

DDC FILE COPY: ADA065046

AFRPL-TR-78-38

AMINE FUELS VIA THE UREA PROCESS

TECHNICAL REPORT

IIT RESEARCH INSTITUTE
10 WEST 35TH STREET
CHICAGO, ILLINOIS 60616

AUTHORS: DR. ALLAN GRAY
MR. EDWARD FOCHTMAN

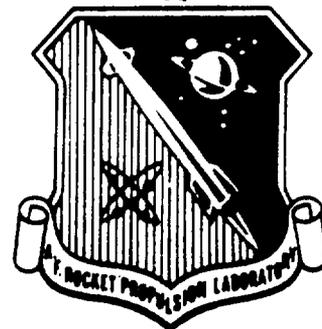
M A Y 1 9 7 8

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED

Prepared for:

AIR FORCE ROCKET PROPULSION LABORATORY
DIRECTOR OF SCIENCE AND TECHNOLOGY
AIR FORCE SYSTEMS COMMAND
EDWARDS AFB, CALIFORNIA 93523

2
LEVEL



DDC
FEB 28 1979
A

79 02 26 225

NOTICES

When U.S. Government drawings, specifications, or other data are used for any purpose other than a definitely related government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications or other data, is not to be regarded by implication or otherwise, or in any manner licensing the holder or any other person or corporation; or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

FOREWORD

This report was submitted by IIT Research Institute, 10 West 35th Street, Chicago, Illinois 60616 under Contract F04611-76-C-0044, Job Order No. 624A00QU with the Air Force Rocket Propulsion Laboratory, Edwards AFB, California 93523.

This report has been reviewed by the information office/XOJ and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations. This technical report has been reviewed and is approved for publication; it is unclassified and suitable for general public release.

Forrest Forbes

FORREST FORBES, Project Manager
Chief, Liquid Propellant Systems

FOR THE COMMANDER

Edward E. Stein
E. E. STEIN, Deputy Chief
Liquid Rocket Division

ACCESSION BY	White Envelope <input checked="" type="checkbox"/>
NTIS	Soft Envelope <input type="checkbox"/>
DDC	<input type="checkbox"/>
UNANNOUNCED	
JUSTIFICATION	
BY	DISTRIBUTION/AVAILABILITY GROUP
Dist	AVAIL. GR. / SPECIAL

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

18 (19) REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER AFRPL-TR-78-38	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER 9 Technical	
4. TITLE (and Subtitle) 6 AMINE FUELS VIA THE UREA PROCESS.		5. TYPE OF REPORT & PERIOD COVERED Tech. Report. 19 Apr 76 - 19 Sep 77	
7. AUTHOR(s) 10 Allan/Gray Edward/Fochtman		8. CONTRACT OR GRANT NUMBER(s) 15 F04611-76-C-0000	
9. PERFORMING ORGANIZATION NAME AND ADDRESS IIT Research Institute 10 West 35th Street Chicago IL 60616		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Program Element 35119F Project 624A JON: 624A90QU	
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Rocket Propulsion Laboratory (AFSC) Edwards AFB CA 93523 LKCP		12. REPORT DATE	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 11 May 78 12 235p.		13. NUMBER OF PAGES	
		15. SECURITY CLASS. (of this report) UNCLASSIFIED	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Amine Fuels UDMH MMH Urea Process			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The distinct possibility that hydrazine fuels would not be available in the quantities required by Air Force and NASA during the late 1970's and early 1980's motivated the Air Force to support research on alternative processes which would have the potential of minimum environmental impact. This is a report of the study of the production of MMH (monomethyl hydrazine) and UDMH (unsymmetrical dimethyl hydrazine) via the urea process. Primary effort of the program was devoted to the study of the chemistry of the reactions.			

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 68 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

175 350 79 02 26 225

LB

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

Engineering design data were developed for several of the unit processes and have permitted a preliminary process design and economic evaluation. Additional engineering data will be required to design a pilot plant.

Prime emphasis was placed on the production of MMH. Best yield of monomethyl urea from urea was 80% on a pilot plant batch. Best yield of MMH from MMU was about 45% (although higher yields could be obtained with greatly increased caustic concentrations). The overall yield, based on urea, was 36%.

Limited laboratory studies indicated the yield of dimethyl urea was 93% and the yield of UDMH was 99%.

The process for formation, separation, and purification of MMH and UDMH follows the processes reported in the literature and appears conventional. A major concern is the production of salt ($\text{NaCl} + \text{Na}_2\text{CO}_3$) since some 18-24 lbs could be produced per pound of MMH product.

The urea process appears to have good potential for the production of UDMH and limited potential for the production of MMH.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

PREFACE

This is a report of the research and development study of the process for the production of hydrazine fuels from urea. The work was conducted by IITRI between April 1976 and September 1977 under Contract No. F04611-76-C-0044. 43

Dr. Allan Gray, Scientific Advisor, supervised the chemistry studies and Mr. Edward Fochtman, Engineering Advisor, supervised the engineering studies. Dr. Jack Veal, Research Chemist, joined the program in November 1976 and developed the hydrazine analytical techniques.

The Air Force Project Officer was Captain Steven Wax; he was reassigned in June 1977 and Mr. Forrest Forbes served as Project Officer for the remainder of the effort.

The staff at the Space and Missile System Organization, notably Mr. Sherwin Lewis, Dr. H. Takimoto, and Major James Kephart, maintained a high level of interest in the program and assisted the Air Force Project Officer.

Data generated during this program are recorded in the following IITRI logbooks: C22720, C22722, C22725, C22729, C22784, C22787, C22856, C22874, C22883, C22910, C22916, D2055, C22920, C22921, C22978, C23229, C23232, and D2058.

TABLE OF CONTENTS

	<u>Page</u>
1. INTRODUCTION	1
1.1 General Background	1
1.2 Alternate Processes for Urea Production	2
1.2.1 Phosgene (COCl ₂) Process	2
1.2.2 Urethane Process	3
1.2.3 Cyanate Process	3
1.2.4 Anhydrous Urea Process	4
1.2.5 Aqueous Urea Process	5
1.3 Preliminary Economic Analysis	5
2. BASIS OF THE STUDY	7
3. PROCESS DESCRIPTION AND TECHNICAL FEASIBILITY STUDY	8
3.1 Introduction	8
3.2 Overview of the Urea:MMH Process	9
3.3 Production of MMU	9
3.3.1 Introduction	9
3.3.2 Laboratory Studies	11
3.3.3 Pilot Studies of MMU Reaction	13
3.4 Stripping of NH ₃ and MMA from Aqueous MMU	16
3.4.1 Introduction	16
3.4.2 Laboratory Stripping of NH ₃	16
3.4.3 Pilot Stripping of NH ₃ and MMA from MMU	18
3.5 Formation of MMH	19
3.5.1 Introduction	19

TABLE OF CONTENTS (cont.)

	<u>Page</u>
3.5.2 Exploratory Laboratory Studies	20
3.5.3 Statistical Study of MMH Formation	23
3.5.4 Pilot Batch Bleach Reaction	28
3.5.4.1 Introduction	28
3.5.4.2 Use of "As Prepared" MMU Solution . .	28
3.5.4.3 Use of MMU Crystallized from Pilot Batch	32
3.5.4.4 Purification of Pilot-Produced MMU .	32
3.5.4.5 Pilot Scale MMH Production	32
3.6 Recovery of MMH from Bleach Reaction Solution	35
3.6.1 Recovery Methods	35
3.6.2 Laboratory Evaporations	38
3.6.3 Pilot Plant Evaporation	41
3.7 Azeotropic Distillation of MMH	48
3.7.1 Introduction	48
3.7.2 Preliminary Laboratory Studies	50
3.7.3 Vapor-Liquid Equilibrium for MMH-Water	53
3.7.4 Verification of MMH Azeotropic Distillation .	57
3.8 Extractive Distillation of MMH	62
3.8.1 Introduction	62
3.8.2 Laboratory Batch Distillation with Purchased MMH	62
3.8.3 Laboratory Distillation with Pilot MMH Batch .	66
3.8.4 Analysis of Pilot-Produced MMH	67
3.8.5 Hydrazine Recovery	67

TABLE OF CONTENTS (cont.)

	<u>Page</u>
3.9 Waste Treatment	57
3.9.1 Sources of Wastes	67
3.9.2 Carbon Adsorption of Hydrazine	70
3.9.3 Oxidation Treatment of Hydrazine	70
3.9.4 Solid Waste Treatment	71
3.10 UDMH Process	71
3.10.1 Introduction	71
3.10.2 Production of UDMU	71
3.10.3 Production of UDMH	75
4. PRELIMINARY PROCESS DESIGN	77
4.1 Introduction	77
4.2 MMU Production	77
4.3 MMH Production	79
4.4 MMH Purification	81
4.5 Waste Treatment	83
5. PRELIMINARY COST ESTIMATE	85
5.1 Purchased Equipment	85
5.2 Total Capital Costs	85
5.3 Raw Materials Costs	85
5.4 Cost of Labor	87
5.5 Utility Cost	87
5.6 Waste Treatment	87
5.7 Cost Summary	90

TABLE OF CONTENTS (cont.)

	<u>Page</u>
6. SUMMARY AND RECOMMENDATIONS	90
APPENDIX A - EQUIPMENT SPECIFICATIONS - Section I	AI-1
APPENDIX A - Section II	AII-1
APPENDIX A - Section III	AIII-1
APPENDIX B - ANALYTICAL PROCEDURES	B-1

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	MMH via the Urea Process	6
2	Aqueous Reaction of Urea and MMA (Runs 21,31)	12
3	Evaporation/Crystallization of Pilot Plant Produced MMU	34
4	Process for the Recovery of MMH From 2.5% Solution	49
5	General Form Vapor/Liquid Equilibrium for MMH/Water	51
6	Graphical Determination of Relative Volatility MMH/H ₂ O	56
7	Azeotropic Column Design Conditions	58
8	Expanded Vapor/Liquid Equilibrium Curve for MMH/ Water	59
9	McCabe-Thiele Diagram, MMH/Water	60
10	McCabe-Thiele Diagram, MMH/Water	61
11	MMH Extractive Distillation Column Results	64
12	MMU Production System	78
13	MMH Production System	80
14	MMH Purification System	82

LIST OF TABLES

<u>Table</u>	<u>Page</u>
3-1 Laboratory Studies of MMU Formation	14
3-2 Ammonia Stripping of Synthetic Mixture	17
3-3 Conversion of MU to MMH by Hypochlorite	21
3-4 Statistical Series on MMH Process Bleach Reaction	24
3-5 "Optimized" Reaction Conditions for MMH Formation	29
3-6 Laboratory Preparation of MMH From Commercial Urea and Monomethylamine	30
3-7 Matrix of Bleach Reactions Using Pilot Plant Produced MMU	31
3-8 Results of Bleach Reaction Using MMU Crystallized from P.P. Run	33
3-9 Analysis of Pilot Bleach Reaction Samples	36
3-10 Material Balance of Bleach Reaction	37
3-11 Laboratory Evaporation of Product From Pilot Bleach Reaction	39
3-12 Laboratory Evaporation of Product From Pilot Bleach Reaction	40
3-13 First Filtration of Pilot Bleach Reaction Mixture	42
3-14 First Evaporation Pilot Bleach Reaction Mixture	43
3-15 Second Filtration After 51% of Bleach Reaction Mixture Had Been Evaporated	44
3-16 Second Evaporation	45
3-17 Third Filtration	46
3-18 Recovery of MMH and HZ From Bleach Reaction Through Evaporation, Crystallation and Filtration	47
3-19 Distillation of MMH at Less Than Azeotropic Concentration	52

LIST OF TABLES (cont.)

<u>Table</u>		<u>Page</u>
3-20	Equilibrium Data of MMH and Water	54
3-21	Performance of 2" Diameter Azeotropic Fractionation Operating During Verification Run	63
3-22	Laboratory Extractive Distillation of MMH	65
3-23	Batch Extractive Distillation of Pilot MMH Batch . . .	68
3-24	Analysis of MMH Produced in Verification Studies . . .	69
3-25	Hydrazine Concentration in Wet Salt Cake	72
3-26	Reaction of DMA With Urea, Aqueous Under Pressure . . .	73
3-27	Reaction of DMA With Urea, Reaction No. 36	74
3-28	UDMH Bleach Reaction	76
5-1	Estimated Capital Costs	86
5-2	Quantities and Costs of Raw Materials	88
5-3	Labor Costs	89
5-4	Summary of Costs for MMH Based on Production Rate of 400 lbs/hr	91

AMINE FUELS VIA THE UREA PROCESS

1. INTRODUCTION

1.1 General Background

The following three storable amine fuels are used for liquid propulsion in rocket engines:

Monomethyl hydrazine (MMH)

Unsymmetrical dimethyl hydrazine (UDMH)

Anhydrous hydrazine (HZ).

As of December, 1975, there were sources for all of these fuels, however, environmentally unacceptable wastes/by-products and limited plant capacity, combined with proprietary production methods, made the supply tenuous. The Air Force decided to develop a chemical synthesis method which could be applied to a moderate scale production facility to produce the fuels in an environmentally acceptable manner in the event that current suppliers could not meet Air Force and NASA needs. The plant was to be designed for a 1,000,000 lb/yr production capacity of MMH and of UDMH.

A promising chemical route to all three fuels is the urea process which had been successful on the plant scale for hydrazine and had been demonstrated on the laboratory scale for MMH and UDMH. When attempted on the plant scale, however, results for MMH and UDMH production were inconclusive.

A contract to determine the economical feasibility of producing MMH and UDMH via the urea process on the pilot plant scale was awarded to IITRI on April 19, 1976. This is a report of that investigation, conducted from April 19, 1976 to September 19, 1977. The program involved a literature review, experimental evaluation of several chemical routes for the production of the urea, preliminary economic evaluations, and more extensive laboratory and pilot plant verification of the selected process.

A summary of the various chemical routes and experimental results are presented here; more details are available in the bi-weekly program reports.

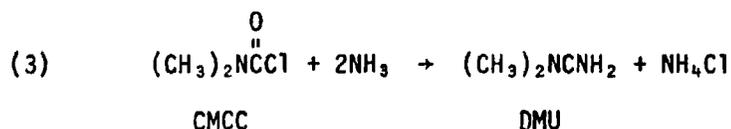
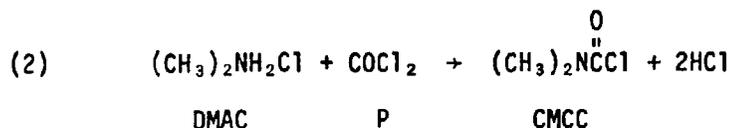
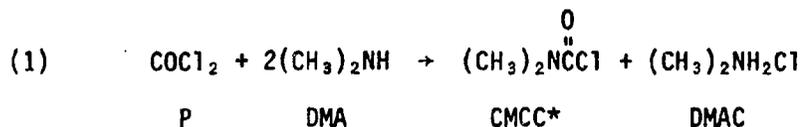
1.2 Alternate Processes for Urea Production

The first step in the urea process involves the production of the monomethyl or the dimethyl urea which is then converted into the corresponding hydrazine.

The alternate process for the production of monomethylurea (MMU) and the unsymmetrical dimethylurea (UDMU) are discussed in the following. Efforts of the program were concentrated on the MMU-MMH process.

1.2.1 Phosgene (COCl₂) Process

Phosgene (P), DMA, and NH₃ have been reacted in a toluene solvent to form DMU with about an 85% yield:



Although this process is of interest, the shipping and handling of phosgene presents both technical and policy problems. In view of these problems, it was decided to concentrate efforts on those chemical processes which did not involve hazardous starting materials. No laboratory work on this process was conducted during the program.

*suspected carcinogen

1.2.2 Urethane Process

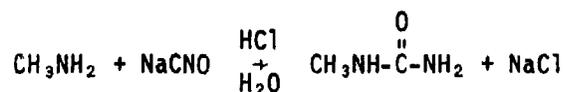
The synthesis of substituted ureas might be accomplished by the reaction of an amine with urethane. The proposed reaction would be:



The reaction was investigated in the laboratory using a solution of 37.7 ml aqueous methylamine (0.5 mole), 40 ml H₂O, 83.0 ml of 6.08 N HCl and 45.0 g (0.5 mole) of urethane. The mixture was refluxed for 2 hours at atmospheric pressure (100-105°C). Little or no reaction occurred under these conditions. Use of excess methylamine and up to 3 hours reaction time did not improve matters. No further work was conducted on the process.

1.2.3 Cyanate Process

Reaction of an amine with sodium cyanate will give the urea:



Such a process would offer several advantages and was investigated in the laboratory using 0.5 moles MMA + 0.5 Moles NaCNO + .5 Moles HCl. The reaction could be conducted at concentrations which would give 90+% yield of methylurea and methylurea concentrations of 10 wt%. The reaction was verified in a 23 gal pilot batch.

MMU from this reaction was reacted with NaOCl to give overall yields that ranged from 50 to 75%.

Only one U.S. commercial source of supply for the sodium cyanate was located; the Diamond Shamrock Corporation. "Off shore" sources that sold through U.S. representatives were located. Practically the total production of the Diamond Shamrock Plant is used internally and their facilities would have to be expanded (almost doubled) to provide for the needs of the Air Force Fuels Program.

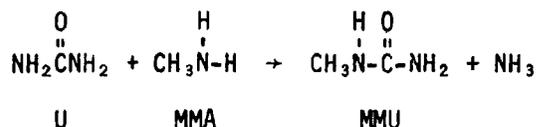
Cost of the sodium cyanate was quoted at about \$.44/lb for 90% material. Slightly lower costs were quoted for less pure material. The major impurity is sodium carbonate.

A preliminary economic analysis indicated little, if any, cost advantage over the urea process which has lower yield but less expensive raw materials.

In view of the time requirements of the Air Force Fuels Program and the need to greatly increase current sodium cyanate plant capacity coupled with marginal, if any, advantages of the process, the IITRI program team recommended that the process be shelved in favor of the urea process.

1.2.4 Anhydrous Urea Process

MMU can be prepared by the reaction of urea (U) with MMA under anhydrous conditions.



This process was investigated in the laboratory using a 2-liter stainless steel stirred reactor. A charge of 120 g (2 moles) of urea and 125 g (4 moles) of MMA were reacted at approximately 110°C. Cooling was applied as necessary.

During this period HPLC (high pressure liquid chromatographic) analysis techniques were under development and exact yield figures were not available; however, estimated yields were above 70% and could have reached 90%. There was an indication of SDMU (symmetrical dimethylurea) formation.

Since the MMU must be dissolved in water for the next step, there would be very little advantage in using an anhydrous high pressure (400-500 psig) process if an aqueous process would yield the same result.

1.2.5 Aqueous Urea Process

This process is essentially the same as the anhydrous urea process except that it is conducted in water and at a lower pressure. This became the process of choice and was studied most extensively in the laboratory and pilot plant verification runs. The process is shown in Figure 1.

Yields of 70-75% MMU and up to 98% UDMU, based on urea, were obtained.

The production of MMU by this process was verified in the pilot plant and the product further processed to produce specification grade MMH.

1.3 Preliminary Economic Analysis

During the screening of the various reaction routes, an attempt was made to develop an economic ranking of each MMH process. The lack of well defined process flow diagrams, yield data, by-product formation, etc., made the analysis very preliminary in nature and simply a gauge of major cost factors. The analysis indicated no significant difference in the estimated cost of MMH produced by the cyanate and the cost of MMH produced by the urea process.

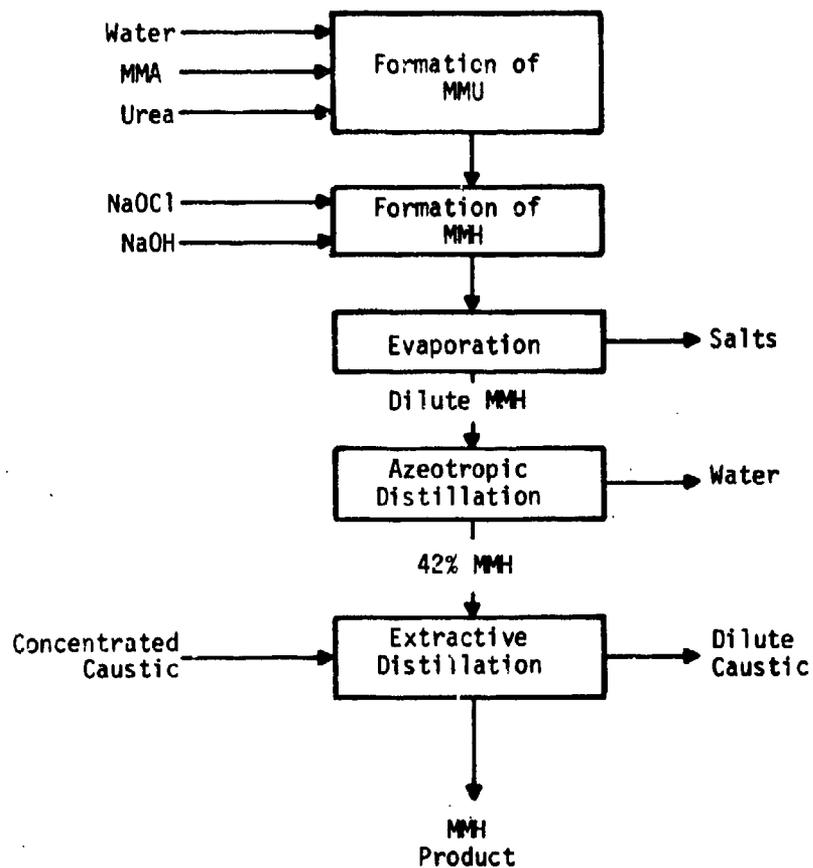


Figure 1. MMH via the Urea Process.

2. BASIS OF THE STUDY

The following factors served as guidelines for the study:

1. The process to be developed should be suitable for production of both MMH and UDMH; production of Hz was of secondary importance.
2. The full-scale plant should produce one million pounds per year of MMH and one million pounds per year of UDMH. Assuming a 2-week changeover from MMH to UDMH, and a 5-day 3-shift operating schedule, production should be 400 lbs/hr.
3. The process should be safe and present no unusual health or environmental impacts.
4. All by-products and waste streams should be fully treated to eliminate hazards to health or the environment.

3. PROCESS DESCRIPTION AND TECHNICAL FEASIBILITY STUDY

3.1 Introduction

In September 1976 the IITRI staff recommended to the Air Force that all further efforts on the program be devoted to the development of the aqueous urea process. The basis for this recommendation were:

1. MMU yields were good
2. Raw material costs were low
3. The reaction was easily controlled
4. Raw materials were readily available in quantities required
5. Equipment and processing costs were considered to be reasonable.

