1964
Problem
Meeting Market Demands—Chloromethanes Plant

FOREWORD

A committee from Solvay Process Division of Allied Chemical Corporation prepared and judged the 1964 Student Contest Problem. The members of the committee were Walter E. Sommerman, chairman; W. F. Kenney; B. E. Kurtz; J. O. Moore; and B. B. Smura. Their comments follow:

Our committee of judges was gratified by the quality of the solutions submitted and fully appreciated the hard work expended by all contestants.

The following comments are offered in the hope that they will benefit the participants and be instructive in their future engineering assignments.

The solutions were judged in four parts including:

Presentation
Conceptual Approach
Theoretical Approach
Numerical Content

A grading system was devised giving equal consideration to each of the above.

The committee evaluated the presentation on the basis of the communication skills exhibited. Many papers were too long to be submitted to a busy executive. Some students dwelled on uneconomical or impractical alternate schemes, although the purpose of the report was to give a concise development of evidence to support the writer's conclusions.

Conceptually, we expected to find an understanding of the importance of employing minor modification in meeting the deadlines for start-up and product distribution. For example, series reactor operation should not be recommended for the initial start-up although it is economically advantageous. Even if the appropriate calculations were completed in time, such a radical departure from pilot plant experience would require additional tests to verify reactor performance and safety aspects. Here qualitative reasoning which minimized unnecessary calculations and engineering time was judged favorably.

In the schemes suggested for the long-term case (1968) we looked for creative thinking based on understanding of the system installed and potential economic advantages of future modifications. Some papers showed a lack of imagination or proposed theoretically unworkable schemes. We judged schemes employing series reactors as offering the greatest economical potential for satisfying the long-term requirements.

In the development of theoretical equations describing the reactions there were two typical errors. These included the omission of the heat balance restriction and the use of kinetic equations for a flow-type reactor rather than the appropriate equations for a back-mixed reactor.

Finally, most students were careful in their numerical manipulations; as we noted, there were very few calculation errors.

For 1964, the A. McLaren White Award winner was Paul R. Bruggink of the University of Illinois; the A. E. Marshall Award winner was Eugene Dykema of the University of Illinois; the third prize winner was Edward Matulevicius of McGill University; and the honorable mention winners were Allyn M. Davis of Clarkson College of Technology, Ramon Luis Espino of Louisiana State University, and Lawrence J. Koth of Oregon State University. The first-prize-winning solution follows on page 143.

INTRODUCTION

Market forecasting is becoming increasingly important in the chemical industry. Changes in product demands frequently tax the ingenuity of the chemical engineer, who becomes responsible for devising methods by which the market demands can be met economically.

This problem centers upon a methane chlorination plant currently under construction. The plant is designed to produce methyl chloride, methylene chloride, chloroform and carbon tetrachloride, the relative amounts of each in balance with market demands. Since the market had remained relatively stable for the past few years, the method for producing a limited range of product distributions was studied in detail to minimize process development time. However, a definite shift in the chloromethanes market has just been verified by the market analysis group. All indications are that the market will stabilize at the new product distribution.

Field construction is on schedule with startup scheduled in one month. The Research Department has already informed the Engineering Department that several alternates for obtaining the new product distribution may exist. Based on this information, the Engineering Department has been instructed by Management to meet not only the new product split, but also the scheduled startup date. To accomplish these objectives, it has been decided that a sound theoretical approach must be used to determine the best method of obtaining the new product distribution; the time limit will not permit pilot plant development of the method chosen.

As a young engineer with extensive academic training, you have been assigned the task of evaluating the routes recommended by Research and, if possible, devising other more economic methods.

STATEMENT OF PROBLEM

A large chemical manufacturer is currently involved in construction of a plant for the manufacture of chloromethanes. The process to be used in the full-scale facility has been pilot planted in detail. Startup of the new facility is scheduled in one month.

All the pilot plant work was directed toward producing a range of product distribution as shown in Figure 1. Present design calls for varying the product distribution by changing the crudes condenser temperature.

