64.7°C was assumed since this is the normal boiling point of methanol.

Therefore: $\log P^\circ_{DEA} = 7.14099 - 1209.9/(229.9 + 64.7)$

$P^\circ_{DEA} = 1083.6$ mm Hg

$P^\circ_{MeOH} = 760.0$ mm Hg (at normal boiling point)

$\log P^\circ_{H_2O} = 7.96681 - 1668.21/(228 + 64.7)$

$P^\circ_{H_2O} = 189.5$ mm Hg

Therefore: $K_{DEA} = 1083.56807/760 = 1.42575$

and similarly: $K_{MeOH} = 1.0$

$K_{H_2O} = 0.24417$

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[12]Dreisbach, Robert R., Physical Properties of Chemical Compounds, vol. III. Washington, D.C.: American Chemical Society, 1951, p. 336.

[13]Dreisbach, p. 463.

[14]Dreisbach, p. 474.

[15]Chemical Engineers' Handbook, Robert H. Perry et al (eds.), Fourth Edition. New York: McGraw-Hill, Inc., 1963, pp. 3-54, 3-60.

TABLE 12

DATA FROM DEW-POINT CALCULATION (EQ. 2)

Component:	y	y/K
Diethylamine:	0.00211	0.00148
Methanol:	0.99696	0.99384
Water:	0.00127	0.00520
Total		1.00052 ~ 1.0

Therefore: $T_{Distillate} = 64.7°C.$

If the summation of y_i/K_i had not been sufficiently close to 1.0, the relative volatilities would have to be calculated from Eq. 6. Then the summation of y_i/α_i would have to be made to determine the new K_r from which a new temperature is obtained to run the next trial.

The next step is to determine the conditions at the bottom of the column. This is done by performing a bubble-point calculation at constant pressure.

Eq. 6 $K_i/K_r = \alpha_i$

Eq. 7 $K_r = 1/\Sigma \alpha_i x_i$

Where: K_i = vapor-liquid equiplibrium constant for component i

K_r = vapor-liquid equilibrium constant for most abundant

light component

x_i = mole fraction of component in liquid

Equation 6 will subsequently be used as the test for completeness of the iteration and as the source of the new K_r for the iteration.

First the bottom pressure is needed in order to calculate K_i using Eq. 4. A pressure drop of 5 mm Hg per theoretical plate was used. A minimum number of theoretical plates is then assumed. In this case, 13.4 was assumed from preliminary calculations. This gave a bottom pressure of 826.98 mm Hg. Next, a temperature of 99.92°C was assumed. The vapor-liquid equilibrium constants, K_i, are calculated, including K_r. Then the relative volatilities, $_i$, are determined by Eq. 6. Finally, the products $\alpha_i x_i$ are summed. The reciprocal of the sum is compared to K_r calculated by Eq. 4. If the two are reasonably close, this part of the calculation is done. If not, the new K_r is used to find a new temperature through Eq. 4 and Antoine's equation, and the calculation is repeated until the newly calculated K_r matches the previous K_r. Then the final relative volatilities are geometrically averaged with the distillate relative volatilities (calculated in the same manner and referred to water) and the number of stages is calculated by Fenske's equation. If this agrees with the original guess as to the number of theoretical stages, the calculation is finished. If not, the new number of stages is used and the process repeated.

TABLE 13

DATA FROM FIRST ITERATION OF BUBBLE-POINT CALCULATION

Component:	x	K		αx
Diethylamine:	0.00135	3.59009	3.91807	0.00529
Methanol:	0.001	3.37785	3.68645	0.003
Water:	0.99393	0.91629	1.000	0.99393
Hydrazine:	0.00472	0.57532	0.62788	0.00296
				1.00218

$\Sigma\alpha$ x = 1.00218

$1/\Sigma\alpha$ x = 0.99782 = K_r, whereas estimated K_r = 0.91629 from Eq. 4 and a temperature of 99.92°C.

Since $K_i = P_i^o(T)/P_T$, $K_r = P_i^o/826.98 = 0.99782$ and P = 825.18
Back-calculating from Antoine's equation, the new temperature at the bottom of the column is 102.3°C.

TABLE 14

DATA FROM SECOND ITERATION OF BUBBLE-POINT CALCULATION

Component:	x	K		αx
Diethylamine:	0.00135	3.81634	3.82468	0.00516
Methanol:	0.001	3.61038	3.61827	0.004
Water:	0.99393	0.99782	1.000	0.99393
Hydrazine:	0.00472	0.62827	0.62964	0.00297
				1.00203

$\Sigma\alpha\ x\ =\ 1.00203$

$1/\Sigma\alpha x\ =\ 0.99795$

K_r (1st iteration) = 0.99782, which is close enough for this purpose.