Subsequent work involved selection of the optimum conditions for production of MMU, the evaluation of optimum conditions for reacting MMU with NaOCl, and the development of the MMH recovery and purification process. Laboratory studies were followed by verification of the process using 25-40 gal batches of starting materials and the production of liter samples of MMH for Air Force evaluation.

In the following section we have presented an overview of the MMH process. This is followed by sections in which we have described each step in the process starting with the literature references, then the laboratory work, and finally the verification runs. This is followed by a description of the proposed process, process flow sheets, material and energy balances, and appendices describing equipment and analytical procedures.

In the conversion of MMU and UDMU to MMH and UDMH, large quantities of salt (NaCl) are produced. This salt could be disposed of by various means; however, it may be best to electrolyze the salt to produce NaOCl, NaOH, and HCl, which can be recycled to the process. The electrolysis of this salt is a commercially available process and is not described in detail here.

Data regarding waste streams and purification of plant discharges are discussed where available.

3.2 Overview of the Urea:MMH Process

Primary emphasis during the program was focused on MMH. Parallel laboratory work for the production of UDMH indicates that better yields will be obtained and that the recovery and purification process will be easier.

The overall process flow diagram for the production of MMH by the urea process is shown in Figure 1. The process involves three major steps:

1. Reaction of aqueous urea and MMA to form MMU
2. Reaction of MMU solution with NaOCl to form MMH
3. Recovery and purification of MMH.

Each of these steps and the associated unit processes are discussed in the following sections.

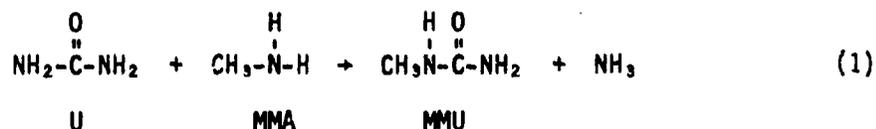
3.3 Production of MMU

3.3.1 Introduction

MMU is readily produced by the reaction, either anhydrous or in an aqueous solvent, of MMA and urea. Both MMA and urea are commercially available chemicals, but MMU is available only through specialty chemical sources.

The overall yield for this reaction has been determined. However, the exact mechanism and rates for the intermediate products are not known.

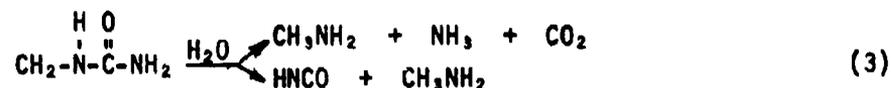
The overall reaction is:



Shaw and Bordeaux have investigated the decomposition of urea in aqueous solution. Their results indicated that urea decomposes by the reaction:

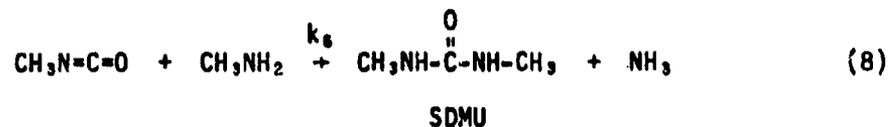
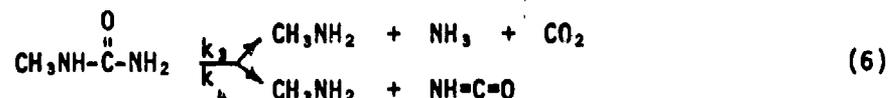
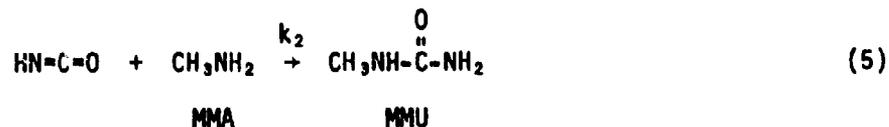
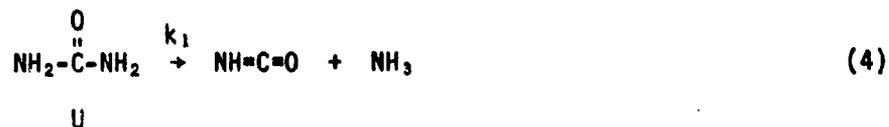


The reaction was shown to be first order with respect to urea over a wide concentration range, with faster rate at higher temperature. They studied a temperature range from 60 to 90°C. Shaw and Grushkin studied the kinetic behavior of methylurea. It was postulated that there were two parallel reactions for methylurea decomposition:



The conclusions of these studies were that (1) the decomposition of urea proceeds at a faster rate than the dissociation of methylurea and (2) both reactions were temperature sensitive.

Based on the understanding of the decomposition of urea and methylurea it is reasonable to postulate the aqueous urea reaction with MMA will be as follows:



For this application reactions (4) and (5) are the desirable reactions, whereas reactions (6), (7), and (8) are undesirable.

If an excess of MMA is used it will effectively consume all the cyanate ($\text{NH}=\text{C}=\text{O}$) produced by the decomposition of urea. As a result it will assist reactions (4) and (5) and, at the same time, will suppress reactions (6) and (7). Excess MMA will increase the production of SDMU (reaction 8). For these reasons it was necessary to find the optimum mole ratio of MMA/Urea, i.e., the ratio that would produce the most MMU with little or no SDMU.

The rate equation for the decomposition of urea can be written in the form

$$dC_A/dt = -k_1 C_A \quad (9)$$

where C_A is the unreacted urea remaining in the reactor. Equation 9 can be solved for C_A :

$$C_A = C_{A0} \exp(-k_1 t) \quad (10)$$

$$\ln(1-X_A) = k_1 t \quad (11)$$

It appears that the urea-amine reaction is a first order reaction. Data from reactions No. 21 and No. 31 are shown in Figure 2. After 120 minutes of reaction time there does not appear to be sufficient MMA to react with the cyanate and the cyanate/ammonia reaction which forms the urea is a strongly competitive reaction at these concentrations. Increasing the MMA concentration tends to increase the formation of SDMU.

3.3.2 Laboratory Studies

Both an anhydrous system and an aqueous reaction system were investigated in the laboratory. However, the lower pressure and the ease of control made the aqueous system more attractive.

Initial laboratory studies were conducted in a closed stirred reactor. It was difficult, however, to withdraw samples during the course of the reaction and a series of six sealed tubes were used in place of the single

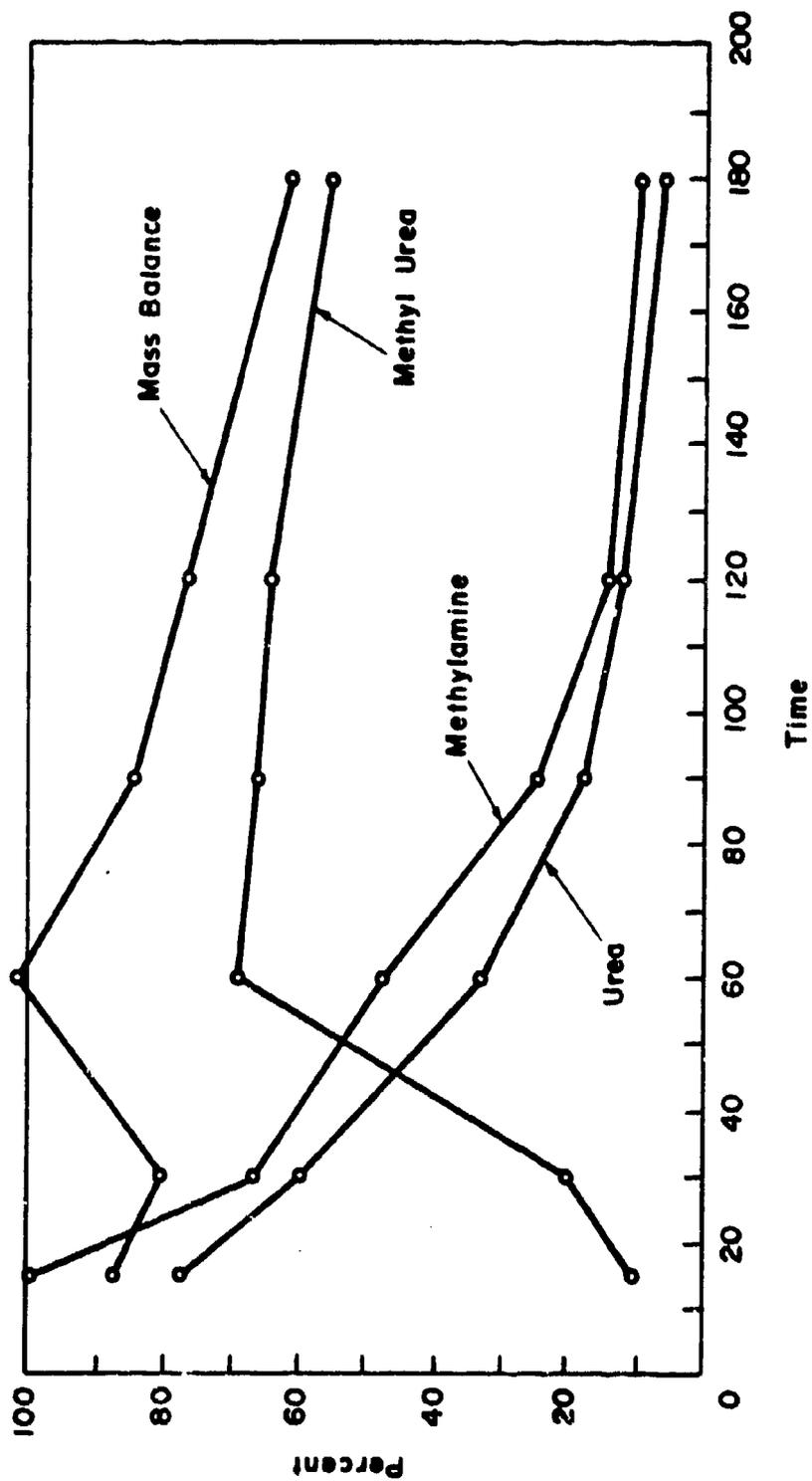


Fig. 2 AQUEOUS REACTION OF UREA AND MMA (Runs 21, 31)

reactor. These tubes were rotated end-for-end in an oil bath and could be removed for analysis as the reaction progressed.

Results of early laboratory runs are given in Table 1. Analysis of this product mixture was done by HPLC and generally resulted in a material balance, based upon urea, of 80-85%. The unaccounted for material probably was a result of the analytical technique. During the investigation it was found that the HPLC column had to be thoroughly washed after each use to obtain satisfactory separation of peaks and accurate results.

Yields of 60-65% MMU could be obtained with a MMA:U mole ratio of 1:1. At this ratio 10 to 25% of the urea was left unreacted. Increasing the time of reaction decreased the unreacted urea but increased the formation of SDMU. Since SDMU might later form symmetrical dimethyl hydrazine (SDMH) it was considered an undesirable by-product. Increasing the MMA:U ratio also increased SDMU formation and had little effect on the amount of unreacted urea.

A review of the results indicated that a system close to the optimum would have:

1. U:MMA mole ratio of 1:1
2. Reaction temperature of 120°C
3. Reaction time of 60 min.

Such a reaction was conducted in the laboratory (Reaction #36, 12/22/76) prior to conducting the pilot scale reaction. Analysis of the 60-minute sample indicated a yield of 65.5% MMU, with 24.5% of the urea unreacted. The SDMU was less than 1.5% of the product.

3.3.3 Pilot Studies of MMU Reaction

A pilot plant reaction, based upon laboratory reaction #36, was conducted to obtain material for the verification of the process.

A 50 gal, 316 SS reactor with internal steam coils and a variable speed agitator was used.

Table 3-1
LABORATORY STUDIES OF MMA FORMATION
Aqueous MMA & Urea

Date	Reaction No.	Remarks	Reaction Time, Min	Reaction Temp, °C	Pressure, psi	Reactant, Moles MMA	Reactant, Moles Urea	Total Volume, ml	% Unreacted MMA	% Unreacted Urea	% Yield MMA	% Yield Urea	Mass Balance %		
7/23/76	20		120	118	140	2	2	-	27	23	76	0.2	99		
7/29/76	21.1	Effect of Reaction Time	15	112		0.106	0.106	13	100	77.2	10.6	-	87.8		
	21.2		30	112		0.106	0.106	13	67	59.7	20.6	-	80.3		
	21.3		60	112		0.106	0.106	13	38	33.2	68.9	-	102.1		
	21.4		90	112		0.106	0.106	13	25	18.4	65.9	-	84.3		
	21.5		120	112		0.106	0.106	13	14	12.6	64.2	-	78.6		
	21.6		180	112		0.106	0.106	13	10	6.2	55.5	0.13	-	61.7	
8/05/76	22.1	Effect of MMA Ratio	120	112		0.106	0.085	12	26	11.1	41.4	-	52.5		
	22.4		180	112		0.106	0.085	12	22	5.4	52.1	7	57.5		
	22.2		120	112		0.196	0.071	11.5	33	7.2	47.1	0.14	-	54.4	
	22.5		180	112		0.106	0.071	11.5	29	4.6	47.7	0.22	-	52.5	
	22.3		120	112		0.106	0.053	10.5	50	9.0	54.3	0.16	-	53.5	
	22.6		180	112		0.106	0.053	10.5	36	5.7	35.1	1.3	-	42.1	
8/19/76	24	Reyeat Reaction 20	-	-	-	-	-	29	26.4	67.0	0	-	93.4		
8/12/76	25	Commercial Urea	120	112		2	2	230	36	29.6	60.8	-	90.4		
8/31/76	28	Commercial Urea	180	125		2	2	234	-	10.5	73.9	7.9	92.3		
	30		120	112		3.0	1.5	-	-	15.7	62.7	0	78.4		
	31.1		15	112		0.106	0.085	13.5	-	-	-	-	-	-	
	31.2		30	112		0.106	0.085	13.5	-	-	-	-	-	-	
	31.3		60	113		0.106	0.085	13.5	-	-	58.4	27.4	0	85.8	
	31.4		90	114		0.106	0.085	13.5	-	-	44.6	40.5	0.56	85.7	
	31.5		120	114		0.106	0.085	13.5	-	-	28.3	43.5	0.1	71.9	
	31.6		180	114		0.106	0.085	13.5	-	-	23.4	54.1	2.0	79.5	
	10/05/76		34.1	60	112		0.106	0.085	13.5	-	-	32.4	45.2	0.5	78.1
			34.2	90	112		0.106	0.085	13.5	-	-	23.2	55.8	1.2	80.2
			34.3	120	112		0.106	0.085	13.5	-	-	19.1	61.5	2.0	82.6
			34.4	180	112		0.106	0.085	13.5	-	-	12.9	56.6	2.5	72.0
34.5		240	112		0.106	0.085	13.5	-	-	10.9	60.9	3.1	74.9		
34.6		180	114		0.106	0.085	13.5	-	-	12.3	64.3	3.5	60.1		
12/22/76	36.1	45	120		0.106	0.106	13.5	-	-	32.7	61.3	<1.5	94.0		
	36.2	60	120		0.106	0.106	13.5	-	-	24.5	65.5	<1.5	90.0		
	36.3	75	120		0.106	0.106	13.5	-	-	19.3	67.9	<1.5	87.2		
	36.4	90	120		0.106	0.106	13.5	-	-	15.4	64.2	<1.5	80.0		
	36.5	105	120		0.106	0.106	13.5	-	-	12.3	63.8	<1.5	76.1		
	36.6	120	120		0.106	0.106	13.5	-	-	11.3	64.6	<1.5	75.9		

The operating procedures were as follows. Exactly 81.0 lb of tap water was charged into the reactor, the reactor was sealed, and the agitator started. Exactly 44.7 lb of anhydrous MMA was charged into the reactor. After the MMA had rapidly dissolved in the water, as indicated by the low gas pressure in the reactor, the reactor was opened and 86.4 lb of solid urea was charged and the reactor was sealed. It required about one hour to completely dissolve the urea in the MMA aqueous solution. The solution was heated with 45 psig steam through an internal heating coil. It took 45 min to heat the solution to 118°C. The solution was maintained between 117 and 120°C for exactly one hour. The reaction was quenched by cooling to room temperature (20°C). Samples were taken for MMU, urea, and SDMU analysis at 45 and 60 min. Since the mixture was at 118°C and under pressure the samples were withdrawn through a single tube heat exchanger. Although the heat exchanger was flushed each time before sampling, it appeared that some MMU crystallized on the heat exchanger surfaces and was not washed out by the flushing. This resulted in non-representative (MMU too high) samples. These samples were discarded.

Overall samples and analysis indicated MMU yields of approximately 80% and a mass balance of 91.5%.

Conditions for the Urea + MMA pilot plant reaction were as follows:

<u>Charge:</u>	water	81.0 lb	
	urea	86.4 lb	1.44 lb-moles
	MMA	44.7 lb	1.44 lb-moles
	Total	212.1 lb	
<u>Reaction:</u>	Time	60 min	
	Temp	118°C	
<u>Product:</u>	Total weight	212.1 lb	
	Total volume	24.6 gal	
	Specific gravity	1.023	
<u>Urea Analysis:</u>	MMU	80%* (approx. 40.2 wt%)	
	MMA	-	
	SDMU	2.2%	
	Urea	9.3%	
	Total	91.5%	

*Based upon urea charged.

3.4 Stripping of NH₃ and MMA from Aqueous MMU

3.4.1 Introduction

Early laboratory studies indicated that the MMA and NH₃ must be stripped from the MMU solution to a mole ratio of 0.02 NH₃/1.0 MMU to maximize the yield of monomethyl hydrazine during the bleach reaction.

Although this had been done in laboratory studies without difficulty, there was some question as to the effectiveness of the stripping operation during one of the commercial attempts to produce MMH.

Removal of NH₃ to below 0.02 mole NH₃/mole MMU would require stripping to:

$$(0.02) \left(\frac{17}{74}\right) (40 \text{ wt\% MMU}) = 0.184 \text{ wt\% NH}_3 \text{ or } 1840 \text{ ppm}$$

Although it was convenient to use nitrogen gas for laboratory stripping of the NH₃, the usual plant practice would utilize reduced pressure with steam. It is important that the pH of the solution be maintained above 11.4 for the release of the ammonia.

3.4.2 Laboratory Stripping of NH₃

A 10 plate sieve plate column 1 in. diameter was used for the study of the stripping process. Results of two runs are given in Table 3-2. These data indicate that the NH₃ concentration can be reduced from 23,000 ppm to 50 ppm in a 10 plate column operating at 270 mm Hg (a) and a feed of pH = 11.5. Plate efficiencies of 25-35% were obtained; these agree with literature values.

The laboratory work indicated the primary factor in the removal of NH₃ was the control of pH and that the process could be conducted without difficulty.

Table 3-2

AMMONIA STRIPPING OF SYNTHETIC MIXTURE

Equipment: ten-plate, glass Oldershaw. 30 mm O.D. x 30 mm plate spacing

Solution	NH ₄ OH	NH ₄ Cl + NaOH
ppm, as NH ₃	6,500	23,000
Feed Rate, ml/min	7.2	7.2
Head Pressure, mm Hg abs.	167	270 (slow increase)
T ^o C, still pot	66	64
T ^o C, head	56	56
Net Steam, g/min	0.51	~ 0.5
Internal Steam, g/min	0.93	~ 0.9
Overhead/Vapor	8.8 (use 9)	~ 9
α , 55-65 ^o C	26.5	26.5
Theoretical Plates	3.5	~ 4
Plate Efficiency, % ¹	33	~30
Viscosity, H ₂ O 60 ^o C, cp	0.5	0.5
O'Connell Factor, $\alpha\mu^2$	13	13
Plate Efficiency, %	25	25
pH Feed	11.29	11.5
pH, bottoms	8.41	8.38
NH ₃ , ppm in bottoms	31	52

¹Peters and Timmerhaus, Plant Design and Economics for Chemical Engineers, 2nd Ed., McGraw-Hill, p. 632, 1968.

²Perry's Handbook, 3rd Ed., p. 172.

3.4.3 Pilot Stripping of NH₃ and MMA from MMU

The MMU solution produced in the 50 gal reactor was stripped of NH₃ and unreacted MMA in a batch operation in the same reactor. Temperature of the solution was maintained at 65°C by drawing a vacuum and heating. Vigorous agitation was provided by mechanical agitation and a nitrogen bleed. It required about 10 hr to strip the solution to approximately 130 ppm NH₃. During the time 144 gm of NaOH were added to maintain the pH above 11.0

ANALYSIS OF THE STRIPPED MMU SOLUTION

Solution weight	157.6 lb
Sp. gr.	1.117
Volume	16.9 gal
Condensate	26.0 lb
Vapors (NH ₃ , MMA, H ₂ O)	not determined

Analysis (hplc)

Urea	0.9 ± .1 m moles/ml, 0.127 lb - moles
MMU	0.69 ± .2 m moles/ml, 0.943 lb - moles
SDMU	0.2 ± .02 m moles/ml, 0.028 lb - moles

Yield

$$\frac{\text{MMU}}{\text{Urea charged}} = \frac{0.943}{1.44} = 65.4\% \text{ MMU}$$
$$\frac{0.127}{1.44} = 8.8\% \text{ Urea}$$
$$\frac{0.028}{1.44} = 1.9\% \text{ SDMU}$$

Unreacted MMA: This could have been as high as 1.44 - .943 = .50 lb moles or 15.4 lb in 212.1 lb soln; 7.26 wt%.

Material Balance: The above analysis indicates a material balance based on urea as:

<u>Input</u>	1.44 lb moles
<u>Output</u>	
Urea	0.127 lb moles
MMU	.943 lb moles
SDMU	.028 lb moles
	<u>1.098 lb moles</u>

Balance

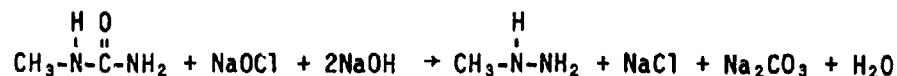
$$\frac{1.098}{1.44} = 76.3\%$$

By hplc analysis the total solids in solution were 51.2 wt%, however, by evaporation the total solids in the solution were 63.8 wt%. Thus it appeared that the hplc analysis did not detect all materials in the solution. By evaporation the material balance based on urea was 95%.

3.5 Formation of MMH

3.5.1 Introduction

Ureas can be oxidized with sodium hypochlorite to form the corresponding hydrazine:



Kobe and McKetta have described the urea process used in Germany before and during World War II to produce hydrazine. Variations of this process were used by Olin Mathieson Chemical Corporation and by Fairmont Chemical Company in the U.S. In general the process involved reacting a 43 wt% solution of urea with a sodium hypochlorite solution. The hypochlorite solution was made by chlorination of 30% NaOH to an available chlorine content of about 15%. This leaves 170-190 g NaOH per liter. The hypochlorite solution reacts rapidly with the urea with considerable frothing as nitrogen is evolved. The nitrogen apparently is the result of a reaction of hypochlorite, chlorourea or chloramine, and hydrazine.