An unexpected shift in sales requires a significantly different product distribution, which is outside the range of pilot plant experience and commercial plant design considerations. Sales demands are now expected to be as follows:

SALES DEMANDS - NET TONS/YEAR*

Compound	1964	1965	1966	1967	1968
CH_3Cl	14,000	17,500	21,000	24,500	28,000
CH_2Cl_2	2,000	2,500	3,000	3,500	4,000
$CHCl_3$	19,000	23,750	25,000	27,500	30,000
CCl_4	7,000	8,750	12,000	16,000	21,000

The Engineering Department has been instructed to determine operating conditions to meet startup requirements. The Chief Engineer has concluded that, because of time limitations, the plant must start up without any major equipment changes.

Since the production rate is expected to double by 1968, eventual physical rearrangement, modifications or additions to equipment may be required to meet the long term sales demands most efficiently. Final recommendations for long term changes should represent the most economic approach.

The problem is twofold:

1. Determine operating conditions within the scope of the present equipment which will result in the required product split and production rate at startup (1964).

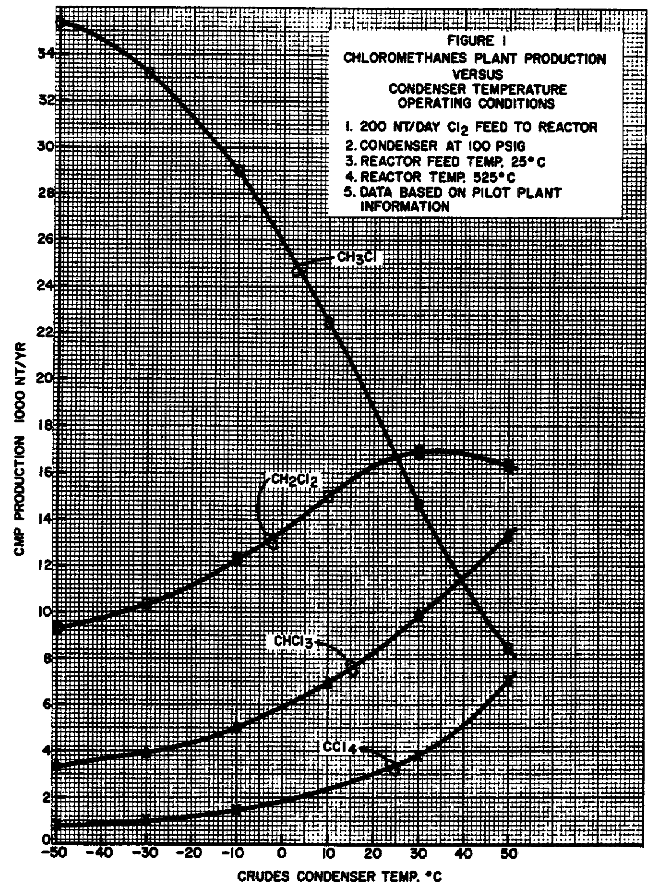
2. Determine the length of time during which the plant could be operated as recommended above and suggest, on a qualitative basis, the most promising avenue of study for meeting the changed product distribution on a long term basis. No detailed calculations are required here, but a clear outline of any process changes and the reasoning behind them is imperative. Obviously, the more complete the analysis of the suggested route, the more likely is Engineering to approve further work along the lines you suggest.

Bear in mind that there may be more than one method of accomplishing the immediate requirement (1964) of placing the plant on stream with the proper product distribution, and the eventual requirement of the most economical processing scheme (1968).

Recycling certain products from the distillation columns has been suggested as one method of altering product distribution within the scope of the present equipment. It is the Engineering Department's opinion that other alternates may exist that are more economical.

Your assignment, therefore, includes an overall analysis of the possible methods for meeting all of the objectives currently visualized. Because of the scope of the assignment, qualitative reasoning may be used to eliminate any case from further consideration.

*Net ton (NT) = 2000 lb



PROCESS DESCRIPTION

The attached flow diagram represents the processing scheme of the commercial facility for a crudes condensing temperature of minus 50 °C.