Then, in Fenske's equation:

$$N = \ln\ (0.00676/0.00127)(0.99393/0.001)\ /\ln(\alpha_{LHavg})$$

$$\alpha_{LHavg} = \sqrt{\alpha_{LHD}\alpha_{LHB}} = 3.85508$$

Substituting, N = 13.47

Using N to calculate the new pressure and assuming the temperature to be 102.3°C, the bubble-point calculation was rerun. The final temperature is 102.3°C, and the final N is 13.47.

When N is finally determined it is substituted into the following equations to determine if it gives the proper separation.

Eq. 8 $b_i = f_i / [1 + \alpha_i^N (d/b)_H]$

Eq. 9 $d_i = \left[f_i (d/b)_H \alpha_i^N \right] / [(d/b)_H \alpha_i^N + 1]$

Where: b_i = moles of i in bottoms

           f_i = moles of i in feed

           d_i = moles of i in distillate

For light components calculate b_i and find d_i by difference. Compare d_i with specification. Light components are those lighter than the light key. The heavy components are the ones heavier than the heavy key. For heavy components, calculate d_i, find b_i by difference, and compare it to the specification. These distribution calculations are taken from Hengstbeck.[16]

In this case, d_i for diethylamine was much greater than the specification. This was of no concern since laboratory distillations showed that the diethylamine did stay behind. The calculation for water was very close. Therefore it was assumed that the desired separation is obtained by 13.47 minimum theoretical stages.

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[16] Hengstbeck, R.J., Distillation Principles and Design. New York: Reinhold Publishing Corporation, 1961, p. 184.

Appendix 2

MINIMUM REFLUX RATIO

These calculations were done using a method developed by Underwood as described by King.[17]

Eq. 10 $1 - q = \sum \dfrac{\alpha_i Z_{if}}{\alpha_i - \Theta}$

Eq. 11 $R_{min} + 1 = \sum \dfrac{\alpha_i Z_{id}}{\alpha_i - \Theta}$

Where: R_{min} = minimum reflux ratio

α_i = relative volatility of component i with respect to the heavy key

Z_i = mole fraction of component i

d   = refers to distillate

f   = refers to feed

Θ = constant $\alpha_{HK} < \Theta < \alpha_{LK}$

q   = fraction of feed that is a liquid

Θ is calculated from Eq. 10 and then substituted in Eq. 11. The feed and distillate compositions are set by the problem specifications. The relative volatilities, α, were calculated during the determination of the minimum number of stages (see Appendix 1). In this case, all of the feed is in the liquid state. Therefore, q equals 1. Substituting the proper numbers in Eq. 10:

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[17]King, p. 449.

$$0.0 = \frac{(4.72581)(0.00169)}{4.72581 - \Theta} + \frac{(3.85483)(0.44)}{3.85483 - \Theta} +$$

$$\frac{(1.00000)(0.55)}{1.00000 - \Theta} + \frac{(0.61249)(0.00262}{0.61249 - \Theta}$$

Θ is calculated by trial and error. By inspection of the substitution in the above equation, it can be seen that Θ lies between 1.0 and 3.855. Starting with an initial guess of 2.0 for the value of Θ, the value determined satisfying the above expression was .0523.

Substitution of this value for Θ into Eq. 11 yielded a minimum reflux ratio of 0.81368, as follows:

$$R_{min} + 1 = \frac{(4.72581)(0.00211)}{(4.72581 - 1.72581)} + \frac{(0.99676)(3.85483)}{(3.85483 - 1.72581)} +$$

$$\frac{(1.00000)(0.00127)}{(1.00000 - 1.72581)} + \frac{(0.61249)(0.0)}{(0.61249 - 1.72581)}$$

$$R_{min} + 1 = 1.81368$$

$$R_{min} = 0.81368$$

Appendix 3

ACTUAL REFLUX RATIO

This calculation was done using the Gilliland correlation. The graph used was taken from King.[18] The actual number of theoretical plates is 23. (Efficiency of 78% was used to obtain the number of theoretical plates).

Eq. 12 $\quad \dfrac{N - N_{min}}{N + 1} = \dfrac{23 - 13.46770}{31} = 0.40$

Where: N = actual number of plates

N_{min} = minimum number of theoretical stages

From the graph:

$$0.24 = \frac{R - 0.81368}{R + 1}$$

$R = 1.4$ = actual reflux ratio.