It has been reported that metal ions, especially iron, decrease the yield of hydrazine from urea. Glue or gelatin at levels up to 0.5 g/liter was added to complex the iron and improve yields.

Lum and Mador patented a process for production of MMH from MMU by reaction of MMU + NaOCl in an alkaline solution. They claimed a 70-73% yield of MMH from MMU. However, they used a molar ratio of NaOH:MMU of 8:1.

The removal of a carbon atom by reaction of the urea with carbonyl-forming metals was patented by Passino, but his process presented additional problems because of the toxic nature of the intermediates.

Since the bleach reaction for the formation of MMH is a key step in the process it was necessary to investigate reaction conditions in the laboratory experiments followed by a series of statistically designed laboratory reactions.

The process involved the reaction of MMU at 0 to 5°C in a NaOH solution with NaOCl (an exothermic reaction) to form the chlorourea. This is a rapid reaction and is completed in 3-5 min or less. The mixture is then heated to 90-100°C for 60-90 min to form the MMH.

3.5.2 Exploratory Laboratory Studies

The reaction of MMU and NaOCl to form MMH is a two-step process which involves a fairly large number of variables. While it would be preferable to study each reaction separately, the lack of a suitable analytical technique makes it necessary to evaluate the effect of the variables on the overall yield.

Preliminary laboratory work established the range of reactant concentrations, temperatures, and time which gave reasonable yields. From these results a statistical matrix was developed and used to evaluate selected reaction conditions.

A series of exploratory bleach reactions were conducted and results are present in Table 3-3.*

During these runs the NaOCl did not appear to react with MMU at 0°C until the NaOH was added. After addition of NaOH to the MMU + NaOCl the disappearance of titratable hypochlorite is rapid.

*Analysis of the MMH product was by glc, direct injection of the sample on the column. This glc technique requires frequent replacement of the column or provision for removal of the solids that accumulate in the vaporization zone. This effect was not fully appreciated in the initial studies and certain of the yield figures are not accurate. A refined analytical technique, which was subsequently developed, did, however, confirm the bulk of the data.

Table 3-3
CONVERSION OF MU TO MH BY HYPOCHLORITE

Reaction No.	Date	Purpose	Reactants, Moles		Addition Temp C	Total Vol ml	MU Conc'n %	Time to Reach Temp Min	Reaction Temp C	Reaction Time Min	% Yield MH (g/c)	Conc'n MH**	Remarks	
			MU	NaOH										
5	7/13/76	Follow lit. procedure	0.27	2	0.35	1/2	2	500	4	60	85	60	42	MU precipitates on adding NaOH
6	7/15/76	Change addn. order. Use higher concn. NaOCl	0.27	2	0.35	2/1	8	370	5.4	60	85	90	30	No precipitate
7	7/15/76	Use addn. order of #5	0.27	2	0.35	1/2	11	370	5.4	60	85	90	45	
8	7/16/76	Use less NaOH	0.27	1	0.35	2/1	2	265	7.5	40	90	60	49	
9	7/16/76	No cooling	0.27	2	0.35	2/1	28-48	370	5.4	60	88	30	0	Exothermic reaction with NaOCl. Decomp.
10	7/19/76	Reagents added at room temp with cooling	0.27	1	0.35	2/1	23	275	7.2	15	80	120	32	
11	7/20/76	Less NaOCl	0.27	1	0.29	2/1	3	260	7.7	10	82	90	31	
12	7/21/76	Calcd amts NaOH, NaOCl longer heating	0.27	0.54	0.27	2/1	2	215	9.3	30	82	180	40	
13	7/21/76	Longer heating	0.27	1	0.35	2/1	5	285	7.0	50	80	180	41	
14	7/22/76	Add NaOH first. Use 1 mole	0.27	1	0.35	1/2	4	285	7.0	15	80	90	54	
15	7/22/76	Half NaOH before, half after NaOCl	0.27	1	0.35	1/2/1/2	4	280	7.1	7	83	90	46	
25	7/28/76	Used MU produced in Urea Reaction #19	0.27	1	0.35	1/2	0	270	7.4	33	81	60	22.5	0.04 moles urea also present in starting material
26	7/28/76	Used 1.5 equiv NaOCl	0.27	1	0.4	1/2	0	305	6.6	12	85	60	68	
54	8/19/76	Use of NaClO product of reaction #23	0.27	1	0.35	1/2	0	320	6.2	8	80	60	53.7	Trace of MA removed by initial warming under vacuum at 50°, before addition of NaOCl
57	8/19/76	NaOH dissolved in NaOCl and combined solution added to MU	0.27	1	0.35	0	-6	295	7.0	8	87	60	63.6	

* Weight/Volume % in initial reaction solution.

** Weight/Volume % in final reaction solution.

Table 3-3 (Contd.)

Reaction No.	Date	Reactants, Moles		Addition Order	Total Vol ml	MU Conc'n %	Time to Reach Temp Min	Reaction Time min	Reaction Temp °C	% Yield NH ₄ Cl (glc)	% Conc'n NH ₄ ⁺	Remarks
		MU	NaOH									
16	7/26/76	0.27	2.0	0.35	1/2	24	2.5	27	60	65	3.1	2% NaOCl, 0.005 mole NH ₄ Cl
17	7/26/76	0.27	1.0	0.35	2/1	-5	6.9	14	30	60	16.1	8.8% NaOCl, 0.005 mole NH ₄ Cl
18	7/26/76	0.27	1.0	0.35	1/2	25°	3.0	20	180	103	27.5	2% NaOCl
19	7/26/76	0.27	1.0	0.35	1/2	21°	7.4	17	50	101	44.2	8.8% NaOCl, 0.005 mole NH ₄ Cl
20	7/26/76	0.27	1.0	0.35	1/2	0	2.7	11	30	83	96.7	2% NaOCl
21	7/27/76	0.27	2.0	0.27	2/1	1°	3.2	23	180	101	54.2	5% NaOCl, 0.005 mole NH ₄ Cl
22	7/27/76	0.27	0.54	0.35	1/2	-6	3.0	50	180	103	58.2	2% NaOCl, 0.001 mole NH ₄ Cl
23	7/27/76	0.27	2.0	0.27	1/2/1	-5	5.0	18	60	81	67.1	5% NaOCl
24	7/27/76	0.27	0.54	0.35	2/1	24	6.5	10	60	83	38.3	5% NaOCl, 0.005 mole NH ₄ Cl
27	7/28/76	0.27	1.0	0.27	1/2	0°	8.5	43	180	82	25.3	8.8% NaOCl
28	7/28/76	0.27	0.54	0.35	1/2/1	2°	8.2	21	30	63	17.9	8.8% NaOCl, 0.005 mole NH ₄ Cl
29	7/28/76	0.27	1.0	0.27	1/2/1	23°	5.8	20	30	101	24.0	8.8% NaOCl, 0.005 mole NH ₄ Cl
30	7/29/76	0.27	2.0	0.35	2/1	2°	4.9	12	60	99	39.0	8.8% NaOCl, 0.005 mole NH ₄ Cl
31	7/29/76	0.27	1.0	0.35	1/2	1°	5.1	22	60	80	35.0	5% NaOCl, 0.001 mole NH ₄ Cl
32	7/29/76	0.27	1.0	0.27	2/1	-8	3.2	11	60	65	28.4	2% NaOCl
33	7/29/76	0.27	2.0	0.35	1/2/1	-3	5.5	10	180	82	30.2	8.8% NaOCl, 0.001 mole NH ₄ Cl
34	7/30/76	0.27	1.0	0.35	2/1	-4	5.5	12	180	65	33.0	5% NaOCl, 0.001 mole NH ₄ Cl
35	7/30/76	0.27	0.54	0.35	1/2/1	0	2.7	41	60	61	50.6	2% NaOCl, 0.001 mole NH ₄ Cl
36	8/2/76	0.27	2.0	0.35	1/2	23	4.8	25	180	63	0	5% NaOCl
37	7/29/76	0.27	2.0	0.27	1/2	21°	4.8	6	30	65	47.3	8.8% NaOCl, 0.001 mole NH ₄ Cl
38	8/2/76	0.27	0.54	0.27	1/2	-5	10.1	19	60	101	41.6	8.4% NaOCl
39	8/3/76	0.27	0.54	0.27	1/2/1	0	6.0	8	180	63		5% NaOCl, 0.005 mole NH ₄ Cl
40	8/2/76	0.27	2.0	0.35	2/1	0	4.4	41	30	105	47.2	5% NaOCl
41	8/3/76	0.27	0.54	0.35	1/2	-5	8.0	8	30	98	44.0	5% NaOCl, 0.005 mole NH ₄ Cl

The best reaction procedure was:

1. Mix NaOCl + NaOH at 0°C
2. Add NaOCl + NaOH to MMU solution at 0°C
3. Heat to 90°C
4. React for 60 min.

3.5.3 Statistical Study of MMH Formation

From the results of the reactions listed in Table 3-3, reasonable levels of the independent variables were developed. After a detailed consideration of the reaction parameters and the statistical analysis procedures a test matrix of reactions was determined. This matrix and the run conditions are given below.

The variables of interest were reaction temperature, reaction time, and reactant concentrations. The matrix is given below:

	<u>-K</u>	<u>-1</u>	<u>0</u>	<u>+1</u>	<u>+K</u>
X ₁	0.25	0.5	0.75	1.0	1.25
X ₂	1.2	2.0	2.8	3.6	4.4
X ₃	0.75	1.0	1.25	1.5	1.65
X ₄	70	80	90	100	110

where X₁ is the MMU concentration, X₂ the NaOH concentration, X₃ the NaOCl concentration all in moles per liter, while X₄ is the reaction temperature, °C.

Results of runs made according to this matrix are given in Table 3-4. It appears that:

- a. the reaction is substantially complete at 60 min
- b. reaction temperature of 70-100°C is satisfactory
- c. the most significant variables are the amounts of NaOCl and NaOH relative to MMU. Best results (in yield of MMH, not concentration) are obtained with 2 moles of NaOCl and 4 moles of NaOH per mole of MMU
- d. runs TM-3 and TM-3D show good reproducibility.

Table 3-4

STATISTICAL SERIES ON MMH PROCESS BLEACH REACTION

Run No.	Date of Run	Concentration, moles/l		Temp °C	Time (min)	MMH		
		MU	NaOH			Concentration, g/100 ml	% Yield	
TM-1	9/21/76	0.956	3.45	1.44	101±2	30	1.74	39.5
						60	2.01	45.6
						90	1.82	41.2
						120	1.98	44.9
					150	2.09	47.4	
TM-2	9/21/76	0.998	3.59	1.50	82±2	30	1.98	43.1
						60	2.37	51.6
						90	2.37	51.6
						120	2.29	49.8
						150	2.39	52.1
TM-3	9/22/76	1.02	3.68	1.02	104±2	30	1.67	35.6
						60	2.17	46.3
						90	2.11	44.8
						120	2.11	44.8
						150	1.94	41.2
TM-3D (TM-3 duplicate)	9/23/76	1.01	3.65	1.01	103±1	30	1.59	34.2
						60	2.02	43.4
						90	1.97	42.3
						120	2.00	42.9
						150	1.93	41.4
TM-5	9/23/76	1.00	2.01	1.50	104±1	30	1.91	41.4
						60	2.13	46.2
						90	2.03	44.0
						120	1.86	40.3
					150	1.99	43.1	
TM-6	9/24/76	1.01	2.01	1.51	83±1	30	1.86	40.2
						60	2.12	45.8
						90	1.99	43.0
						120	2.15	46.6
					150	2.14	46.3	

Table 3-4 (Contd.)

Run No.	Date of Run	Concentration, moles/l		Temp °C	Time (min)	MMH	
		MU	NaOH			Concentration, g/100 ml	% Yield
TM-7	9/24/76	1.01	2.03	102±2	30	1.72	36.9
					60	1.78	38.2
					90	1.60	34.3
					120	2.14	45.9
					150	1.65	35.4
TM-8	9/27/76	1.01	2.02	83±1	30	1.13	24.4
					60	1.54	33.1
					90	1.56	33.7
					120	1.58	34.0
					150	1.55	33.3
TM-9	9/27/76	0.51	3.67	107±1	30	1.32	56.4
					60	1.32	56.5
					90	1.34	57.2
					120	1.34	57.0
					150	1.22	51.9
TM-10	9/28/76	0.52	3.71	85±1	30	1.50	63.6
					60	1.52	64.1
					90	1.61	67.9
					120	1.55	65.3
TM-11	9/28/76	0.51	3.64	103±1	30	0.21	10.3
					60	1.35	58.2
					90	1.48	63.7
					120	1.57	67.6
TM-12	9/28/76	0.50	3.62	85±1	30	1.33	57.5
					60	1.33	57.5
					90	1.36	58.8
					120	1.33	57.5
TM-13	9/29/76	0.50	2.01	104±1	30	1.07	46.4
					60	1.05	45.5
					90	1.18	51.5
					120	1.16	50.4

Table 3-4 (Contd.)

Run No.	Date of Run	Concentration, moles/l		Temp °C	Time (min)	MMH	
		MU	NaOH			Concentration, g/100 ml	% Yield
TM-14	9/29/76	0.51	2.02	86±1	30	1.20	51.6
					60	1.28	55.0
					90	1.26	54.2
					120	1.34	57.6
TM-15	9/29/76	0.51	2.03	102±1	30	1.25	53.5
					60	1.19	50.9
					90	1.18	50.5
					120	1.23	52.6
TM-16	9/29/76	0.50	2.01	82±1	30	1.21	52.7
					60	1.16	50.4
					90	1.20	52.3
					120	1.18	51.1
TM-17	9/30/76	0.75	2.81	93	30	1.63	47.1
					60	1.84	53.0
					90	1.88	54.2
					120	2.01	57.9
A-1*	9/30/76	1.01	2.83	92±1	30	1.96	42.2
					60	2.21	47.5
					90	2.19	47.1
					120	2.30	49.5
A-2	9/30/76	0.76	3.64	93±1	30	2.05	58.6
					60	2.01	57.3
					90	2.00	57.3
					120	1.91	54.7
A-3	10/1/76	0.75	2.81	90±1	30	1.78	51.4
					60	1.95	56.3
					90	1.97	56.9
					120	1.90	54.9

* Runs A-1 through A-3 not in the statistical series.

Table 3-4 (Contd.)

Run No.	Date of Run	Concentration, moles/l		Temp °C	Time (min)	MMH	
		MU	NaOH			Concentration, g/100 ml	% Yield
A-4	10/1/76	0.75	2.81	100	30	2.07	59.8
					60	1.93	55.8
					90	1.97	56.9
					120	1.80	52.0
TM-18	10/1/76	1.26	2.82	91±1	30	2.49	42.9
					60	2.50	43.1
					90	2.53	43.6
					120	2.35	40.5
TM-19	10/1/76	0.754	4.42	91±1	30	1.94	55.9
					60	2.00	57.7
					90	2.00	57.7
					120	2.04	58.8
TM-22	10/29/76	0.253	2.84	90±1	30	0.37	31.7
					60	0.36	30.8
					90	0.37	31.7
					120	0.37	31.7
TM-23	10/29/76	0.752	1.20	90±1	30	0.85	24.5
					60	1.01	29.2
					90	1.04	30.0
					120	0.99	28.6
TM-24	10/29/76	0.750	2.80	90±1	30	1.11	32.2
					60	1.31	38.0
					90	1.25	36.2
					120	1.31	38.0
TM-25	10/29/76	0.750	2.80	70±2	30	1.40	40.6
					60	1.55	44.9
					90	1.50	43.5
					120	1.67	48.4

* Run A-4 not in the statistical series.

The best conditions for the reaction are close to the conditions given for run TM-2; these are listed in Table 3-5. Approximately 50% excess of NaOCl is used under these conditions.

A preliminary evaluation of the overall urea process was made by laboratory preparation of MMH from commercially available urea and MMA. Two runs of this type are reported in Table 3-6.

3.5.4 Pilot Batch Bleach Reaction

3.5.4.1 Introduction

The program intended to use the MMU solution prepared in the pilot batches for the production of MMH by reaction with NaOCl. Before reacting the pilot batch of MMU an aliquot was taken and reacted with NaOCl in the laboratory. MMH yield of this laboratory reaction was low. Several laboratory reactions were conducted to define optimum conditions, however, in all cases the MMH yield was lower than expected. It was decided to crystallize the MMU and use this purified material for the production of MMH.

3.5.4.2 Use of "As Prepared" MMU Solution

The MMU produced in the pilot plant contained some unreacted urea and some unknowns. This solution was used to study the optimization of the bleach reaction conditions by a matrix of reaction conditions. Results of these reactions are given in Table 3-7.

Yield of MMH from the laboratory runs (aliquots) using MMU solution prepared in the pilot plant were low, i.e., 35-40% as compared to the yields of about 60-75% obtained during laboratory runs with pure MMU starting material. The highest yield was obtained from Run 2 and was 40% based on the MMU in the solution as determined by hplc analysis. The yield was only 26% based upon the urea charged to the MMU reactor.

As a result of these tests it was decided to crystallize the MMU from the solution and use this purified MMU for the bleach reaction.

Table 3-5

"OPTIMIZED" REACTION CONDITIONS FOR MMH FORMATION

Best Reactant Ratios and Concentrations

	<u>g-moles/liter</u>
MMU	1.0
NaOH	3.6
NaOCl	1.5

Best Yields and Concentrations

Using the above procedure and reactants
the yield and concentration should be:

52% MMH based upon MMU
2.4 wt% MMH

Table 3-6

LABORATORY PREPARATION OF MMH FROM COMMERCIAL UREA & MONOMETHYLAMINE

<u>Date</u>	<u>Run #25</u> <u>8/12/76</u>	<u>Run #28</u> <u>8/31/75</u>
<u>MMU Preparation</u>		
Reaction time, min	120	180
Reaction temp., °C	112	125
Reaction pressure, psi	140	140
Urea, g-moles	2.0	2.0
MMA, g-moles	2.0	2.0
Total volume, ml	230	234
Yield, % on urea		
MMU	60.8	74
U	29.6	10
SDMU	-	8
<u>MMH Preparation</u>		
<u>Date</u>	<u>9/10/76</u>	
Reaction time,	82	
Reaction temp., °C	1.22	
MMU, g-moles	1.22	
NaOH, g-moles	1.0	
NaOCl, g-moles	.79	
Yield, % on urea		
MMH	62	
Overall yield, %	46	

Table 3-7
MATRIX OF BLEACH REACTIONS USING
PILOT PLANT PRODUCED MMU¹

Run No.	Vol. Urea Soln., ml	M Moles ¹		Reaction Mixture, Moles		Time Min.	Product, mg/ml		% Yield ³ MMH	Overall % Yield ⁴		Reaction Vol., ml
		Urea	MMU	Urea ²	NaOH		MMH	HZ		MMH	HZ	
1	28.4	26.5	197	5.9	1.24	3.93	2.07	14.7	4.45	26	11	242
1R	29.4	26.5	197	5.9	1.20	3.80	2.00	14.7	4.00	26	10	--
2	36.7	33.0	246	7.3	1.41	4.14	2.26	13.0	5.25	24	14	250
3	36.7	33.0	246	7.3	1.58	4.62	1.58	12.6	5.06	23	13	266
4	36.7	33.0	246	7.3	1.30	2.78	2.08	16.9	7.34	26	16	--
5	36.7	33.0	246	7.3	1.50	3.20	1.50	15.6	5.06	24	11	238
6	19.6	17.6	131	3.9	0.766	4.21	2.30	11.8	5.08	16	10	--
7	19.6	17.6	131	3.9	0.813	4.47	1.52	10.5	4.36	20	11	288
8	19.6	17.6	131	3.9	0.794	3.17	2.38	11.7	4.71	20	11	250
9	19.6	17.6	131	3.9	0.806	3.23	1.51	9.44	4.00	14	9	--
10	46.5	41.9	311	9.3	1.90	3.80	2.00	9.70	4.41	19	8	261
9R	19.6	17.6	131	3.9	0.806	3.23	1.51	6.40	1.94	19	8	--
11	29.4	26.5	197	5.9	1.12	3.56	2.25	8.53	2.55	23	10	246
12	29.4	26.5	197	5.9	1.12	3.56	2.25	8.25	2.06	22	8	--
13	12.25	11.0	82.0	2.5	0.517	3.93	2.07	6.59	2.38	18	10	252
14	29.4	26.5	197	5.9	1.19	2.66	1.98	6.51	2.48	23	10	248
								8.62	2.53	23	10	--
								7.21	2.80	19	11	250
								10.64	5.60	12	9	--
								8.51	2.80	35	11	248
								6.77	2.16	18	8	--
								10.96	3.51	20	9	248
								9.36	2.58	17	7	--
								7.89	1.91	15	5	267
								7.68	2.11	15	5	--
								3.55	1.76	15	11	242
								3.27	1.72	14	10	--
								11.52	4.81	21	13	252
								10.43	4.74	19	12	--

1 Solution: 0.9 M Urea, 6.69 M-MMU, 0.2M SDMH by hplc analysis

2 Based on Urea charged

3 Based on analysis of MMU in stripped solution

4 Based on Urea charged

3.5.4.3 Use of MMU Crystallized from Pilot Batch

The pure MMU provided by crystallization from the reaction mixture was evaluated by a series of bleach reactions on a laboratory scale. Results are given in Table 3-8 and indicate a maximum yield of MMH based upon MMU of 39-40%. This was considerably below the 60-75% obtained with neat MMU, but time limitations did not permit investigating the reasons for the lower yield.

3.5.4.4 Purification of Pilot-Produced MMU

The pilot plant MMU solution was cooled to 19°F and the crystals formed removed by filtration. Attempts to dry the crystals at 125°F were not successful. The crystals dissolved in the approximately 5% water present and made removal of water very difficult.

A series of evaporation/crystallizations were conducted by evaporation of water at atmospheric pressure in a thin film evaporator and crystallization by cooling the liquid in a refrigerated room. Typical results of the evaporation crystallization are shown in Figure 3.

3.5.4.5 Pilot Scale MMH Production

The bleach reaction was conducted in the pilot plant using TM-2T reaction conditions: MMU 1.03 moles/liter, NaOH 3.70 moles/liter, and NaOCl 1.54 moles/liter. Reaction temperature was 81°C, reaction time 90 min. This reaction is discussed in detail below.