Methane and chlorine are mixed with recycle gas and the combined stream is fed to an adiabatic catalytic reactor. Reactor effluent is cooled by a waste heat recovery system and then scrubbed with water to remove HCl, followed by a drying operation. The gas is next compressed to 100 psig, partially condensed in a refrigerated unit and collected in a receiver. The gas stream containing unreacted methane with some chloromethanes is recycled to the reactor.

Crude chloromethanes from the receiver are transferred to a continuous distillation unit consisting of four columns. The purified products are then piped to their respective storage and loading facilities.

EQUIPMENT DETAILS

Reactors

The chlorinations are performed in a catalyzed reactor at 525 °C where the concentrations of all constituents and the temperature may be considered uniform throughout.

Two reactors have been installed based on early design parameters; however, further studies showed only one reactor will be needed to operate as shown in the flow diagram. Consequently, the second reactor is currently functioning as a spare.

Each reactor is estimated to have a capacity of about 200 net tons per day of chlorine input. Since the reactors are essentially adiabatic, the recycled gas rate is fixed by the chorine rate, desired reaction temperature, and reactor feed composition.

Reactor Waste Heat Recovery

Each reactor is equipped with a waste heat recovery unit in which the reactor effluent is cooled with Tetralin (an organic heat transfer fluid). These units are capable of cooling the reactor effluent gas to 25 °C at a reactor chlorine input up to 200 net tons per day at any product distribution.

HCl Absorber, Gas Dryer & Recycle Compressor

The size of the towers and their associated piping will limit the recycle gas rate to about 800# mole/hr as feed to recycle compressors. The plant has five adiabatic recycle compressors. When the plant is operating at capacity, one unit will spare the other four. Each unit has a gas capacity of 200# mole/hr.

Crudes Condenser

The crudes condenser and refrigeration equipment were taken from an obsolete plant and have a capacity of 10,000,000 Btu/hr. This unit is capable of condensing down to minus 50 °C.

Distillation Equipment

The distillation equipment was also taken from an obsolete plant. The capacity of each of these units is given on Figure 2.

ASSUMPTIONS

In making this study, the following assumptions may be made:

1. The combined feed temperature to the reactor is 25 °C.
2. Final reaction temperature is 525 °C.*
3. Feed to the reactor contains a negligible amount of carbon tetrachloride.
4. The reactions can be correlated by the following equations:

$$CH_4 + Cl_2 \xrightarrow{k_1} CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{k_2} CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{k_3} CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{k_4} CCl_4 + HCl$$

$r_i = k_i \ (C_i)(Cl_2)$ General rate equation

Where $k_i = k_1, k_2, k_3$ or k_4 and are specific rate constants. The reactions are first order with respect to the chloromethanes and chlorine, and are irreversible.

(C_i) = mole fraction of CH_4, CH_3Cl, CH_2Cl_2 or $CHCl_3$.

(Cl_2) = mole fraction of chlorine.

Product distribution must be calculated using relative reaction rates. (See Ref. 1 & 2)