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[18]King, p. 460

Appendix 4

CALCULATIONS FOR THE McCABE-THIELE DIAGRAM

By using standard techniques the equations of the operating lines were found to be:

Stripping Section:

$$y = 1.52 \quad x \quad + \quad .00052.$$

Rectifying Section:

$$y = 0.58 \quad x \quad + \quad .41$$

Figure 4 is a replica of the original McCabe-Thiele diagram used.

Appendix 5

DATA AND ANALYSIS OF LABORATORY DISTILLATONS

Table 15

FIRST DISTILLATION

Sample Units	Still pot Temperature	Upper Column temp.	Total Volume of distillate
	35°C	25°C	0
	55	25	0
	65	25	0
	70	25	
	77	70	Start collecting
1-1	78	71	100 ml
1-2	78	71	200
1-3	78	71	300
1-4	79	71	400
1-5	80	72	500
1-6	80	72	600
1-7	81	72	700
1-8	81	73	800
1-9	82	74	900
1-10	83	75	1000
1-11	84	75	1100
1-12	86	75	1200
1-13	87	76	1300
1-14	90	78	1400
1-15	92	80	1500
1-16	95	82	1600
1-17	99	85	1600
1-18	residue volume 1100 ml		

Table 16

ANALYSIS OF SAMPLES FROM FIRST LABORATORY DISTILLATION

	H_2O, N_2H_4 (Vol. %)	CH_3OH (Vol. %)	DEA (Vol. %)	Unknown (Vol. %)
1-1	10.1%	88.4	1.5	
1-2	10.4	88.3	1.3	
1-3	11.0	87.5	1.4	
1-4	11.7	85.1	3.2	
1-5	12.1	84.5	3.4	
1-6	12.4	83.9	3.7	
1-7	12.9	83.2	3.9	
1-8	13.8	82.0	4.2	
1-9	14.7	81.1	4.2	
1-10	15.4	80.1	4.5	
1-11	16.3	78.8	4.9	
1-12	17.5	76.8	5.7	
1-13	18.8	74.8	6.4	
1-14	20.4	72.5	7.1	
1-15	23.5	68.1	8.4	
1-16	27.9	62.2	9.9	
1-17	34.9	52.7	12.4	
1-18	83.8	8.28	5.84	1.93

Table 17

DATA FROM SECOND LABORATORY DISTILLATION

Sample	Still pot Temperature	Upper Column temp.	Total Volume of distillate
–	25 °C	25 °C	
	77	64.0	
	77	62.0	
	77	62.0	distillate starts over
2-1	77	63.0	10 ml
2-2	77	63.0	20
2-3	77	63.0	90
2-4	77	63.0	140
2-5	78	63.0	215
2-6	79	63.0	290
2-7	80	63.5	365
2-8	81	63.5	455

Table 18

ANALYSIS OF SAMPLES FROM SECOND LABORATORY DISTILLATION

	H_2O, N_2H_4 (Vol. %)	CH_3OH (Vol. %)	DEA (Vol. %)	NH_3 (Vol. %)	Unknown (Vol. %)
2-1	.39	89.39	.03	.35%	9.84
2-2	.46	98.67	.01	.26	.80
2-3	.11	99.4	.06	.17	.26
2-4	.17	99.76	--	.03	.04
2-5	.23	99.69	.04	.01	.03
2-6	.27	99.54	.16	--	.03
2-7	.20	99.49	.29	--	.02
2-8	.16	99.06	.76	--	.02

Appendix 6

SPECIFICATIONS FOR RESTORED METHANOL

1. Description: Clear, colorless, liquid having a characteristic but not pungent odor.

2. Volatile Impurities by Gas Chromatography: 1.0% maximum (excluding water.

3. Identification by Gas Chromatography: Conforms.

4. Solubility in Water: Clear.

5. Specific Gravity 20°/20°: 0.7900 - 0.7940.

6. Non-Volatile Residue: 1 mg/100 ml.

7. Water (by Karl Fischer): 0.1% maximum.

8. Acidity: 0.75 ml of 0.02N NaOH maximum.

9. Alkalinity: 0.2 ml of 0.02N Sulfuric Acid maximum.

10. Substance Darkening Sulfuric Acid: To pass test.

11. Substance Reducing Permanganate: To pass test.

12. Acetone, Aldehydes: 10 ppm maximum.

13. Refractive Index at 20°C: 1.326 - 1.331.

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