The MMU solution was made by dissolving 44.65 lb MMU crystals feed in distilled water to make a 40% by weight solution. The total diluted weight was 111.5 lb (50.58 kg), volume was 12.34 gal (46.7 liters), and specific gravity was 1.083. The hplc analysis of this solution indicated that urea was 17.3 mg/ml, MMU was 357 mg/ml, and SDMU was 4.48 mg/ml.

To make up the 35 gal (132.5 liters) required for the bleach reaction required 62.3 lb (28.26 kg) of MMU solution, 96.1 lb (43.59 kg) of 45% by weight of NaOH, and 155.4 lb (70.49 kg) of NaOCl (11% Cl by weight). The NaOCl used was 1.55 moles/liter, which was 0.11 moles/liter more than TM-2T requirement because of the presence of urea and SDMU in the MMU solution.

Table 3-8
RESULTS OF BLEACH REACTION USING MMU CRYSTALLIZED FROM P.P. RUN

Sample	Reaction Mixture		Total Volume ml	MMU Content, m moles ²	Reaction Temp °C	Reaction Time Min.	Yield		HZ mg/ml	% Yield MMH ²	Overall MMH ¹	% Yield HZ ¹
	Urea ¹ Moles/l	NaOH NaOCl					MMH ¹ mg/ml	HZ mg/ml				
1 ³	1.21	3.31	1.81	246	105	45	9.77	2.21	26.8	17.6	5.7	
						60	9.32	2.02	25.6	16.8	5.2	
						70	10.45	3.22	28.7	18.8	8.3	
						100	10.2	3.26	28.0	18.4	8.4	
2 ⁴	1.28	3.49	1.91	247	105	45	10.74	3.15	27.9	18.3	7.7	
						60	10.0	2.79	26.0	17.1	6.8	
						70	8.98	2.92	23.4	15.3	7.2	
						100	8.95	3.05	23.3	15.3	7.5	

1. Based on moles of urea charged.
2. Based on MMU content as determined by original hplc analysis of reaction product mixture.
3. Stripped with steam at atmospheric pressure.
4. Stripped with steam at reduced pressure.

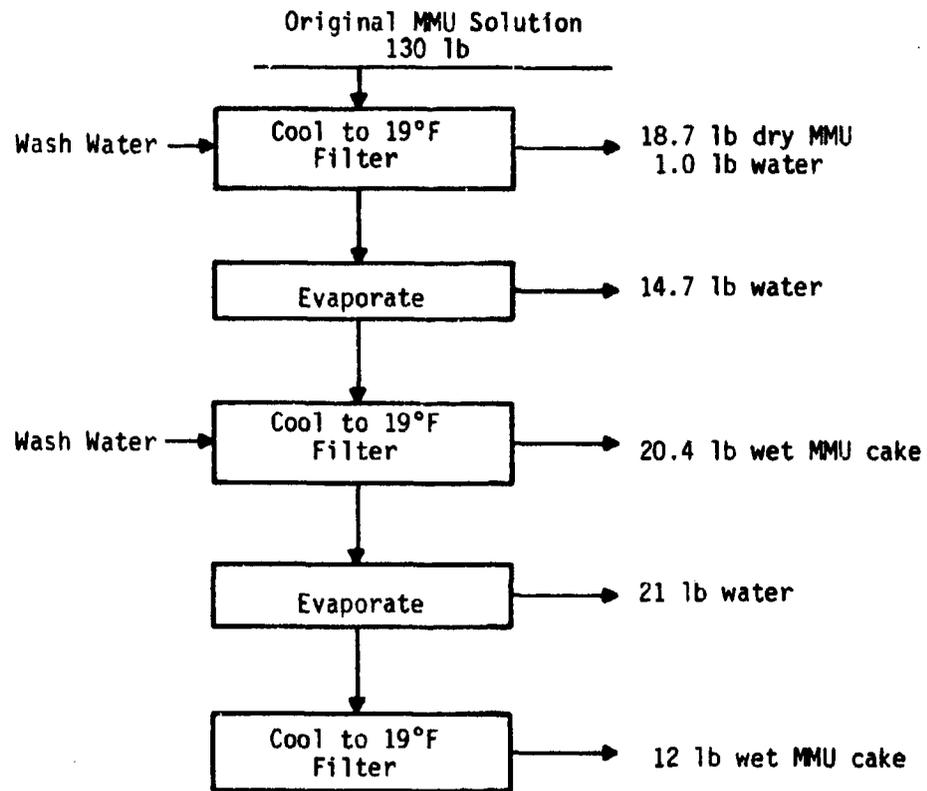


Figure 3 EVAPORATION/CRYSTALLIZATION OF PILOT
PLANT PRODUCED MMU

The MMU solution was charged into a 50 gal reactor which was equipped with a pump-around and heat exchanger. Methanol/dry ice was used as the coolant and was kept at -20 to -30°F. After the MMU solution in the reactor was cooled to -12°C, the cooled pre-mixed NaOCl and NaOH was pumped into the circulation line just upstream of the pump. A thermometer in the effluent of this pump was closely watched and the temperature of the solution was maintained below 7°C by controlling the feed rate. It took 2.5 hours to complete the addition of NaOH/NaOCl. The reaction mixture was milk-white during the course of addition. After a 20 min waiting period, the reaction mixture was heated to 88°C in 35 min with steam. During heating, the reaction mixture degassed and caused a foam. After degassing, the reaction went smoothly and the solution color changed from milk-white to light yellow. The reaction mixture was kept at 82-88°C for 90 min and then quenched by cooling. Three samples were taken from MMH analysis at 30, 60, and 90 min intervals.

The analysis results are given in Table 3-9 and the overall material balance of the bleach reaction is given in Table 3-10.

The pilot bleach reaction had a yield of MMH of 41.1% as compared to laboratory run TM-2T (11/12/76) of 56.2%. This is a significant (27%) loss in yield. The reason for this lower yield was not determined, but it should be noted that the laboratory studies were conducted in glassware, while the pilot reactions were conducted in 316 ss (with gelatin added).

3.6 Recovery of MMH from Bleach Reaction Solution

3.6.1 Recovery Methods

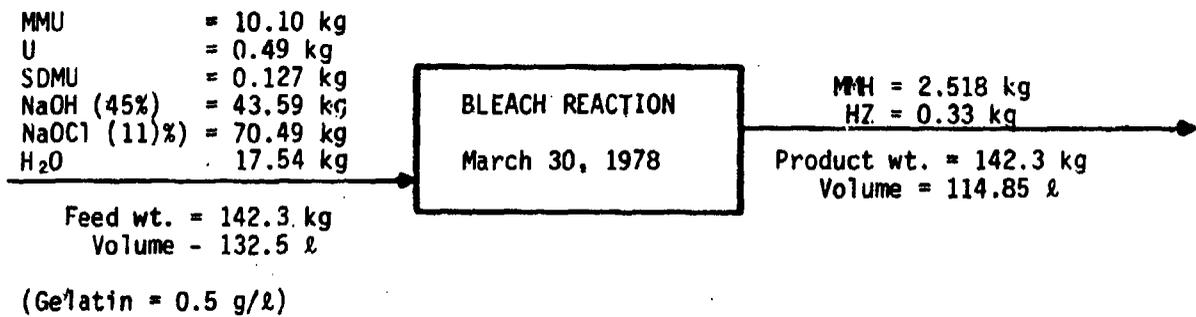
The reaction mixture from the bleach reaction contains about 2 wt% MMH, about 0.2% hydrazine hydrate, and several volatile contaminants. The solution contains one mole of NaCl for every mole of NaOCl used as well as some NaOH and Na₂CO₃.

MMH must be recovered from this dilute salt-containing solution; this process represents one of the major energy-intensive steps in the production of the hydrazine fuels.

Table 3-9
ANALYSIS OF PILOT BLEACH
REACTION SAMPLES
(35 gal Batch)

<u>Time, min.</u>	<u>Analysis, mg/ml</u>	
	<u>MMH</u>	<u>HZ</u>
30	16.75	1.78
50	22.26	2.70
90	21.92	2.90

Table 3-10
MATERIAL BALANCE OF BLEACH REACTION



Note: Based on charged MMU, MMH yield was 41.1%
Based on charged Urea, HZ yield was 127.3%

Previous processes have relied upon evaporation for the separation and this course was followed during the study reported here. This technique offers the best possibility of producing a salt type by-product with minimum loss of MMH or Hz.

3.6.2 Laboratory Evaporations

The product from the pilot plant bleach reaction was used for a series of laboratory evaporations to determine the best conditions for the pilot plant batch.

The bleach reaction product was used in two laboratory evaporations to determine the operating conditions for maximum recovery of MMH. Table 3-11 shows the results of the laboratory evaporation at a slight vacuum (660 mm Hg absolute). The results indicated a 54.2% recovery of MMH. The salt slurry in the pot was very thick at the conclusion of the evaporation. The amount of MMH in the reboiler was reduced from 20,370 mg to 1489 mg by evaporation of 577 ml of the 1000 ml charge.

The material balance indicated 61.2% recovery of MMH, but over 100% recovery of hydrazine. It appeared that some decomposition of MMH was taking place. Most of the collected condensate samples had an ammonia odor and analysis of these samples showed unidentified peaks.

A second laboratory evaporation was made at a higher vacuum. The results are shown in Table 3-12. In addition to operating at a higher vacuum, the original bleach reaction product, which contained suspended salts at 5°C (40°F) was filtered before the evaporation. After collection of distillate equal to about 50% of the original charge, the bottom product was cooled and filtered to remove the precipitate. The filtrate was further distilled after the addition of two drops of anti-foaming agent. A total of 928 ml of distillate was collected from 1,195 ml of bleach reaction product. Only a trace of MMH was detected in the last two samples of distillate. The recovery of MMH was 93.2%; the material balance of MMH was 93.9%. The analysis indicated only very small impurity peaks.

Table 3-11

LABORATORY EVAPORATION OF PRODUCT FROM PILOT BLEACH REACTION

Pressure: 600 mmHg

Date: April 1, 1977

Time Min.	Temp, °C		Reboiler volume, ml	Distillate Volume, ml		G.C. Analysis of Distillate mg/ml		Weight, mg			
	Pot	Vapor		Collected	Accum.	MMH	HZ	Reboiler MMH	HZ	Distillate MMH	HZ
0	13	22	1,000	-	0	22.35	3.25	20,370	2950	-	-
75	104	95	-	50	50	22.28	2.10	-	-	1114	105
85	105	95	-	50	100	20.91	1.48	-	-	1045.5	74
95	105	96	-	50	150	19.73	1.36	-	-	986.5	68
105	105	97	-	50	200	19.35	1.38	-	-	967.5	69
115	107	97	-	50	250	29.40	1.39	-	-	970	69.5
125	107	97	-	50	300	19.34	1.40	-	-	967	60
135	107	98	-	50	350	21.23	1.42	-	-	1061.5	71
160	108	96	-	50	400	20.20	1.42	-	-	1010	71
165	108	N.D.	-	15	415	19.72	1.40	-	-	295.8	21
190	103	?	-	50	465	15.19	1.36	-	-	759.5	68
205	107	?	-	50	515	17.10	1.40	-	-	855	70
215	109	?	-	62.5	577	16.20	1.60	-	-	1012.3	100
		Room Temp.				3.52		14.89	3519		

SUMMARY

Material Balance %		Recovery, %	
MMH	HZ	MMH	HZ
61.5	148.3	54.2	29.0

Table 3-12

LABORATORY EVAPORATION OF PRODUCT FROM PILOT BLEACH REACTION

Pressure: 70~75 mmHg April 4, 1977

Time, Min.	Pressure mmHg	Temp, °C		Reboiler Volume, MI	Distillate Volume, ml		G.C. Analysis, mg/ml		Weight, mg			
		Pot	Vapor		Collected	Accum.	MHI	HZ	MHI	HZ	MHI	HZ
0	75	-	-	1195	0	0	22.82	2.72	27.270	3,250	-	-
25	75	50	42		50	50	13.02	1.61	-	-	651.0	80.5
43	75	50	43		53	103	14.05	1.63	-	-	744.7	86.5
63	75	51	44		53	156	16.45	1.43	-	-	871.9	75.8
80	75	51	44		53	209	21.07	1.29	-	-	1116.7	68.4
100	75	51	44		52	261	23.65	1.14	-	-	1229.8	59.3
113	75	51	43		54	315	22.47	1.02	-	-	1213.4	53.0
133	75	51	44		52	367	27.79	1.04	-	-	1445.1	54.1
163	75	51	44		51	418	29.32	1.00	-	-	1487.7	50.0
192	75	51	44		48	466	31.82	1.05	-	-	1527.4	50.9
220	75	53	44		46	512	42.44	1.26	-	-	1952.2	58.9
245	75	53	45		58	570	48.50	1.28	-	-	2816.5	74.8
Pot cooled 25°C. Filtered Crystals. Washed with 155 ml cold water. Met Crystals 281 g* Filtrate 495 g (inc. wash)												
0	70	-	-	495	-	570	23.77	1.63	11,766.0	806.9	-	-
38	70	62	48		53	623	47.72	1.49	-	-	2529.2	79.0
53	70	62	50		52	675	55.30	1.54	-	-	2875.6	80.1
70	70	65.5	50.5		52	727	55.34	2.47	-	-	2877.7	128.4
85	70	73	59		52	779	34.0	5.87	-	-	1766.0	305.2
105	67	84	64		53	832	5.71	12.53	-	-	302.6	664.1
125	67	81	64		51	883	Trace	16.60	-	-	Trace	864.6
140	67	110	60		45	928	Trace	5.72	-	-	Trace	257.4

* Sample of crystals dissolved in water (4.5 g wet cake in 10 ml water) 3.32. Trace 202.8 Trace

SUMMARY

	Material Balance %		Recovery %	
	MHI	HZ	MHI	HZ
1st Distillation	99.1	46.7	55.2	21.9
2nd Distillation	88.0	292.5	38.0	72.6
Overall	92.9	94.5	93.2	93.5

Attempts to detail the recovery of hydrazine was inconclusive, probably due to contaminants that affected the analysis. In the first step of the distillation 21.9% was recovered and the material balance was only 46.7%. On the other hand, in the second step of distillation recovery was 72.6% and the material balance was far beyond 100%. The overall recovery and material balance for hydrazine appear to be very good.

These laboratory evaporation studies indicate that evaporation of the bleach reaction product at low pressure, 50-75 mm Hg, was preferred because: (1) there was better MMH recovery, (2) there was better Hz recovery and (3) the g.c. analysis indicated fewer unidentified peaks.

3.6.3 Pilot Plant Evaporation

Based upon the information obtained from laboratory studies, the pilot bleach reaction product was first cooled and filtered, then evaporated using a thin-film evaporator at high vacuum to obtain 50-50 cut in volume. The bottom product was cooled, the crystallized salt removed by filtration, and the filtrate was evaporated under vacuum. The bottom product from the second evaporation was cooled and filtered. Tables 3-13 through 3-17 show the material balance and the analysis of each step of this operation. Analysis of samples indicated from 0.15 to 0.76 mg/ml SDMH in the reboiler. These limited results suggest that the SDMH was not stable under the evaporating conditions.

The results summarized in Table 3-18 show that of the 2346 g MMH charged, only 20 g would be lost in the filtrate from the third filtration.

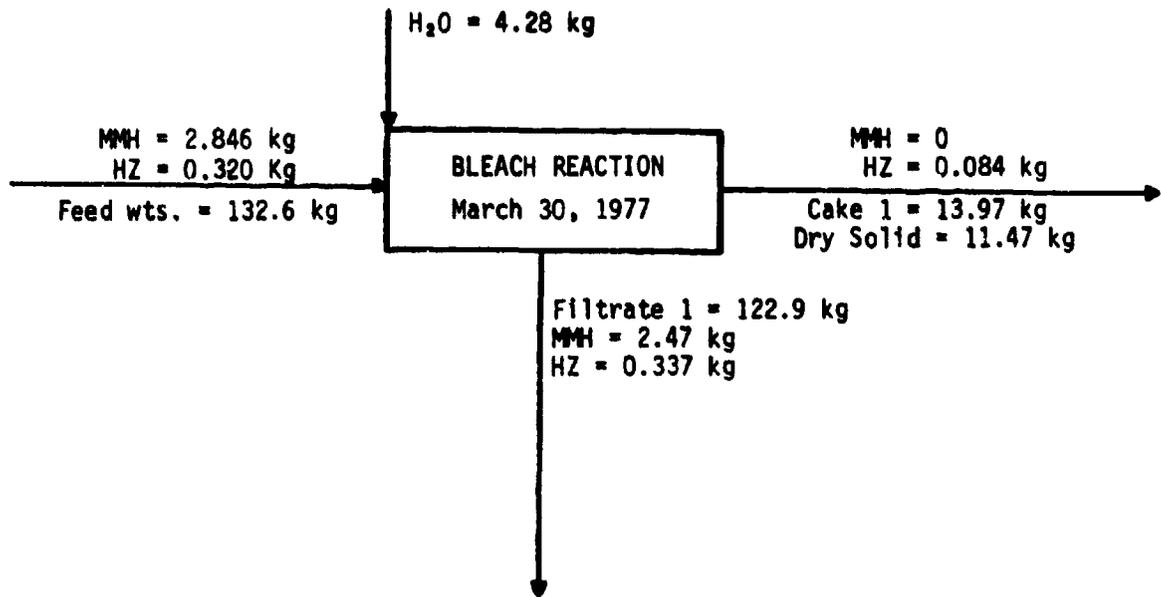
There are several interesting results:

- 1.85 kg of MMH in 79.6 l of distillate was recovered
- 20.6 lb of salts were generated per lb of MMH product
- Very little MMH remained in the salt cake
- The salt cake had a very low moisture content.

Highly accurate analysis of the product from the bleach reaction is required to complete an accurate material balance for this portion of the process. The MMH material balance was approached in two ways:

Table 3-13

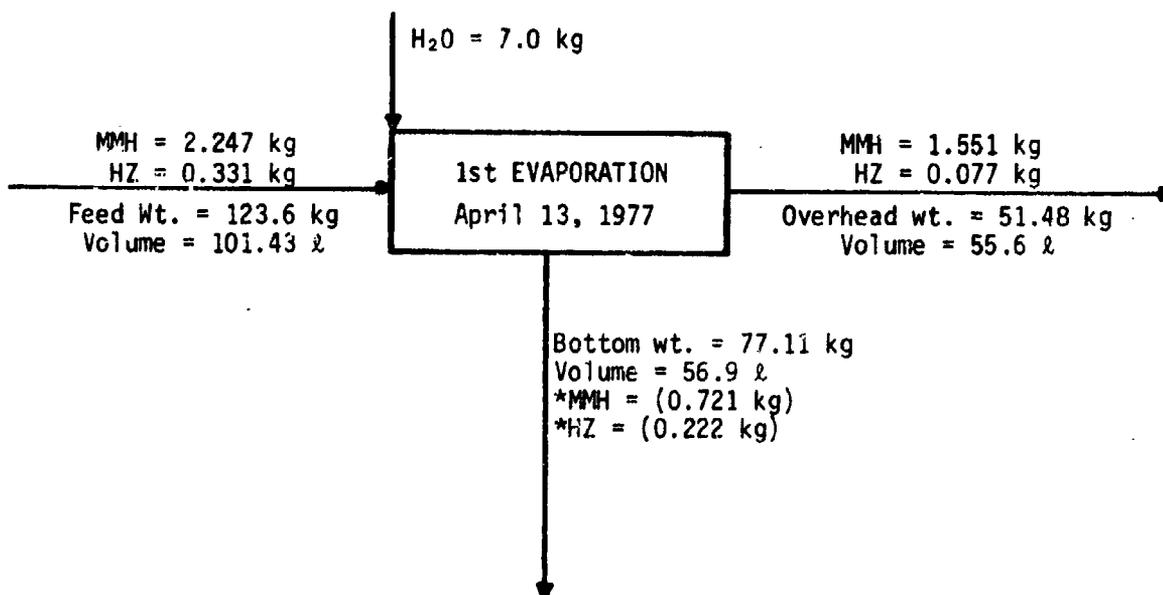
FIRST FILTRATION OF PILOT BLEACH REACTION MIXTURE
April 7, 1977



Note: Recovery of MMH during the filtration was 105%
Material balance of MMH was 105%
Recovery of HZ was 105%
Material balance of HZ was 132%
Filtration was rapid on glass cloth septum; 0.3 gal/ft²/min
Cake quite dry

Table 3-14

FIRST EVAPORATION PILOT BLEACH REACTION MIXTURE
April 13, 1977

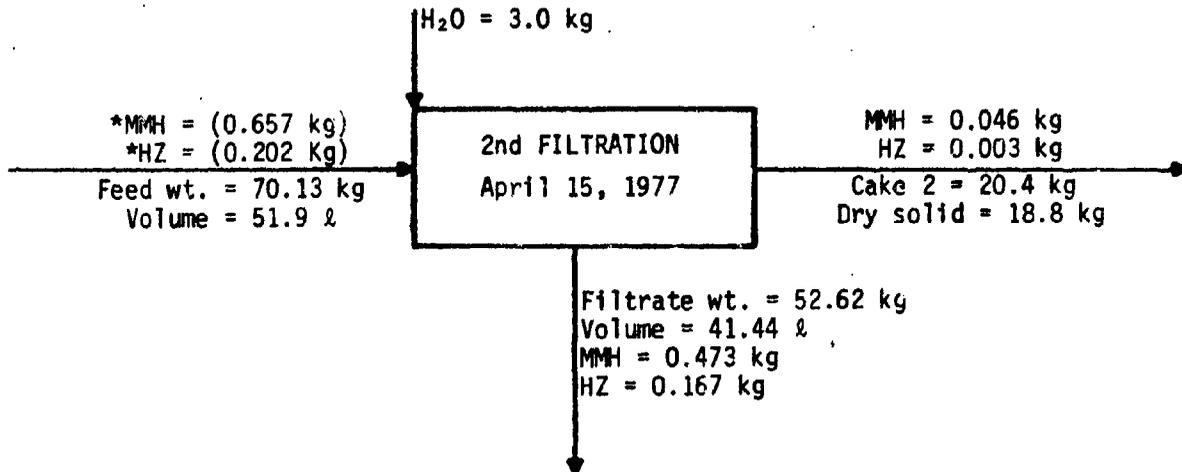


*This is calculated value.