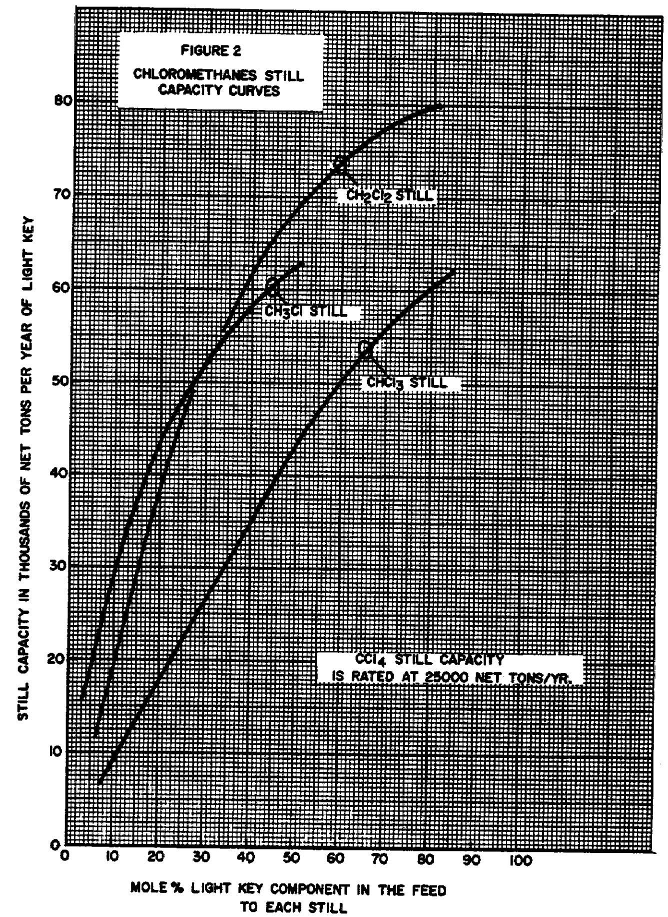
5. Relative rates are constant and

$$\frac{k_1}{k_2} = 1.83$$

$$\frac{k_1}{k_3} = 1.06$$

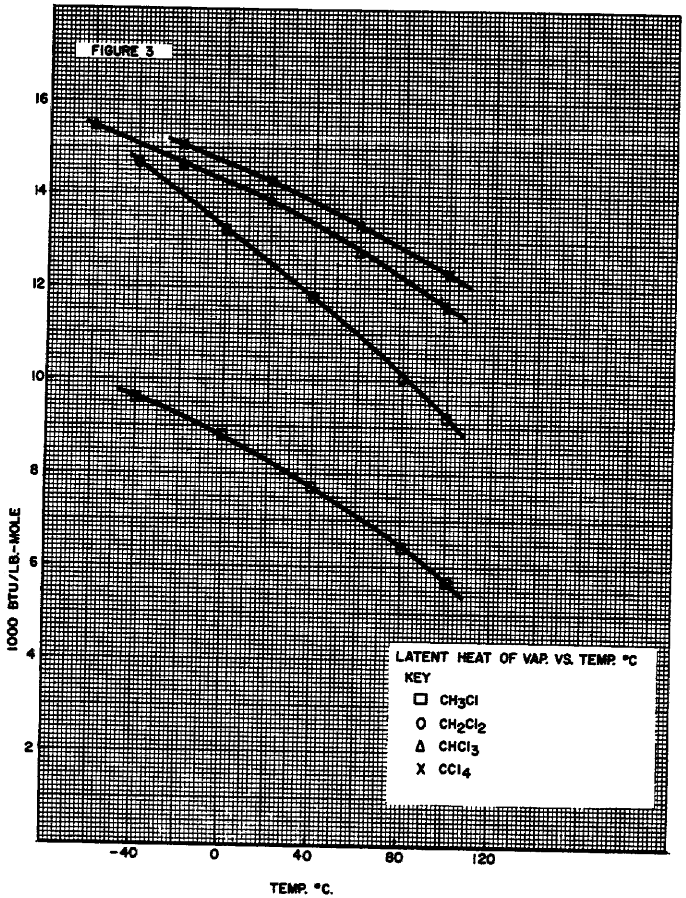
$$\frac{k_1}{k_4} = 1.61$$

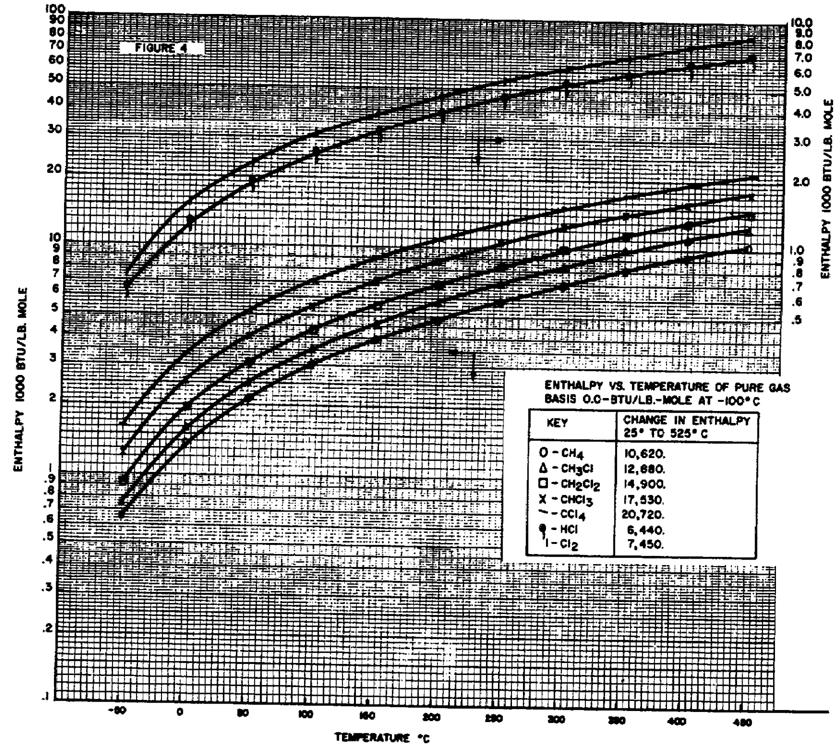
*This value has been chosen as optimum for the catalyst and reactor design used. Consider it a fixed value for the purposes of this problem.



6. Raoult's law holds.
7. Physical properties on Figures 3-5 apply.
8. Pressure drop across the reaction system is small compared to the remaining recycle system.
9. The reactor waste heat unit can cool the effluent gas to 25 °C.
10. The crudes condenser can be operated down to minus 50 °C.
11. Compression costs are $0.06/100 lb mole of recycle gas.
12. Drying costs are—$0.80/100 lb mole of recycle gas.
13. Crudes condensing costs are:

$0.40/100 lb mole CH_3Cl condensed.
$0.20/100 lb mole CH_2Cl_2 condensed.
$0.15/100 lb mole $CHCl_3$ condensed.
$0.12/100 lb mole CCl_4 condensed.





14. Distillation costs are:
    $3/NT of CH_3Cl.
    $4/NT of CH_2Cl_2.
    $10/NT of $CHCl_4$.
    $10/NT of CCl_4.
    (Note: These costs cover steam, power and water only.)

15. The heat of reaction is 43,000 Btu/lb mole Cl_2 at 525°C for all four reactions.

16. Losses of organics are negligible.

17. Compressor discharge temperature is fixed at ———————— 135°C.

18. All Cl_2 fed is completely consumed in the reactions.

19. CH_4 is insoluble in the liquid crudes.

REPORT FORMAT

Your report will be read by the Chief Engineer and will form the basis of his recommendation to Management. Consequently, the Introduction to the report should include a clear concise statement of the problem. This should be followed by a Summary section including:

a. The schemes you considered to meet the immediate demand.

b. The scheme you recommend.

c. The basis for your selection and its time limitations for practical application.

d. The route you recommend for further study to arrive at the solution for the long term problem.