Pressure; mmHg	50~55 mmHg
Steam pressure; psig	45
Temperature of Liquid °C	60-70
Feed rate	0.7 liter/min
Estimated time at temperature:	1 minute

Table 3-15

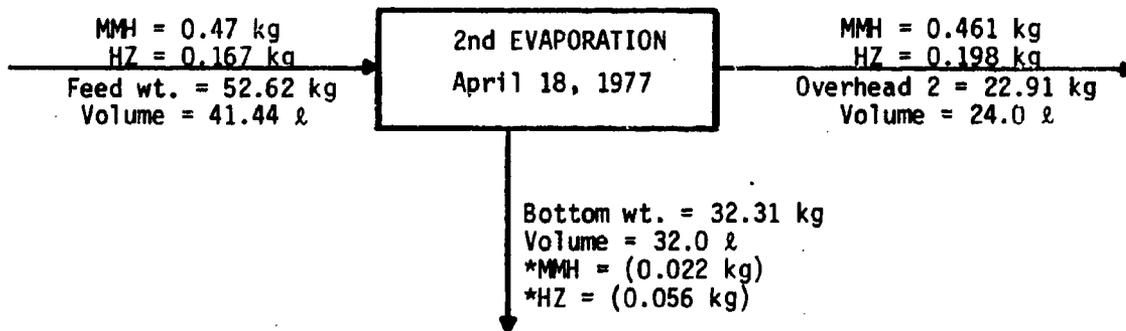
SECOND FILTRATION AFTER 51% OF BLEACH REACTION MIXTURE
HAD BEEN EVAPORATED



*This is calculated value.

Filtration was rapid on glass cloth septum; 0.3 gal/ft²/min
Temperature: Ambient
Cake was fairly dry.

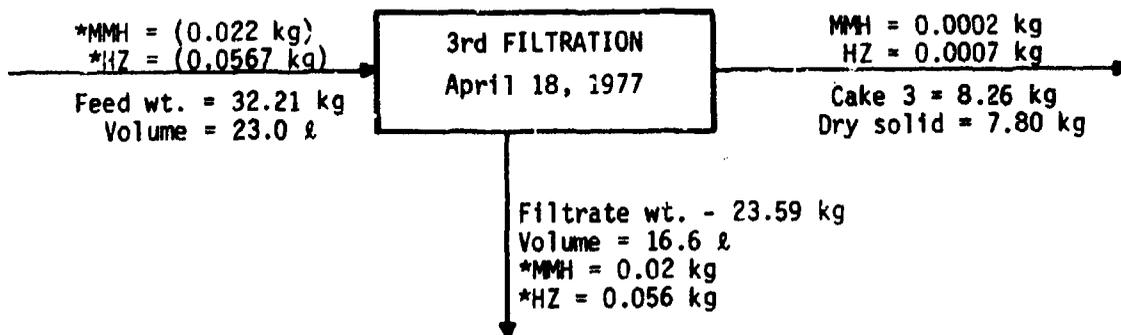
Table 3-16
SECOND EVAPORATION



*This is calculated value.

Pressure, mmHg: 50
 Steam pressure, psig: 45
 Temp of liquid °C: 75-75-85
 Feed rat l/m: 0.7
 Estimate time of liquid at temperature, 1 min

Table 3-17
 THIRD FILTRATION



*This is calculated value.

Filtration was rapid on glass cloth septum; 0.3 gal/ft²/min
 Temperature: Ambient
 Cake fairly dry

Table 3-18

RECOVERY OF MMH AND HZ FROM BLEACH REACTION
THROUGH EVAPORATION, CRYSTALLATION AND FILTRATION

Run. No.	Mass in, kg MMH HZ	Mass out, kg MMH HZ	Recovery, kg MMH HZ	Process Lost, kg MMH HZ	Recovery, % MMH HZ	Material Balance, % MMH HZ
1st Filtration	2.346	2.472	-	0.0(2)	105	105
1st Evaporation	2.346	2.315	1.58	0.0078	67.3	24
2nd Filtration	0.735(1)	0.580	-	0.051(2)	72.0	62.6
2nd Evaporation	0.529(1)	0.1856	0.540	0.025(2)	97.4	119
					102	153

Overall MMH recovery = $\frac{0.515 + 1.58}{2.346} \times 100\% = 83.3\%$

Overall MMH process loss = $\frac{0.051 + 0.025}{2.346} \times 100\% = 3.1\%$ (or 96.9% recovery)

Overall HZ recovery = $\frac{0.0078 + 0.221}{.32} \times 100\% = 68.4\%$

Overall HZ process loss = $\frac{0.063 + 0.0034 + 0.084}{.32} \times 100\% = 47.0\%$

(1) corrected for handling loss.

(2) based on cake analysis.

(1) the total product in compared to the total product out and (2) the total product in compared to the loss of product in the salt cake. The first method showed a 89.3% product recovery, the second method showed a 3.1% loss of MMH in the salt cake or a 96.9% MMH recovery.

A material balance for Hz indicates a recovery of 53-68%. Accuracy of the hydrazine analysis at these low concentrations may account for the relatively poor material balance.

3.7 Azeotropic Distillation of MMH

3.7.1 Introduction

The MMH is recovered from the bleach reaction solution by evaporation of water and MMH to give a concentration of 2 to 3% MMH in water. This dilute solution is distilled and a high boiling-point azeotrope containing about 42 wt% MMH in water is withdrawn from the reboiler. The azeotrope is extractively distilled to obtain a specification grade product. A series of distillations, shown in Figure 4, are required to recover 98.5% MMH.

The first fractionation column is called the MMH azeotropic distillation column, where the 2% MMH stream is separated into relatively pure water (>10 ppm of MMH) as the overhead stream and a bottom stream which approaches the azeotropic composition of 42% MMH. A flash drum on the overhead stream may be necessary to remove any light ends, such as methanol. The water can be returned to the process and the light ends incinerated.

The 42% MMH azeotrope mixture is then sent to the extractive distillation column, where NaOH is used to suppress the vapor pressure of the H₂O to allow separation of MMH and H₂O. The bottom stream contains hydrazine (Hz), which is produced from urea during the bleach reaction. This bottom stream is sent to an evaporator to separate the water, Hz, and MMH from the NaOH, which can be used again for the extractive distillation operation. Some Hz + MMH are collected with water from the caustic evaporator. The vapor liquid equilibria for the NaOH, water, and MMH in the reboiler of the extractive distillation column was not determined. One laboratory result

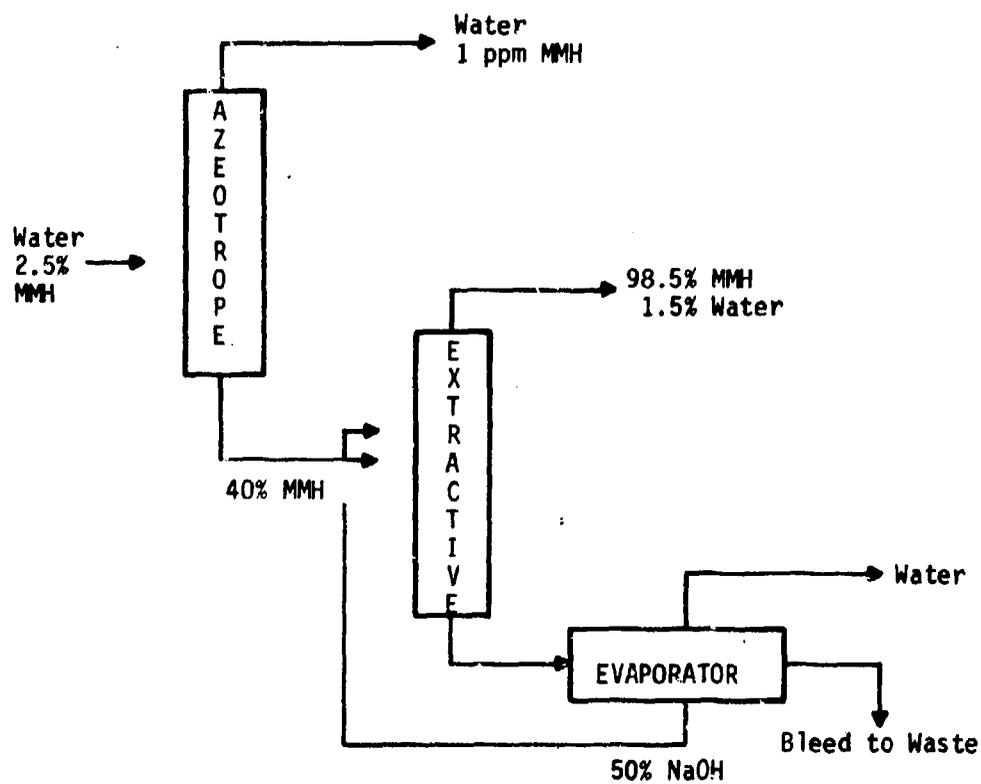


Figure 4. PROCESS FOR THE RECOVERY OF MMH FROM 2.5% SOLUTION

indicated 3 wt% MMH in this stream, this is a significant quantity and must be recovered. Further laboratory studies are required to define the limits of operation.

There is some Hz in the vapors from the caustic evaporator and these must be separated. The proposed process includes an extractive distillation with caustic to give Hz + MMH followed by a binary distillation to separate Hz + MMH.

The azeotropic distillation of the dilute aqueous MMH solution produced by the evaporation represents a significant heat input to the process. This stream enters the column at approximately 2.5 wt% MMH in water and must be concentrated to approximately 42 wt%. The most useful design information for such a separation is the vapor/liquid equilibria data. The literature contains references to recovery of MMH by distillation but does not contain the required design information. The data in a general sense is represented in Figure 5.

Although this information is not sufficient for design, the curve and accompanying text indicate:

- A 2% solution can be concentrated to a high boiling azeotrope of about 35-45 wt% MMH.
- There is a definite pinch point at the azeotrope concentration and additional distillation plates will result in only small increases in concentration.

Laboratory efforts were conducted to obtain further design data.

3.7.2 Preliminary Laboratory Studies

In order to confirm the azeotrope composition and determine one point on the vapor/liquid equilibrium curve, a brief laboratory study was conducted. A 10 plate 30 mm dia. Oldershaw column was used at a pressure of ~700 mm Hg (a). Nitrogen was introduced into the reboiler at ~5% of the vapor flow. Three tests at different reflux ratios were made using 42.5 wt% MMH as a charge to the bottom. One test was made using a charge of 48 wt%. Results are shown in Table 3-19.

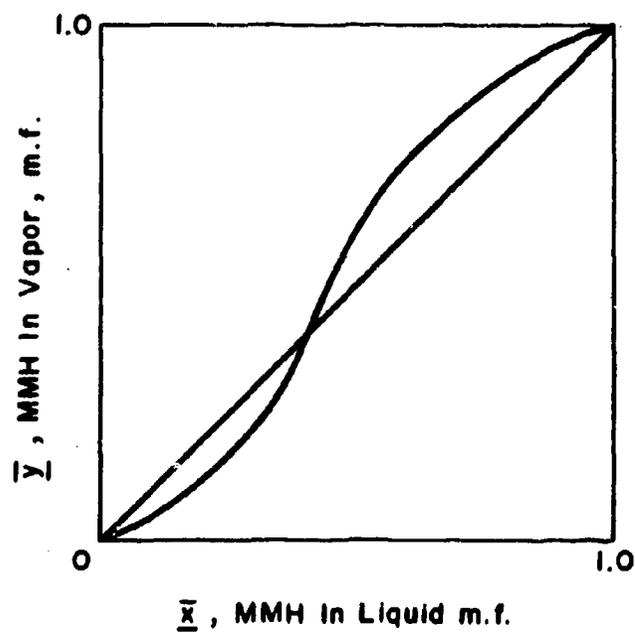


Fig. 5 GENERAL FORM VAPOR/LIQUID EQUILIBRIUM FOR MMH/WATER

Table 3-19

DISTILLATION OF MMH AT LESS THAN
AZEOTROPIC CONCENTRATION
at 700 mmHg (a)

Reflux Ratio L/D	Temp °C		wt% MMH	
	Reboiler	Overhead	Reboiler	Overhead
∞	101	86	42.5	0
3			42.5	Trace (0.1)
1			42.5	~5
∞			48.0	11.1
∞	102	88	48.0	12.5

The results indicate that the azeotropic concentration of MMH in water is very close to 45 wt% at a pressure of 700 mm Hg (a).*

These data indicated there would be no difficulty in this first distillation. Since the pinch point in the distillation occurs at the bottom of the column, there would be no difficulty approaching to within 5% of the azeotrope in a 10 plate column at practical reflux ratios and the column could be designed to give "pure" water overhead.

From these data a reflux ratio of 3/1 was tentatively selected for preliminary design in order to maximize the purity of the overhead water. The design resulted in a very large column with a high heat load. Further work was indicated and is reported below.

- The column should operate at the lowest possible reflux ratio which will give column stability, in order to conserve heat energy.
- Produce overhead water with little or no MMH; goal of 10 ppm was set.
- Produce a bottom concentration close to the 42 wt% azeotrope concentration and not less than 35 wt%.

With these goals in mind it was decided to measure the MMH-water vapor-liquid equilibrium. These equilibria data permit the calculation of the reflux ratio and the number of plates for any given feed and overhead concentrations.

3.7.3 Vapor-Liquid Equilibrium for MMH-Water

A laboratory scale apparatus consisting of a 500 ml round bottom flask, a two plate sieve-tray column, and a total condenser was set up to measure the MMH concentration of the vapor (overhead) and liquid (reboiler) when the system was in equilibrium and operating at total reflux. These measurements were conducted at two pressures for different concentrations of MMH in water. The resulting data and calculated separation factor and relative volatility are presented in Table 3-20.

*Knight, O.A. Jr., Hydrocarbon Processing & Petroleum Refiner 41, 179 (1962) indicates the azeotrope concentration is 35% MMH at atmospheric pressure.

Table 3-20
EQUILIBRIUM DATA OF MMH AND WATER

Pressure, mmHg abs	Reboiler Temp, °C	MMH, Mt. %		Mole Fraction		Separation Factor, F	Plate Efficiency %	Relative Volatility α
		\bar{x} liq.	\bar{y} vap.	\bar{x}	\bar{y}			
180	65	.53	.0006	2.08×10^{-3}	2.34×10^{-6}	1/889	75	1/15.1
180	65	7.0	.064	.028	2.5×10^{-4}	1/115	75	1/6.67
180	65	14.4	.30	.0617	.00117	1/56	75	1/5.00
180	65	22.2	2.03	.1	.00803	1/13.7	75	1/2.85
690	97	.056	.00275	2.19×10^{-4}	1.07×10^{-6}	1/205	75	1/8.41
690	98	.54	.001	2.12×10^{-3}	3.91×10^{-6}	1/542	75	1/12.4
690	99	7.50	.18	0.0306	7.04×10^{-4}	1/44.8	75	1/4.58
690	104	14.8	.69	.0635	2.71×10^{-3}	1/24.9	75	1/3.62
690	23.3	3.34	3.34	0.106	0.0133	1/8.80	75	1/2.39

54

Nomenclature

- \bar{x} = wt% MMH in liquid (reboiler)
- \bar{y} = wt% MMH in liquid (overhead)
- \bar{x} = mol fraction of MMH in liquid (reboiler)
- \bar{y} = mol fraction in vapor (overhead)

Separate factor = $\frac{\bar{y}}{\bar{x}} \left[\frac{1 - \bar{y}}{1 - \bar{x}} \right] / \bar{x}$

Relative volatility = α

where

α^{n+1} = separation factor and

n = number of theoretical plate, $(0.75)(2) = 1.5$

A separation factor is calculated from the composition of the overhead and the reboiler. The relative volatility can then be calculated based upon the number of theoretical plates.

The problem then becomes one of determining an average α from the data presented in Table 3-20 where $1/\alpha$ varies from 1/12.4 to 1/2.39 for the pressure of interest.

α can be determined graphically, as shown in Figure 6. Although there is considerable scatter of the data at low concentrations, the $1/\alpha$ values increase rapidly at low concentrations of MMH in the liquid phase. A value of $1/\alpha = 8$ appears reasonable. (Note that a value of $\alpha = 1/8$ to $1/15$ would not greatly influence column design.)

For the very low values of \bar{y} the vapor-liquid equilibrium curve can be represented by a straight line with a slope of 1/8.

\bar{y} = mole fraction of MMH in overhead

\bar{x} = mole fraction of MMH in reboiler

F = separation factor

$$F = \frac{\left[\frac{\bar{y}}{1 - \bar{y}} \right]}{\left[\frac{1 - \bar{x}}{\bar{x}} \right]}$$

α = relative volatility

n = number of theoretical plates assuming a 75% plate efficiency for the 2 plate column

$$n = 1 + (.75)(2) = 2.5$$

α^{n+1} = separation factor = F

$$\frac{\left[\frac{2.34 \times 10^{-6}}{1 - 2.34 \times 10^{-6}} \right]}{\left[\frac{1 - 2.08 \times 10^{-3}}{2.08 \times 10^{-3}} \right]}$$

$$F = 1/889$$

$$\alpha^{2.5} = F$$

$$\alpha = 1/15.1$$

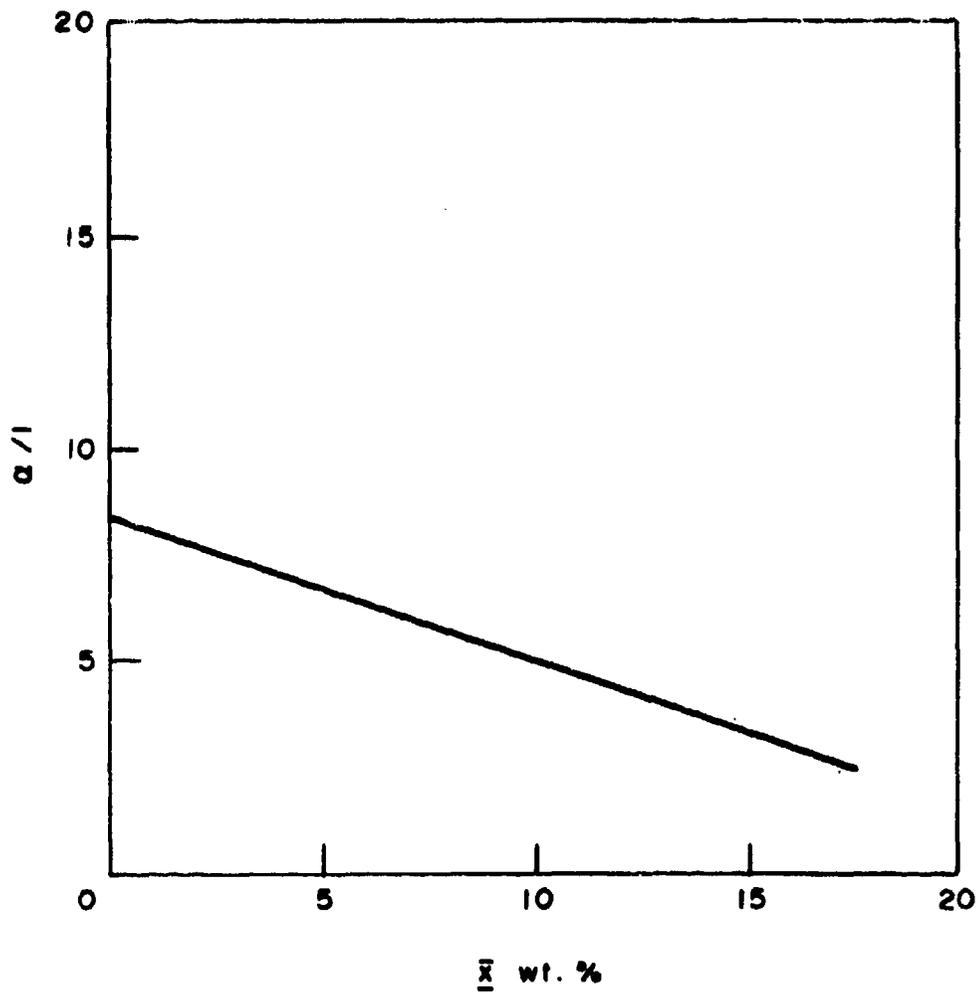


Fig. 6 GRAPHICAL DETERMINATION OF RELATIVE VOLATILITY, MMH/H₂O

The vapor/liquid equilibrium can then be calculated from:

$$\bar{x} = \frac{\bar{y} \frac{1}{\alpha}}{1 + (\frac{1}{\alpha} - 1) \bar{y}}$$

Column conditions for $L/V = 1/2$, $L/D = 1/1$ with a feed of 2.5 wt% MMH concentration of 10 ppm are shown in Figure 7.

Using $\alpha = 1/8$, an expanded vapor-liquid curve can be drawn for $L/D = 1/2$ as shown in Figure 8.

The desired product (vapor y_D) has 10 ppm or 4×10^{-6} m.f. of MMH. A reflux ratio of $L/D = 1/2$ is assumed and the relative volatility of $1/8$ is used. The liquid in equilibrium with y_D is x_1 with 16×10^{-6} m.f. MMH. The theoretical plates can be stepped off graphically as illustrated in Figures 8, 9 and 10. The approximate compositions are:

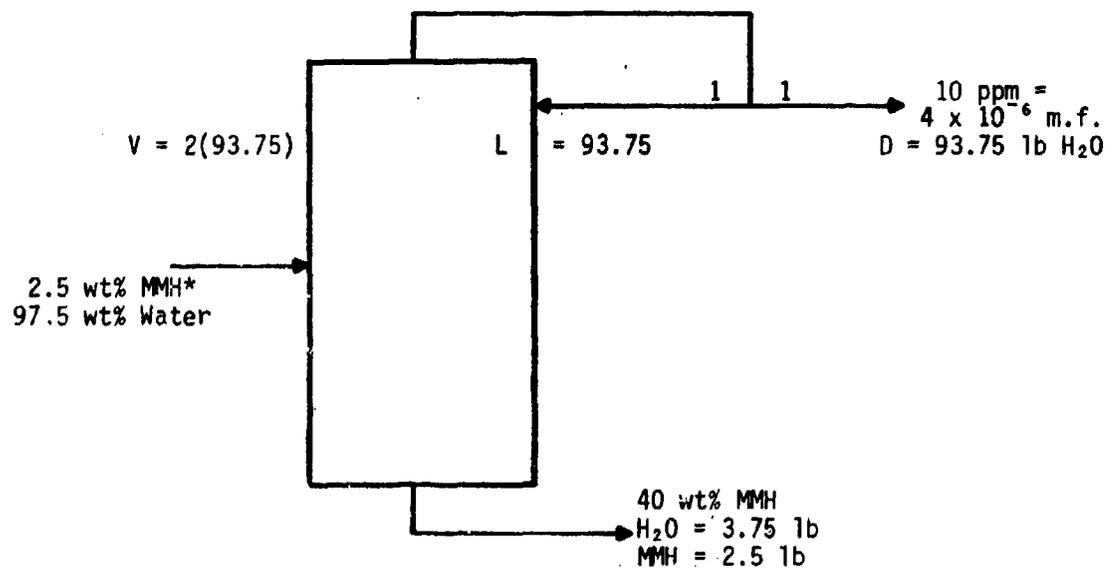
Plate	m.f. $\times 10^{-6}$	
	\bar{y}	\bar{x}
Top	4	32
2	18	150
3	76	600
4	310	2200
5	1200	9200

Since the feed is .01 MMH it could be fed to the 5th or 6th plate.