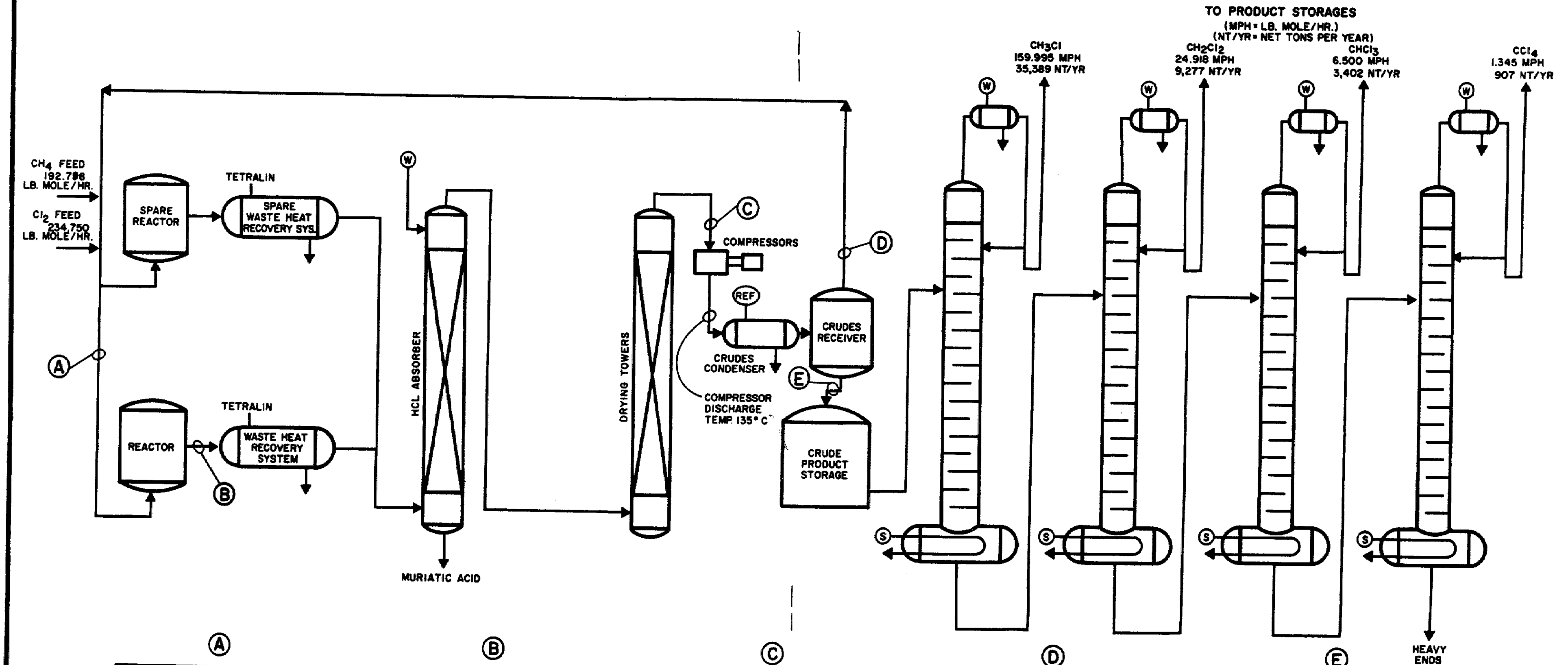
The entire report so far should require no more than five to ten minutes reading time.

The Text of the report should present the details of your problem analyses and recommended solutions. A detailed flow sheet for immediate mode of operation and at least a qualitative one for the suggested long term solution should be provided. Calculations should be placed in an Appendix.

In addition to the report, a letter of transmittal to the Vice President for Production should be prepared for the Chief Engineer's signature. This letter should identify the problem treated in the report and contain a very brief statement of the recommended solution.

Your report will be judged on clarity, accuracy and originality.

CHLOROMETHANES
SCHEMATIC FLOW DIAGRAM
BASIS–FEED RATE OF 200 NT Cl_2/DAY



(A)

Combined Reactor Feed Temp. 25°C		
Compound	#Mole/Hr	Mole %
CH_4	765.531	75.224
CH_3Cl	17.255	1.700
CH_2Cl_2	0.080	0.008
$CHCl_3$	0.006	trace
CCl_4	Nil	Nil
Cl_2	234.750	23.068
HCl	Nil	Nil
Total	1017.622	100.000

(B)

Reactor Product Temp. 525°C		
Compound	#Mole/Hr	Mole %
CH_4	572.773	56.286
CH_3Cl	177.250	17.418
CH_2Cl_2	24.998	2.457
$CHCl_3$	6.506	0.639
CCl_4	1.345	0.132
Cl_2	Nil	Nil
HCl	234.750	23.068
Total	1017.622	100.000

(C)