3.7.4 Verification of MMH Azeotropic Distillation

The MMH recovered from the bleach reaction solution by a series of filtrations and evaporations was 2.7% by weight in water solution. A 2 inch sieve-tray fractionation column was set up (20 plates above and 10 plates below the feed) to concentrate the feed solution to azeotropic composition.

Because of the limited capacity of this column it took more than 150 hours of continuous operation to obtain about 2.4 kg of the "azeotropic" composition mixture (34% MMH). Two different reflux ratios were investigated



* 0.0089 m.f., use .01 m.f.

Figure 7. AZEOTROPIC COLUMN DESIGN CONDITIONS
Based on 100 lb feed

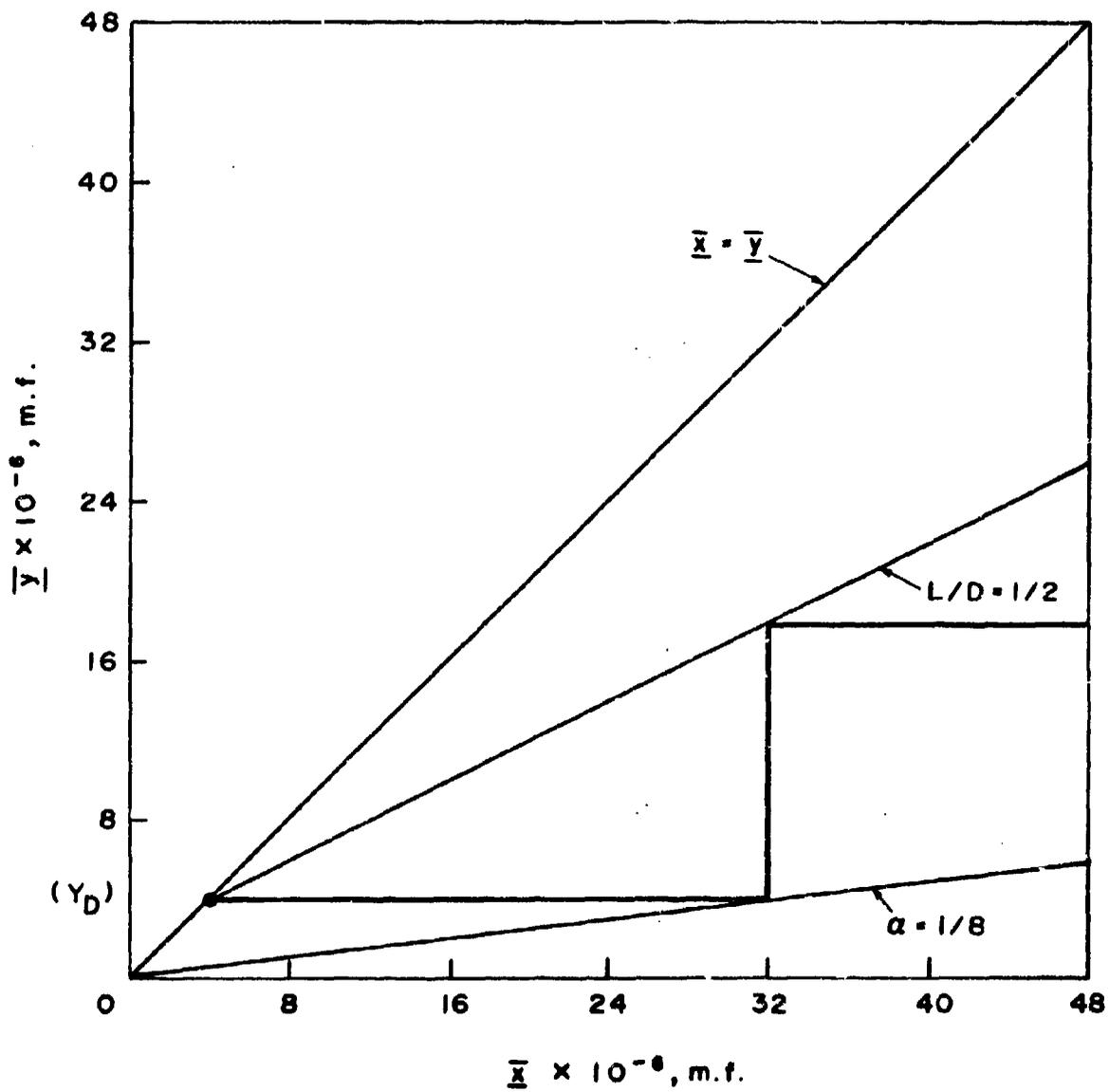


Fig. 8 EXPANDED VAPOR/LIQUID EQUILIBRIUM CURVE FOR MMH/WATER

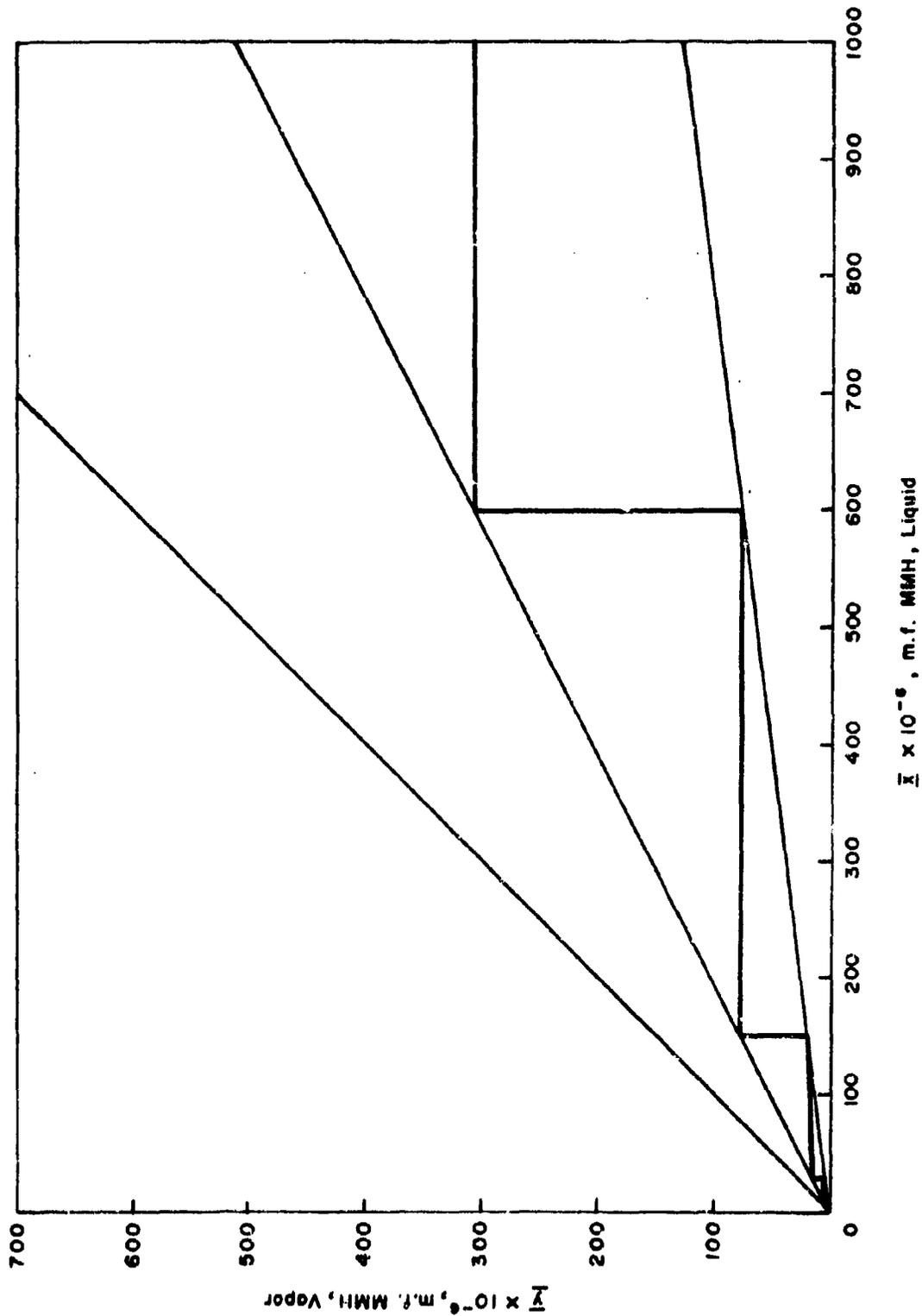


Fig. 9 MCCABE - THIELE DIAGRAM, MMH/WATER

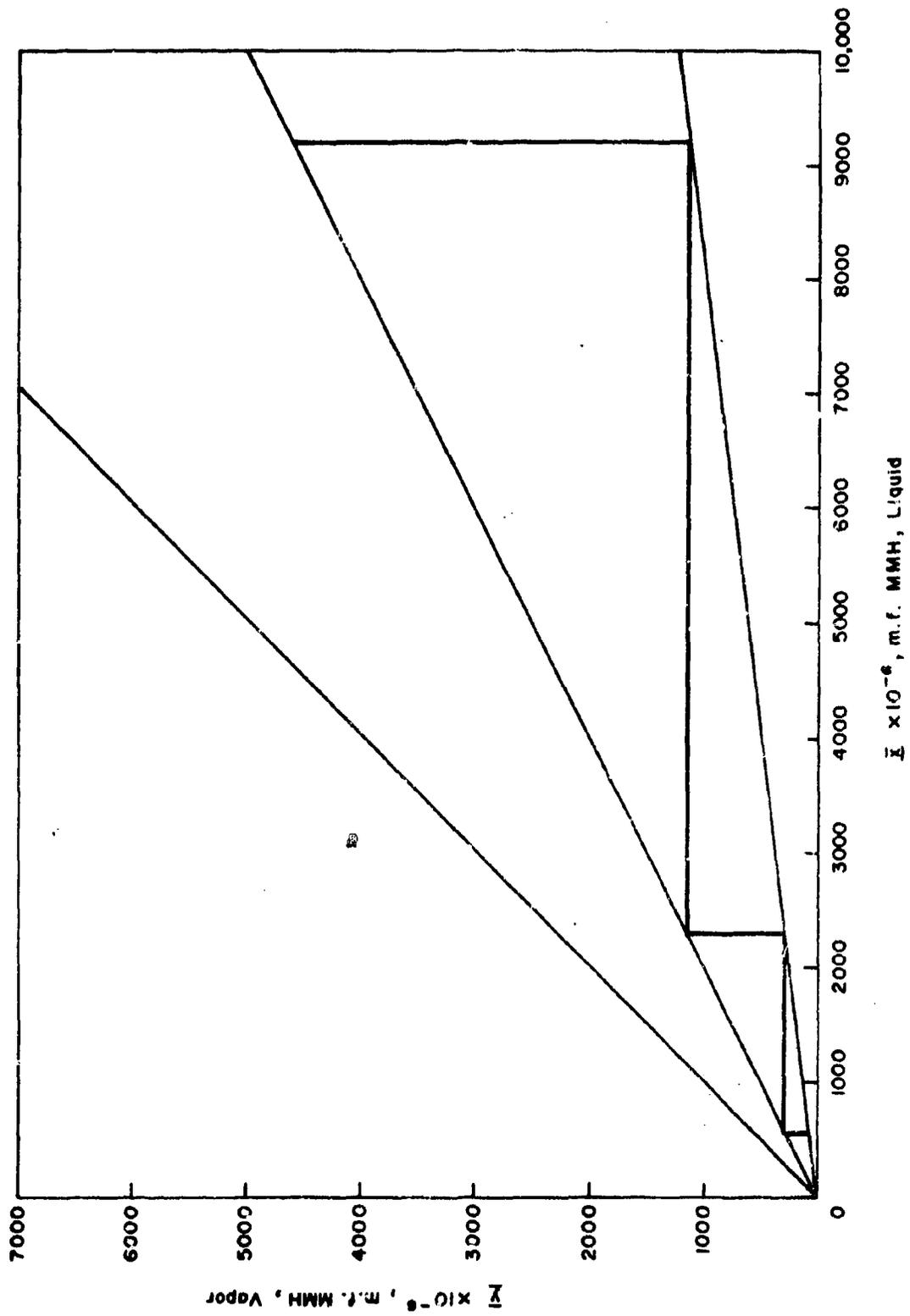


Fig. 10 McCABE - THIELE DIAGRAM . MMH/WATER

during the course of the continuous distillation, and various overhead samples were taken for MMH analysis. These data are presented in Table 3-21.

The data were somewhat inconsistent and the results did not entirely agree with calculated overhead MMH concentrations based on equilibrium data. It is possible that:

- (1) The feed and overhead take-off pumps were not stable enough to keep the feed and withdrawal rates constant at all times.
- (2) The 2 in sieve-tray columns used for the study was unstable; at times some of the plates above the feed either contained no liquid or were flooded.

The azeotropic fractionation would be improved by using more stable feed and product pumps and/or a larger distillation column.

3.8 Extractive Distillation of MMH

3.8.1 Introduction

The bottoms of the azeotropic distillation column are a constant boiling mixture with about 42% wt MMH. The specification grade MMH is recovered from this mixture by extractive distillation using caustic to suppress the vapor pressure of the water. This extractive distillation was investigated with a 1 in. diameter glass column and the same laboratory column was later used to prepare specification grade MMH from the pilot plant batch.

3.8.2 Laboratory Batch Distillation with Purchased MMH

Laboratory studies of the extractive distillation were conducted to determine the concentration of NaOH necessary to minimize the carry-over of MMH in the still bottoms.

Test conditions for the extractive distillation with purchased MMH are shown in Figure 11. Results of the laboratory studies are given in Table 3-22 and indicate that the concentration of MMH in the still bottoms decreases to less than 3 wt% when the NaOH concentration is 25 wt% of the

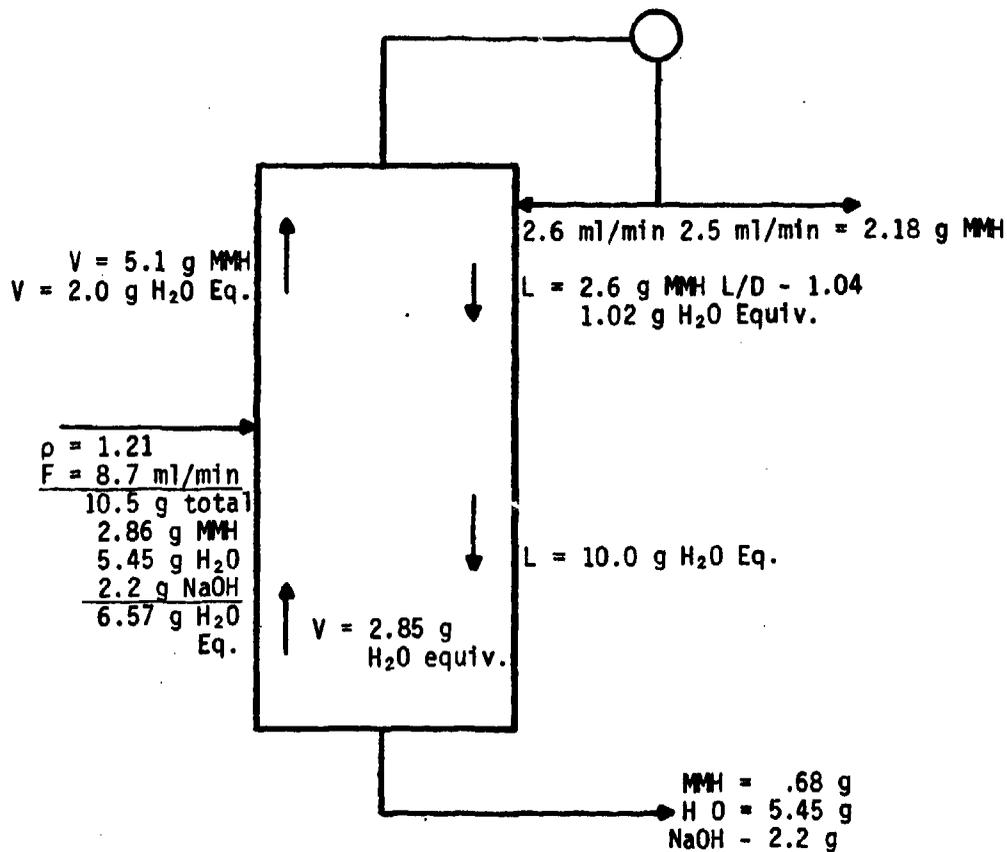
Table 3-21

PERFORMANCE OF 2" DIAMETER AZEOTROPIC FRACTIONATION
OPERATING DURING VERIFICATION RUN

<u>Pressure,</u> <u>mmHg (a)</u>	<u>Reboiler</u> <u>Temp, °C</u>	<u>Feed</u> <u>Rate</u> <u>ml/min</u>	<u>Boil-up</u> <u>Rate,</u> <u>ml/min</u>	<u>Reflux Ratio,</u> <u>L/D*</u>	<u>Overhead MMH Conc.</u> <u>ppm</u>
640	96	4.1	8.0	1.5	290
640	96	4.7	8.0	1.5	259
640	96	2.5	8.0	1.0	54
640	96	5.0	8.0	1.22	231
640	96	0.	8.0	1.5	134
640	96	4.7	8.0	1.16	135
640	96	5.5	8.0	0.78	150
640	96	4.8	8.0	1.35	180
640	96	5.5	8.0	1.0	225

*L = Liquid returned to column,

D = Liquid product



O.H. Analysis	% MMH
6/1/77 1330	99.67
6/1/77 1400	99.78
6/1/77 1500	99.84
6/1/77 1530	00.61

NOTE: For description of distillation column conditions MMH has been expressed in terms of water equivalents as follows:

$$\text{g-MMH} \times \frac{18}{46} = \text{g-water equivalents}$$

Figure 11. MMH EXTRACTIVE DISTILLATION COLUMN RESULTS
(Purchased MMH)

Table 3-22
 LABORATORY EXTRACTIVE DISTILLATION OF MMH

Run	Feed	Wt % MMH		NaOH in Feed*	L/V
		Overhead	Bottoms		
6	45.1	62.6	12.6	10	2.0
7	41.0	62.0	14.0	10	1.5
8	33.3	52.7	<3.0	25	1.25

*Based upon total water content

total water in feed. Although this is a relatively low MMH concentration, it is a very significant loss and suggested the use of a higher caustic concentration.

It should be noted that this column has a relatively low heat requirement and therefore the reflux ratio does not greatly affect the overall heat requirements of the plant.

3.8.3 Laboratory Distillation with Pilot MMH Batch

A 20 plate Oldershaw Column (30 mm/I.D.) with the feed on the 11th plate from the top was operated continuously under the conditions of Figure 11. The column was put on line using a simulated feed made up with MMH obtained from Aldrich Chemical Co. The column operated for several hours, producing 140 g of overhead (OH) with compositions better than 99.5% MMH. This corresponds to a final product recovery of 76%. (The other 25% in the bottoms was recovered in a subsequent distillation.)

During subsequent batch distillations it was found that the charge (both simulated and from the pilot plant) foamed and frothed to varying degrees on being brought to a boil. The pilot plant charge which had been mixed with the alkali and stored for 7 days foamed so vigorously that foam started up the column and the still pot had to be quenched. The simulated charge showed less frothing. In commercial practice where hold-up times are much smaller and severe foaming without flooding or plugging can be handled, this effect should be minimized.

In view of the foaming difficulties when operating this small laboratory column on a continuous basis it was decided to use batch distillation to produce the MMH required for a verification of the process. In these batch distillations the reboiler was charged with 200-300 g of MMH in water plus solid NaOH to give a feed composition the same as in Figure 11. The overhead was collected in several fractions, which contained less than 1.5% water and were considered specification grade MMH. Subsequent fractions contained increasing amounts of water. These later fractions (wet) were used as a part of the charge to the still in subsequent distillations.

Examination of the data in Table 3-23 indicates a 50-60% MMH recovery and a 95% total material balance for these batch distillations. The MMH loss was due to the discard of still bottoms containing less than 35 wt% MMH. This large loss would not occur in a continuous column; however, some MMH and Hz may remain in the still bottoms and would have to be recovered. The process design provides for this recovery.

3.8.4 Analysis of Pilot-Produced MMH

The four batches of MMH produced by the above extractive distillation procedure were analyzed at IITRI using the gas chromatographic techniques specified in MIL-P-27404A, 20 May 1969. Samples were submitted to Edwards Air Force Base and were analyzed in their laboratories. Results are given in Table 3-24. According to Edwards Air Force Base analysis, Batch A contained 0.4% water; Batch C had 2.4% water.

3.8.5 Hydrazine Recovery

In the proposed urea process, about 10% of the charged urea remains as urea after the amine reaction. It was proposed to leave this unreacted urea in solution and to let it form hydrazine during the bleach reaction. The hydrazine would be carried with the MMH to the extractive distillation where hydrazine hydrate (HH) would be removed with the 25% caustic from the still bottoms. The HH would come over with the water vapor during the caustic reconstitution step.

3.9 Waste Treatment

3.9.1 Sources of Wastes

The primary wastes generated in the urea process are:

- Water (overhead) in the azeotropic distillation of crude MMH solution
- Salts from filtration during concentration of the crude MMH or UDMH product
- Water from the caustic reconstitution process
- Miscellaneous volatile by-product and gaseous products from decomposition.

Table 3-23

BATCH EXTRACTIVE DISTILLATION OF PILOT MMH BATCH

<u>CHARGE</u>	Run	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
MMH, g		290.6	222.8	171	277.7
Water, g		263.2	288	459	420
NaOH, g (Pellets)		107.5	135	121	151
<u>RECOVERED OVERHEAD</u>					
<u>Specification grade MMH</u>					
MMH, g		142.5	94.3	35.4	160
Water, g		0	0	0	0
<u>Wet MMH</u>					
MMH, g		51.2	56.8	51.6	0
Water, g		63.8	65.2	47.5	0
<u>MMH RECOVERY</u>					
<u>Specification grade MMH, g</u>		142.5	94.3	35.4	160
<u>Wet MMH, g</u>		51.2	56.8	51.6	-
Total, g		193.2	151.1	87.0	-
% of Charge		67%	68%	51%	-
<u>OVERALL MATERIAL BALANCE</u>					
Charge, g		662.0	746	630	849
Overhead, g		115.0	216.3	132.5	160
Bottoms, g		323.5	216.3	132.5	680
% Accounted For		90%	101%	89%	99%

Table 3-24

ANALYSIS OF MMH PRODUCED IN VERIFICATION STUDIES

<u>Batch</u>	<u>IITRI Analysis, wt%</u>		<u>EAFB Analysis, wt%</u>	
	<u>MMH</u>	<u>H₂O</u>	<u>MMH</u>	<u>H₂O</u>
A	99.2	.2	99.9	.4
B	98.9	.5	97.6	1.5
C	99.0	.4	97.0	2.4
D	99.3	.2	98.3	1.1

All waste products must be treated to insure no environmental impact. Exploratory laboratory experiments were conducted to determine the extent of this problem.