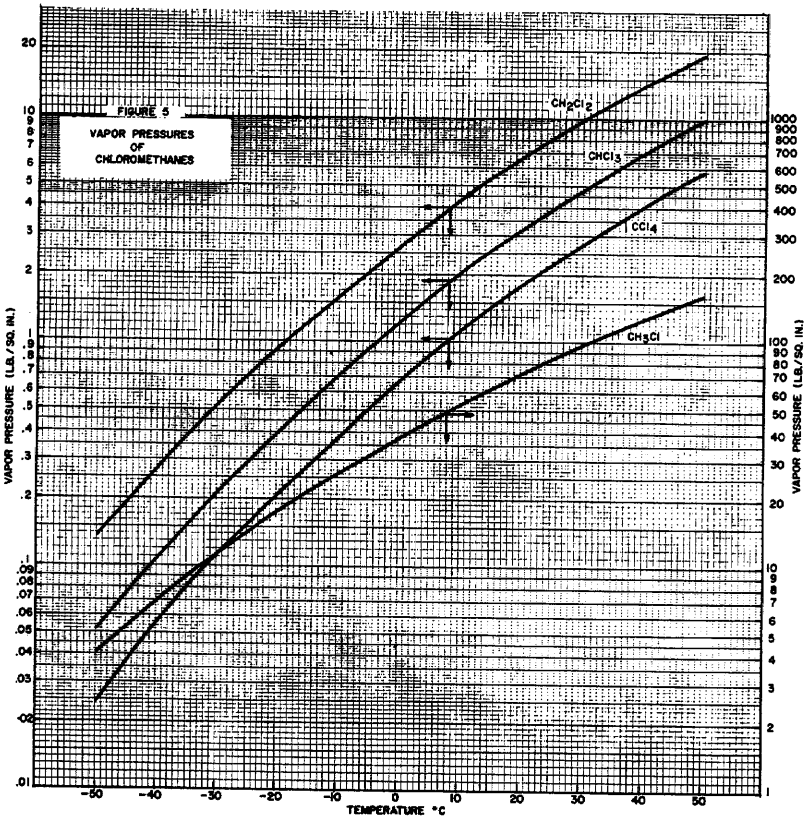
Compressor Feed Temp. 25°C Press. 1 PSIG		
Compound	#Mole/Hr	Mole %
CH_4	572.773	73.163
CH_3Cl	177.250	22.641
CH_2Cl_2	24.998	3.193
$CHCl_3$	6.506	0.831
CCl_4	1.345	0.172
Cl_2	Nil	Nil
HCl	Nil	Nil
Total	782.872	100.000

(D)

Recycle Gas Temp. -50°C Press. 100 PSIG		
Compound	#Mole/Hr	Mole %
CH_4	572.773	97.061
CH_3Cl	17.255	2.924
CH_2Cl_2	0.080	0.015
$CHCl_3$	0.006	Trace
CCl_4	Nil	Nil
Cl_2	Nil	Nil
HCl	Nil	Nil
Total	590.114	100.000

(E)

Crude - Still Feed Temp. -50°C Press. 100 PSIG		
Compound	#Mole/Hr	Mole%
CH_4	Nil	Nil
CH_3Cl	159.995	82.999
CH_2Cl_2	24.918	12.930
$CHCl_3$	6.500	3.373
CCl_4	1.345	0.698
Cl_2	Nil	Nil
HCl	Nil	Nil
Total	192.758	100.000



LITERATURE CITED

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2. Johnson, P.R., Parsons, J.L., and Roberts, J.B.—"Making Chloromethanes" —Industrial & Engineering Chemistry 51 No. 4, April 1959, Page 499.

3. Chilton, Cecil H.—"Cost Engineering in the Process Industries," McGraw-Hill Book Company, Inc.—1960.

FIRST PRIZE WINNING SOLUTION—1964

ABC Chemical Company
Engineering Department
Chicago, Illinois

November 30, 1963

Mr. J. W. Jones
Vice President for Production
ABC Chemical Company
Pittsburgh, Pennsylvania

Dear Mr. Jones:

The enclosed report is a study of the operating conditions necessary to meet the revised sales demands for the chloromethanes plant currently under construction. Also included are qualitative recommendations for meeting the long-term product demand.

The solution recommended involves recycling CH_3Cl and CH_2Cl_2, and operating the condenser at +25°C. It is also recommended that operation of the reactors in series be looked into for the long-term solution.

Yours truly,

J. Blow, Chief Engineer
Engineering Department