3.9.2 Carbon Adsorption of Hydrazine

Exploratory studies of adsorption of Hz, MMH, and UDMH on two types of carbon were conducted. The samples, however, apparently underwent change between the time of sampling and the time of analysis so results were inconclusive.

Carbon adsorption studies were also conducted by Verzino (June 1976) of the Aerospace Corporation. Three carbons, Filtrasorb 400, Nuchar WV-W, and Witco 235 were used. Solutions containing 1000 ppm UDMH were treated with 40 g/l of the carbon. Treated samples contained 30-40 ppm UDMH, equivalent to 95% removal. Carbon capacity was approximately 0.0002 g UDMH/g carbon at the 30 ppm final concentration.

Verzino conducted a second set of experiments in August 1976 using 20 ppm of UDMH and treating with 20 g carbon/liter reduced the UDMH concentration to below 0.001 ppm.

While these results indicate carbon does adsorb the hydrazines, the adsorption capacity is very low. Further investigations of the adsorption capacity of activated carbon are required before the potential of this means of treating wastewater can be assessed.

3.9.3 Oxidation Treatment of Hydrazine

Hoke has indicated that hydrazines in wastewater can be oxidized by atmospheric oxygen as well as by sodium hypochlorite. Coughling has reported that activated carbon serves as a catalyst in the oxidation of a large number of organics. Emel (a reference obtained after completion of the laboratory work) indicates that alumina acts as a catalyst for ozone oxidation.

Initial attempts to oxidize Hz, MMH, and UDMH with ozone resulted in significant reductions of these compounds. In the case of UDMH, however, considerable nitroso dimethylamine was formed.

Experiments by Verzino to test the activated carbon/air oxidation of UDMH were encouraging and indicate this approach should be further investigated.

3.9.4 Solid Waste Treatment

According to the material balance for the proposed process, some 18 lb of dry salts or 26 lb of wet salt cake are generated per lb of MMH produced. The salts consist of NaCl, Na₂CO₃, and NaOH. The salts must be free (probably less than 0.4 ppm) of hydrazine before disposal. Composition of the salt obtained during the verification studies is given in Table 3-25. The wet cake has approximately 5% water and 3000 ppm hydrazine. This water could be evaporated in a salt dryer and condensed to give hydrazine-containing water which could be returned to the system.

3.10 UDMH Process

3.10.1 Introduction

During this study efforts were concentrated on the development of the urea process for the production of MMH and only limited efforts were expended in the study of the UDMH process. The laboratory work indicated good yields and few processing problems. No attempt was made to verify the laboratory results on a large scale.

3.10.2 Production of UDMU

UDMU was produced by the reaction of urea and DMA in an aqueous solution at 118°C (Table 3-26). A 25% excess of DMA was used and a yield of UDMU of 87%, based on urea, was obtained with a 240 min reaction time. Data from a second run is shown in Table 3-27. In this run a 50% excess of DMA was used and the yield, based on urea, was 98% at 240 min reaction time.

These two reactions indicate that good yields can be obtained without difficulty.

Table 3-25

HYDRAZINE CONCENTRATION IN WET SALT CAKE

<u>Cake</u>	<u>Total Weight,kg</u>	<u>MMH Weight,kg</u>	<u>HZ Weight,kg</u>
1	13.97	0	.084
2	20.4	.046	.003
3	8.26	.002	.0007
Total	<u>42.63</u>	<u>.048</u>	<u>.0877</u>

$$\text{Concentration} = \frac{.048 + .0877}{42.63} = 3200 \text{ ppm}$$

Table 3-25

REACTION OF DMA WITH UREA, AQUEOUS UNDER PRESSURE
 Reaction No. 35: 10/14/76, 0.075 mole DMA + 0.06
 mole urea (1.25:1) Temperature 113-118°C

Sample Time (min)	m. moles		% Recovery		% Yield 1,1-DMU	Mass Balance % Urea + % DMU
	DMA	Urea	DMA	Urea		
30	45.6	29.5	60.8	49.2	39.8	89.0
60	31.9	19.4	42.5	32.3	64.0	96.3
90	21.6	13.5	28.8	22.5	71.3	93.8
120	14.8	11.4	19.7	19.4	83.45	102.9
180	25.6	10.3	34.1	17.2	83.6	100.8
240	25.9	10.3	34.5	17.2	87.1	104.3

Table 3-27

REACTION OF DMA WITH UREA, REACTION NO. 36
 10/18/76, 0.075 mole DMA (34.4% Aqueous) +
 0.05 mole Urea (1.5:1), Temp 113-118°C

Sample Time (min)	m moles		% Recovery		% Yield 1,1-DMU	Mass Balance % Urea + % DMU	
	DMA	Urea	DMA	Urea			
30	46.6	34.5	16.0	62.2	69.0	32.1	101.1
60	45.8	20.7	22.8	61.0	41.4	45.7	87.1
90	38.0	16.7	31.6	50.7	33.3	63.2	96.5
120	34.0	10.5	36.7	45.3	20.9	73.4	94.3
190	33.7	6.5	44.3	44.9	13.0	88.6	101.6
240	33.7	6.2	49.4	45.0	6.3	98.0	104.3

3.10.3 Production of UDMH

UDMH was produced in the laboratory by the procedure used by Vickburg Chemical Company and described by Wax. They reported a 95% yield of UDMH.

The Vickburg procedure is given below:

- (a) 19.9 g DMU (.2227 moles DMU: .0052 NH_4Cl) is dissolved in 160 ml H_2O and 35.3 g 50% caustic (.4450 moles).
- (b) The DMU/caustic solution is cooled to -10°C with stirring.
- (c) 142 g of 11.1% NaOCl (.223 moles) at -10°C is added rapidly to the cold DMU solution.
- (d) The reaction mixture is allowed to sit in an ice/methanol bath for 10 minutes at which time 35.3 g 50% caustic are added and the solution brought rapidly to distillation temperature.
- (e) Approximately 70 g of distillate are caught in a cold trap and weighed accurately.

They stated that it was essential that the UDMH be distilled rapidly to insure good yields.

This procedure was duplicated and results of the experiment are given in Table 3-28. A UDMH yield of 99% was obtained.

On the basis of these laboratory experiments, it appears that UDMH can be produced by the urea process without difficulty.

Table 3-28
UDMH BLEACH REACTION

Reaction No. 4

Concentration, moles/l:		
	UDMU	0.677
	NH ₄ Cl	0.016
	NaOH (total)	2.74
	NaOCl	1.08
Temp °C, initial		-10
	Distillation	98
Reaction time, min		30
Volume, ml, reaction mixture		186
	Distillate	47
Yield, mg/ml	UDMH	159.2
	Hydrazine	0.2
Yield UDMH, %		99

4. PRELIMINARY PROCESS DESIGN

4.1 Introduction

During the laboratory studies a continuing effort was made to develop the process design for the full scale plant. These efforts served to highlight areas of particular concern as to costs, yields, and waste production which were then studied in the laboratory effort. The time frame of the work did not permit an in-depth study of every aspect of the process; however, the concurrent development of the design and laboratory effort insured a maximum of useful results for the effort expended. Results of this design effort are reported here.

The process design was based upon a production rate of 400 lbs MMH/hr using urea and monomethylamine. At this point in the overall development there are many unanswered questions regarding the best modes of operation, the exact size of equipment, some of the materials of construction, waste treatment, and build-up of impurities in recycle streams which will influence the design of the plant. The information available is sufficient to delineate the process steps, to develop approximate equipment sizes and costs, to prepare the first mass and energy balances, and to prepare early cost estimates.

For convenience the process is considered in three sections:

- (1) MMU Production
- (2) MMH Production
- (3) MMH Purification

Each section is presented separately. Specifications for major equipment are given in the Appendix.

4.2 MMU Production

Section (1), MMU Production, is shown in Figure 12.

Urea pellets are delivered by truck and a 10-day supply held in a silo (101). Urea is dissolved in water in a batch operation. The urea is fed through a weigh feeder (102) to an intermediate hopper (103) and into a

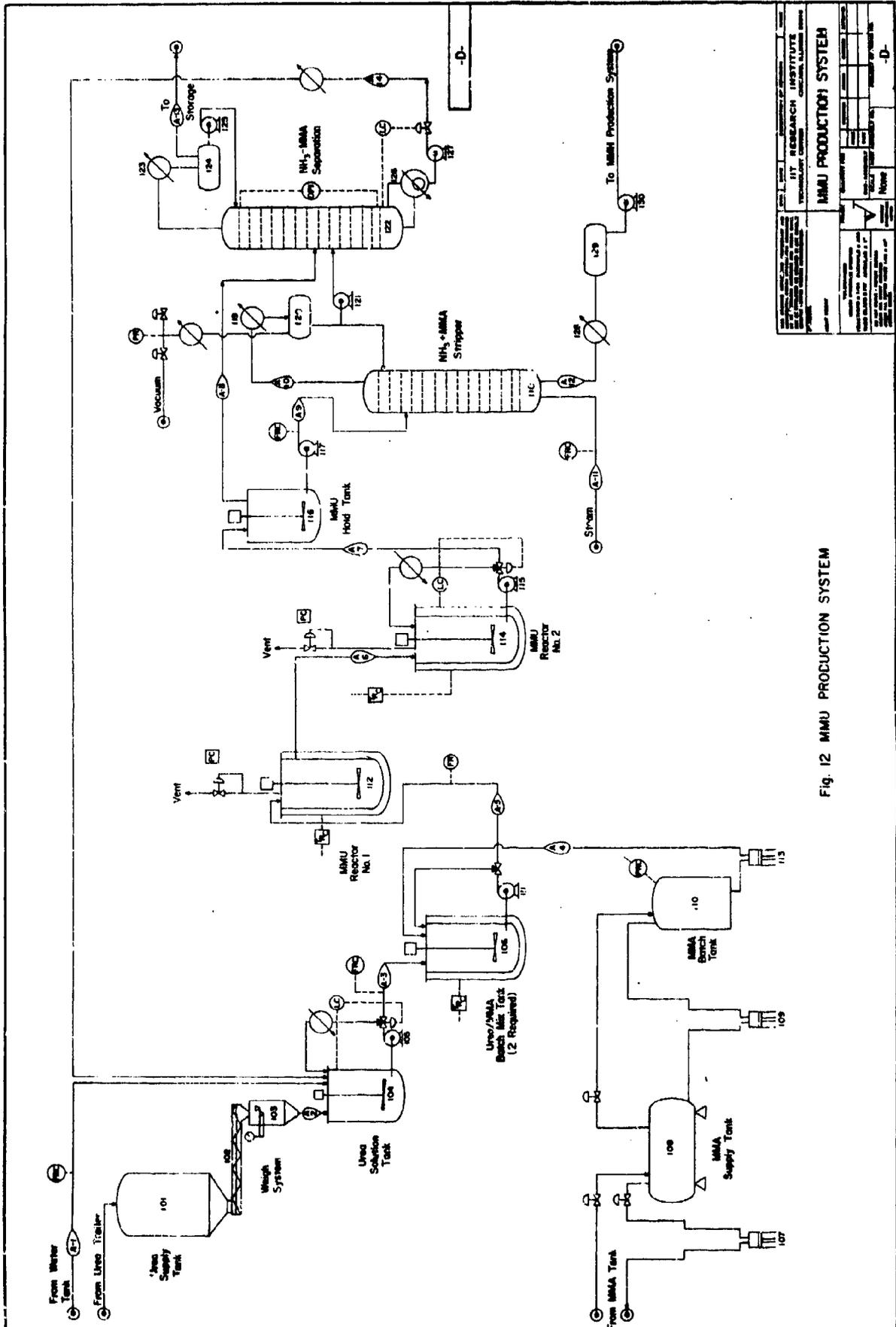


Fig. 12 MMAU PRODUCTION SYSTEM

IIT RESEARCH INSTITUTE THERMAL CENTER P.O. BOX 700 KANPUR-208002 U.P., INDIA		MMAU PRODUCTION SYSTEM	
PROJECT NO. 108 DATE 10/10/80 DRAWN BY S. S. SINGH CHECKED BY S. S. SINGH APPROVED BY S. S. SINGH	SHEET NO. 1 OF 1	NAME S. S. SINGH	-D-

mix tank (104) with water at the proper level for the concentration desired. As urea dissolves considerable heat is adsorbed and a heat exchanger is provided. This tank also receives the recycle MMA (A-14). The 48% urea solution (A-3) flows to a mix tank (106) where MMA is added.

MMA (100%) is received by tank truck and stored in a low pressure tank (108) for use as needed. The MMA is pumped to a weigh tank (110) and is then batch-mixed with the urea water solution in a mix tank (106). The MMA readily dissolves in water and no heat exchanger is necessary. Pressure of the system at this point is less than 5 psi. Two batch make-up tanks are used to provide continuous feed to the rest of the plant.

The 40% urea/20% MMA solution (A-5) is then pumped (A-5) to a two stage reactor system (112 and 114). Total reaction time is approximately 60 min at 120°C. The pressure in the system increases to approximately 125 psig. During laboratory studies attempts were made to react all of the urea and to minimize the formation of SDMU. The two reactor system provided may assist in achieving this goal.

After the MMU has formed it is pumped (A-9) to a stripper tower (118) where unreacted MMA and NH_3 are removed under vacuum using steam as the inert gas. (Although a vacuum system is shown, a pressure system, perhaps at 15-30 psig would work as well and could operate with warmer cooling water). The overhead from the stripper H_2O , NH_3 /MMA goes to the separation tower (122) and the MMA is reclaimed for reuse. The ammonia would be recovered in aqueous solution.

Since ammonia in the solution decreases the MMH yield the stripped MMU solution (A-12) should have less than 30 ppm ammonia before being sent to the next section of the plant; the MMH Production Section.

4.3 MMH Production

In this section of the plant the MMU is reacted with NaOCl/NaOH to form the crude MMH solution. The process flow diagram is shown in Figure 13.

The MMU stream is filtered and gelatin added before entering the bleach reactors. In the verification studies some uncharacterized sludge

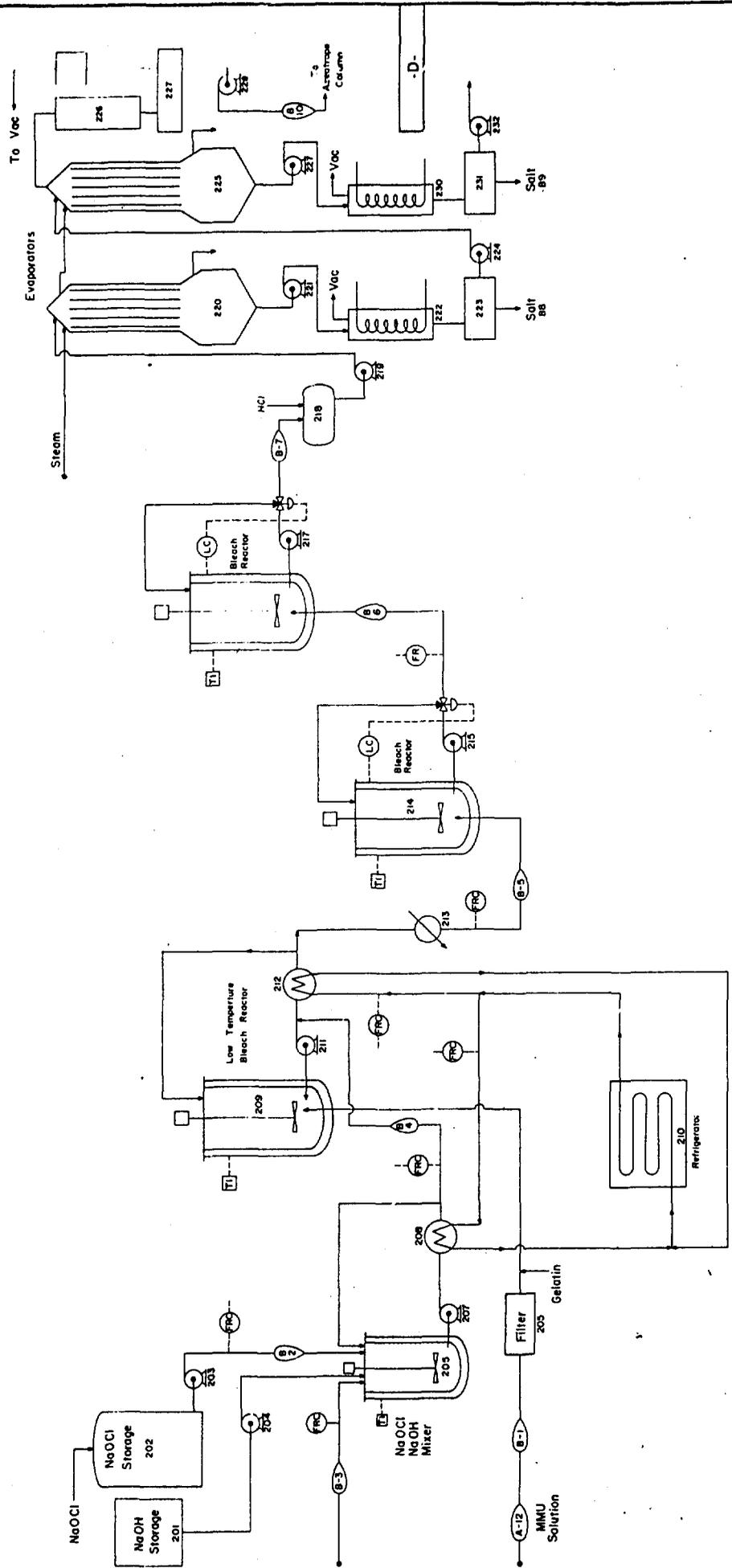


Fig. 13 MMH PRODUCTION SYSTEM

DATE	REVISIONS BY	REVISIONS

IIT RESEARCH INSTITUTE
 TECHNOLOGY CENTER
MMH PRODUCTION SYSTEM

NO.	DESCRIPTION	DATE	BY	CHKD.	APPROVED
1	AS SHOWN				
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					
25					
26					
27					
28					
29					
30					
31					
32					
33					
34					
35					
36					
37					
38					
39					
40					
41					
42					
43					
44					
45					
46					
47					
48					
49					
50					
51					
52					
53					
54					
55					
56					
57					
58					
59					
60					
61					
62					
63					
64					
65					
66					
67					
68					
69					
70					
71					
72					
73					
74					
75					
76					
77					
78					
79					
80					
81					
82					
83					
84					
85					
86					
87					
88					
89					
90					
91					
92					
93					
94					
95					
96					
97					
98					
99					
100					

(approximately 0.1 g/liter) was noted in this solution. The MMU was prepared in 316 stainless steel reactors and may have been contaminated by iron. Gelatin was added to prevent decomposition of MMH due to the presence of dissolved iron.

NaOCl, 12-15% Cl, is received by tank truck and stored (202). NaOH is returned from the caustic recycle (B-3) section and/or received as a 50 wt% solution. For best yields, the NaOCl/NaOH must be mixed and cooled before reacting with MMU. Mixing of NaOCl/NaOH is accomplished in a jacketed tank (206) equipped with a pump-around external titanium heat exchanger (208). The temperature is kept at about 0°C by a refrigeration system (210).

MMU and the NaOCl/NaOH react at 0-5°C to form the chlorourea in a jacketed stirred reactor (209) which is equipped with a pump-around heat exchanger system. This reaction is fast (less than 5 min) and the process can be operated continuously.

The reaction mixture (B-5) is rapidly brought to 80°C (heat exchanger 213) and MMH is formed in two reactors in series (214 and 216). Degassing due to the decomposition occurs, primarily in the first reactor.

The crude MMH product (B-7) (about 2-3% MMH) which contains NaCl, Na₂CO₃, NaOH, HH, and probably some light ends is sent to the evaporators (220) (225) where the water/MMH is evaporated and the solids removed by centrifuges (223) (231). The salt cake (B-8 and B-9) is sent to the waste treatment section. A two stage evaporation (220-225) appears necessary to recover most (99 + %) of the MMH. In the verification studies the salt from the second stage evaporation contained about 1% by weight hydrazine hydrate.

The condensate from the evaporators contains the 400 lbs of MMH in a total stream of 14,716 lbs (B-10).

4.4 MMH Purification

The MMH purification system is shown in Figure 14.

The crude MMH product (about 3% MMH in water, C-1) is sent to a surge tank (300) and then to the azeotropic distillation column (301). In this column the MMH concentration is increased to about 40 wt% at the bottom

of the column. The column is designed to produce "clean" water, less than 10 ppm MMH, as overhead. Since the separation factor for the system is relatively high it may be possible to operate the column with an overhead concentration of less than 0.1 ppm MMH in the water. Some light ends (possibly methanol) and ammonia from decomposition would be expected in this water. The light ends are removed by a simple purge system (308, 309, 312) and the product (bottoms at about 40 wt% MMH, C-7) is sent to the extractive distillation column (314).

The extractive distillation is conducted using 50 wt% NaOH (C-8) to suppress the vapor pressure of the water. The overhead product (C-10) is 99 + wt% MMH and is sent to product storage. The still bottoms contain NaOH, H₂O, Hz, and probably some decomposition products. The column should be designed for little or no (less than 0.5%) MMH in the still bottoms.

The caustic (C-11) used for extractive distillation is reconstituted to 50 wt% in an evaporator (320). During the evaporation any remaining Hz and MMH come over with the vapors and are concentrated to close to the 40 wt% MMH azeotrope by feeding the vapors to a fractionation column (322). The overhead from this column is pure water (C-14) and is returned to the process. The bottoms which contain MMH and Hz and water (C-16) are fed to a small extractive distillation column (329) where Hz and MMH are separated in a refining column (335). While the separation appears somewhat complex it is required to remove the Hz from the system. If the pilot plant could demonstrate the reaction of all of the urea to MMU the formation of Hz would be minimized and this separation system could be avoided.

4.5 Waste Treatment

The major waste product is NaCl which is contaminated with traces of Hz and MMH. This waste is removed during the evaporation/centrifugation process and pilot studies indicate it will contain relatively low concentrations of water. Some consideration was given to the installation of a sodium hypochlorite generating plant which would use this waste as a feed. This plant is relatively complex and requires a major capital expenditure.

In view of these factors it was decided that a better approach would be to install an incinerator to heat the by-product salt to a temperature sufficient to insure removal of any contaminants.

Such an incinerator was estimated to cost \$400,000 and have a fuel cost of \$0.03/lb salt treated. Solid waste disposal costs at the plant location were estimated at \$0.05/lb. Thus the disposal cost of the wet waste salt was estimated as \$0.08/lb salt or \$1.60/lb MMH.

Most water will be recycled. Water entering the plant with NaOCl amounts to about 10 lbs water per lb MMH. The excess water could be used in the cooling tower provided it does not represent a health or safety hazard. No provision was made for cost of treating this water.

Vent gases are assumed to be of very low volume and would be incinerated in the by-product salt incinerator.

Some NaOH may remain in the bottoms stream of the evaporator and contaminate the salt. No provision was made to treat this NaOH.

No provision was made to treat the NaOH purge stream from the extractive distillation. This purge is necessary to avoid build-up of concentrations of hazardous compounds. If the purge is relatively small it may be neutralized by the CO₂ in the flue gas of the incinerator.

5. PRELIMINARY COST ESTIMATE

A preliminary cost estimate can be made on the basis of the cost of purchased equipment, raw materials, and labor. Such an estimate has been developed for a MMH plant rated at a capacity of 400 lbs/hr.

5.1 Purchased Equipment

Brief specifications and cost of individual equipment items are given in the Appendix. These costs were based on published literature and data in IITRI files from previous studies. Costs are as of November 1977. The installed equipment costs for the three major sections of the plant are:

MMH Production	\$ 239,000
MMH Production	970,000
MMH Production	291,000
	<hr/>
	\$1,500,000

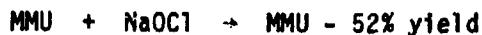
5.2 Total Capital Costs

Purchased equipment can be used as a basis for estimating the total capital cost of the plant. Since this is a very small plant some costs, such as instrumentation, represent a higher proportion of the total than they would in a large scale chemical plant. Total capital costs are presented in Table 5-1. These costs were charged against 6-1/2 years' production at 2×10^6 lb/yr or

$$\frac{\$9,550,000}{6.5 \times 2 \times 10^6} = \$0.734/\text{lb MMH}$$

5.3 Raw Materials Costs

Raw materials costs are primarily based upon two reactions



Laboratory yields of MMU were about 65% whereas the pilot plant verification yields were about 80%. A portion of this difference may be due to changes in the analytical procedures and part may be due to the better

Table 5-1 Estimated Capital Costs

Purchased equipment, installed	\$1,500,000
Instruments + controls, installed	300,000
Piping	600,000
Electrical	400,000
Buildings	500,000
Site improvements, facilities	1,200,000
Services	800,000
Land	-0-
Incinerator	500,000
Unspecified equipment	400,000
Site preparation	1,200,000
	<hr/>
	\$7,400,000
Engineering and supervision	600,000
Construction expense	550,000
Contractors fee	250,000
Contingency	750,000
	<hr/>
	\$9,550,000

agitation and temperature control of the pilot plant reactor. A yield of 70% has been assumed for the cost calculation, further pilot plant work may result in the yield of 85-90%.

Conversion of MMU to MMH by the bleach reaction is a complex series of reactions and laboratory yields of 52% were obtained as a result of a statistical series of experiments. This yield could not be duplicated in the verification runs and the reason for the lower yield was not ascertained. A major difference was the use of glass reactors in the laboratory and stainless steel reactors in the pilot plant. Yield in the verification runs was 41.1%; a yield of 52% was assumed for the cost estimate. Quantities of raw materials necessary for 400 lb/hr production are shown in Table 5-2.

Cost of the raw materials were taken as of Fall 1977 from the Chemical Marketing Reporter and a quotation on NaOCl delivered in 4,000 gal tank trucks to Chicago. These costs are given in Table 5-3.

5.4 Cost of Labor

The cost of labor is shown in Table 5-3.

Maintenance is assumed to be 6% of the plant cost or \$573,000/yr (or \$0.286 lb MMH at a production of 2,000,000 lbs/hr).

Miscellaneous plant expense is estimated at \$200,000/yr or \$0.10/lb of MMH.

5.5 Utility Costs

Steam economy will be highly dependent upon the ability to make good yields and relatively good, say 4% MMH concentrations. There are some opportunities for steam savings, however, control difficulties may cancel any steam savings. No special steam conservation measures were considered in the cost estimate. The steam usage was estimated at 70 lbs steam per lb MMH. Steam cost was estimated at \$3.50/1000 lb or 0.245/lb MMH. Electrical power was estimated to cost \$0.02 kw-hr or \$0.05/lb MMH.

5.6 Waste Treatment

The major waste steam is NaCl which is generated at the rate of about 8,000 lbs/hr. This salt will be heated to 1500°F to insure that it is free of contamination. Cost of heating was estimated at \$0.03/lb MMH. Cost of disposal was estimated at \$0.05/lb salt or \$1.00/lb MMH.

Table 5-2 Quantities and Costs of Raw Materials

	<u>Urea</u>	<u>MMA</u>	<u>NaOC1</u>	<u>NaOH</u>
1b mole/1b mole MMH	2.74	2.74	2.88	6.92
1b/1b MMH	3.56	1.84	4.63	6.62
1b/400 1b MMH	1424	736	1852	2648
Cost, \$/lb	.08	.30	.128	.08
Cost, \$/lb MMH	0.085	0.552	.593	0.554
Total Raw Material, \$/lb MMH	1.984			

Table 5-3 Labor Costs

(Production 400 lbs/hr, 9600 lbs/day)

<u>Type</u>	<u>Number per shift</u>	<u>Wage \$/hr</u>	<u>Shifts per day</u>	<u>Cost per day</u>
Operators	8	7.00	3	1,344
Chemist	1	10.00	3	240
Supervisors	1	12.00	3	288
Plant Manager	1	20.00	1	160
			Total	<u>2,032</u>
		Salary related costs, 30%		607
				<u>2,639</u>
		Overhead 150%		3,944
				<u>6,583</u>
		Cost per lb MMH		.686

5.7 Cost Summary

A summary of the cost for MMH is given in Table 5-4. The estimated cost of \$7.06/lb is believed to be accurated to \pm 20% based on the process and yields as stated.

6. SUMMARY AND RECOMMENDATIONS

Production of MMH via the urea process is technically feasible. The relatively low yield in the bleach reaction results in large amounts of NaCl which presents a disposal problem.

A preliminary estimate of the cost of MMH is 7.06/lb this is believed to be accurate to \pm 20%.

Production of UDMH via the urea process is technically feasible and may be economically attractive. High yields result in good production with reasonable waste generation.

One area not adequately addressed during the program was the optimization of the bleach reaction for formation of MMH. All studies were conducted with a simple batch reactor under a statistically designed set of experiments. This reaction appears to be suitable for a continuous reactor system which may result in higher yields.

Further process design work is required to more completely define the vapor/liquid equilibrium of the MMH/water system and the MMH/NaOH water system and the wastewater treatment system.

Table 5-4 Summary of Costs for MMH Based on
Production Rate of 400 lbs/hr

<u>Cost Element</u>	<u>Amount \$/lb MMH</u>
Capital costs	0.734
Raw Material	1.984
Burden (40 %)	.794
Labor	.686
Maintenance	.286
Plant Expense	.100
Steam	.245
Electrical power	.050
Waste treatment	1.030
	<hr/>
Total cost of production	5.909
Administrative overhead 24%	.341
Total cost of manufacture	6.250
Profit (13 %)	.812
	<hr/>
	7.062

REFERENCES

- Coughling, R.W., I & EC Product Research Division 8 (1), 12-23 1969.
- Hoke, B., Decontamination and Purification of Waste Water Containing Hydrazine, Dimethyl Hydrazine and Nitrogen Oxides, German Patent No. 1,517,634, August 30 1973.
- Kobe, H.H. and J.J. McKetta Jr., Editors. Advances in Petroleum Chemistry Series, Interscience Publications, Inc., NY, 1959. See Chapter 9, Nicolaisen, B.H., R.C. Harshman and C.C. Clark, "Commercial Production of Hydrazine". (all authors employed by Olin Mathieson Chemical Corp.)
- Lum, D.W. and Mador, I.L., Preparation of N-Substituted Hydrazine Derivatives, U.S. Patent 2,917,545, assigned to National Distillers & Chemical Corp., New York, NY December 15, 1959
- Shaw, W.H.R., and J.J. Bordeaux, The Decomposition of Urea in Aqueous Media, J. Chem. Soc. 77,4729 (1955).
- Verzino, W.J. Activated Carbon Treatment of UDMH Wastewater. Internal Memo 76-4050-C & D-13 September 17, 1976
- Verzino, W.J. Activated Carbon Treatment of UDMH Wastewater. Internal Memo 76-4050-CP-1, August 27, 1976
- Yanova, Emel G.I., et al., Study of the Kinetics and Mechanism of the Heterogeneous Oxidation of Dimethylhydrazine by Ozone ZH.Fiz.KHIM. 51 (1) 85-8. 1977

APPENDIX A
EQUIPMENT SPECIFICATIONS
SECTION I - MMU PRODUCTION

Unit Number and Name: 101 - Urea Receiving Hopper

Function: To store urea for 10 working days of capacity

Specifications:

Type: conical bottom

Capacity: 180,000 lbs urea, approximately 4,000 ft³

Material of construction: mild steel

Use tanks 12 ft diameter by 35 ft high

Assume urea is delivered in tank truck which can feed top of storage tank by self-contained pneumatic conveyor.

Estimated Cost:

Purchased cost: \$16,800

Installed cost: 22,500

Unit Number and Name: 102 - Screw Conveyor

Function: To feed urea pellets to weigh scale

Specifications:

Type: horizontal

Capacity: 16 ft long x 6 in. diameter

Material of construction: carbon steel approximately 760 lb urea/hr
(12 ft³/hr)

Utilities:

Electricity: 0.746 Kw

Estimated Cost:

Purchased cost: \$6,000

Installed cost: 7,500

Unit Number and Name: 103 - Batch Weight Tank

Function: To weigh urea for batch make-up

Specifications:

Capacity: 2,000 lbs

Material of construction: carbon steel

Estimated Cost:

Purchased cost: \$ 7,000

Installed cost: 10,000

Unit Number and Name: 104 - Batch Make-up Tank

Function: To dissolve urea in water and mix with the recycle MMA solution
2 tanks required.

Specifications:

Type: conical
Capacity: 250 gal
Agitation: Mechanical seal
Material of construction: 304 stainless steel
Design Pressure: 100 psi
Steam sparger for heating

Utilities:

Steam: 60,000 Btu/hr
Electricity: 1 kw

Estimated Cost:

Purchased cost: \$16,000 each
32,000 total
Installed cost: 40,000 total

Unit Number and Name: 105 - Pump

Function: To pump urea solution from make up tank

Specifications:

Type: centrifugal

Capacity: 10 gpm

Material of construction: 304 stainless steel

Design temperature: 250°F

Design pressure: 150 psi

Utilities:

Electricity: 1 Kw

Estimated Cost:

Purchased cost: \$ 600

Installed cost: 1,200

Unit Number and Name: 106 - Reactor Feed Tank (2 required)

Function: To dissolve anhydrous MMA in aqueous urea solution

Specifications:

Type: conical

Capacity: 500 gal

Agitation: double mechanical seal

Jacketed: yes

Material of construction: 304 stainless steel

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 70 - 100°F

Operating pressure: 5 - 25

Utilities:

Cooling water: 70°F, 10 gpm

Electricity: 1 Kw

Estimated Cost:

Purchased cost: \$15,000

Installed cost 18,000

Total for 2: 36,000

Unit Number and Name: 107 - Pump

Function: To pump anhydrous MMA from tank car into storage tank

Specifications:

Type: positive displacement

Capacity: 5 gpm

Material of construction: carbon steel

Operating Conditions:

Operating temperature: 75°F

Operating pressure: 50 psi

Utilities:

Electricity: 3 Kw

Estimated Cost:

Purchased cost: \$2,500

Installed cost: 3,500

Unit Number and Name: 108 - Storage Tank

Function: Receive and store anhydrous MMA from tank car or tank truck

Specifications:

Type: horizontal ASME code pressure vessel

Capacity: 72,000 lb MMA

Material of construction: carbon steel

Operating Conditions:

Operating temperature: 75°F

Operating pressure: 100 psig, maximum

Others: designed for full vacuum and with safety relief valves

Estimated Cost:

Purchased cost: \$14,000

Installed cost: 17,500

Unit Number and Name: 109 - Pump

Function: To pump anhydrous MMA from storage tank to batch tank

Specifications:

Type: positive displacement

Capacity: 5 gpm

Material of construction: carbon steel

Operating Conditions:

Operating temperature: 75°F

Operating pressure: 50 psi

Utilities:

Electricity: 3 Kw

Estimated Cost:

Purchased cost: \$2,500

Installed cost: 3,500

Unit Number and Name: 110 - MMA Batch Tank

Function: To make up batch of MMA

Specifications:

Type: conical

Capacity: 500 gal

Material of construction: carbon steel

Design pressure: 100 psi

Operating condiftons:

Operating temperature: 75°F

Operating pressure: 50 psi

Estimated Cost:

Purchased cost: \$3,000

Installed cost: 4,200

Unit Number and Name: 111 - Transfer Pump

Function: Transfer urea/MMA solution to reactor

Specifications:

Type: positive pressure (Moyno)

Capacity: 10 gpm

Material of construction: 304 stainless steel

Design temperature: 100°F

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 75°F

Operating pressure: 130 psi

Utilities:

Electricity: 2 Kw

Estimated Cost:

Purchased cost: \$2,000

Installed cost: 4,000

Unit Number and Name: 112 - Pressurized Reactor

Function: Reactor for MMU production

Specifications:

Type: conical

Capacity: 500 gal

Agitation: double mechanical seal

Jacketed: yes

Material of construction: 304 stainless steel

Design pressure: 300 psi

Operating Conditions:

Operating temperature: 250°F

Operating pressure: 130 psig

Utilities:

Steam: 100 psig (800 lbs/hr)

Electricity: 3 Kw

Estimated Cost:

Purchased cost: \$18,000

Installed cost: 21,000

Unit Number and Name: 113 - Pump

Function: To pump MMA to make-up tank

Specifications:

Type: positive displacement

Capacity: 5 gpm

Material of construction: carbon steel

Operating Conditions:

Operating temperature: 75°F

Operating pressure: 50 psi

Utilities:

Electricity: 3 Kw

Estimated Cost:

Purchased cost: \$2,500

Installed cost: 3,500

Unit Number and Name: 114 - Pressurized Reactor

Function: Reactor for MMU production

Specifications:

Type: conical

Capacity: 500 gal

Agitation: double mechanical seal

Jacketed: yes

Material of construction: 304 stainless steel

Design pressure: 300 psi

Operating Conditions:

Operating temperature: 250°F

Operating pressure: 130 psi

Utilities:

Steam: 30 psi

Electricity: 3 Kw

Estimated Cost:

Purchased cost: \$18,000

Installed cost: 21,000

Unit Number and Name: 115 - Pump

Function: To transfer MMU solution to hold tank

Specifications:

Type: centrifugal

Capacity: 10 gpm

Material of construction: 304 stainless steel

Design temperature: 250°F

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 250°F

Operating pressure: 130 psi

Utilities:

Electricity: 1.5 Kw

Estimated Cost:

Purchased cost: \$ 600

Installed cost: 1,200

Unit Number and Name: 116 - Hold Tank

Function: To serve as a feed tank for stripper

Specifications:

Type: conical

Capacity: 500 gal

Agitation: yes

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 75°F

Operating pressure: 25 psi

Utilities:

Cooling water: 50 gpm

Electricity: 2.5 Kw

Estimated Cost:

Purchased cost: \$4,000

Installed cost: 6,000

Unit Number and Name: 117 - Transfer Pump

Function: Feed to stripper

Specifications:

Type: centrifugal pump

Capacity: 10 gpm

Material of construction: 304 stainless steel

Design temperature: 100°F

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 75°F

Operating pressure: 25 psi

Utilities:

Electricity: 1.5 Kw

Estimated Cost:

Purchased cost: \$ 600

Installed cost: 1,200

Unit Number and Name: 118 - Stripping Column

Function: To remove ammonia and MMA from MMU solution

Specifications:

Type: Bubble cap column

Diameter: 1 ft

Number of trays: 10

Tray spacing: 18 in.

Height: 15 ft

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 150°F

Operating pressure: 30 psi

Utilities:

Steam: 500 lb/hr at 14.7 psi

Estimated Cost:

Purchased cost: \$6,000

Installed cost: 8,000

Unit Number and Name: 119 - Condenser

Function: Condense NH₃ and MMA

Specifications:

Type: Fixed tube sheet

Capacity: 50 ft

Material of construction: carbon steel/stainless steel

Design pressure: 30 psig

Utilities:

Cooling Water: 30 gpm

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 120 - Hold Tank

Function: Reflux hold tank

Specifications:

Type: vertical

Capacity: 50 gal

Agitation: no

Jacketed: no

Material of construction: 304 stainless steel

Cover: yes

Estimated Cost:

Purchased cost: \$200

Installed cost: 300

Unit Number and Name: 121 - Transfer Pump

Function: Feed MMA/NH₃ distillation column

Specifications:

Type: centrifugal pump

Capacity: 10 gpm

Material of construction: 304 stainless steel

Design temperature: 100°F

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 150°F

Operating pressure: 25 psi

Utilities:

Electricity: 1 Kw

Estimated Cost:

Purchased cost: \$ 600

Installed cost: 1,200

Unit Number and Name: 122 - NH₃/MMA Fractionation Column

Function: Separate NH₃ from MMA and return MMA to system

Specifications:

Type: bubble cap column

Diameter: 1 ft

Tray spacing: 1 ft

Number of trays: 10

Height: 18 ft

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 25 - 65°C

Operating pressure: 30 psi

Utilities:

Steam: 200,000 Btu/hr

Estimated Cost:

Purchased cost: \$6,000

Installed cost: 8,000

Unit Number and Name: 123 NH₃ Condenser

Function: Condenser on NH₃/MMA separating column

Specifications:

Type: fixed tube sheet

Capacity: 50 ft²

Material of construction: carbon steel and stainless steel

Operating Conditions:

Operating temperature: 80°F

Operating Pressure: 150 psi

Utilities:

Cooling Water: 80 gpm

Estimated Cost:

Purchased cost: \$2,000

Installed cost: 3,000

Unit Number and Name: 124 - Hold Tank

Function: Reflux hold tank

Specifications:

Type: vertical

Capacity: 50 gal

Material of construction: 304 stainless steel

Estimated Cost:

Purchased cost: \$200

Installed cost: 300

Unit Number and Name: 125 - Reflux Pump

Function: Return condensed NH₃ to column

Specifications:

Type: positive displacement

Capacity: 15 gph

Material of construction: 304 stainless steel

Design pressure: 500 psi

Operating Conditions:

Operating temperature: 70°F

Operating pressure: 200 psig

Utilities:

Electricity: 1 Kw

Estimated Cost:

Purchased cost: \$2,500

Installed cost: 3,500

Unit Number and Name: 126 - Heater Exchanger

Function: Boiler heater, NH₃/MMA column

Specifications:

Type: fixed tube sheet

Capacity: 50 ft²

Material of construction: carbon steel and stainless steel

Design pressure: 250 psi

Operating Conditions:

Operating temperature: 70°F

Operating pressure: 200 psig

Utilities:

Steam: 200,000 Btu/hr

Estimated Cost:

Purchased cost: \$2,000

Installed cost: 3,000

Unit Number and Name: 127 - Pump

Function: Transfer recycle MMA to reactor

Specifications:

Type: positive displacement

Capacity: 5 gpm

Material of construction: 304 stainless steel

Design pressure: 150 psi

Design temperature: 250°F

Operating Conditions:

Operating temperature: 76°F

Operating pressure: 50 psi

Utilities:

Electricity: 1.5 Kw

Estimated Cost:

Purchased cost: \$ 600

Installed cost: 1,200

Unit Number and Name: 128 - Heat Exchanger

Function: Cool stripped MMU solution

Specifications:

Type: fixed tube sheet

Capacity: 50 ft²

Material of construction: carbon steel and stainless steel

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 150°F

Operating pressure: 30 psig

Utilities:

Cooling water: 80 gpm

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 129 - Holding Tank

Function: To hold MMU solution after stripping

Specifications:

Type: vertical

Capacity: 150 gal

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 75°F

Operating pressure: 15 psi

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 1,500

Unit Number and Name: 130 - Pump

Function: Transfer MMU solution to next operation

Specifications:

Type: centrifugal/motor pump

Capacity: 10 gpm

Material of construction: 304 stainless steel

Design temperate: 70°F

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 76°F

Operating pressure: 15 psi

Utilities:

Electricity: 1.5 Kw

Estimated Cost:

Purchased cost: \$ 600

Installed cost: 1,200

APPENDIX A
SECTION II - MMH PRODUCTION

MMH PRODUCTION SYSTEM

<u>Identification</u>	<u>Description</u>	<u>Purchased Cost</u>	<u>Installed Cost</u>
201.	50% Caustic Supply	\$ 16,000	\$ 26,000
202.	NaOCl Supply	16,000	20,000
203.	Caustic Feed Pump	1,000	2,000
204.	NaOCl Feed Pump	2,000	4,000
205.	Polishing Filter	600	2,000
206.	Mixing Tank	18,000	24,000
207.	Pump	8,000	12,000
208.	Heat Exchanger	20,000	28,000
209.	Chloramine Reactor	18,000	24,000
210.	Refrigeration System	214,000	286,000
211.	Pump	8,000	12,000
212.	Heat Exchanger	20,000	28,000
213.	Heat Exchanger	14,000	19,000
214.	Reactor	39,000	65,000
215.	Pump	6,000	12,000
216.	Reactor	39,000	65,000
217.	Pump	2,000	4,000
218.	Holding Tank	1,500	3,000
219.	Pump	2,000	4,000
220.	1st Stage Evaporator	12,000	17,000
221.	Pump	3,500	5,000
222.	Cooler/Crystallizer	25,000	35,000
223.	Continuous Discharge Centrifuge	63,000	80,000
224.	Transfer Pump	2,000	4,000
225.	2nd Stage Evaporator	12,000	17,000
226.	Condenser	26,800	40,000
227.	Receiver Tank	1,000	2,000
228.	Pump	3,500	5,000
229.	Pump	3,500	5,000
230.	Cooler/Crystallizer	25,000	35,000
231.	Centrifuge	63,000	80,000
232.	Transfer Pump	3,500	5,000
	Total	\$688,900	\$970,000

Unit Number and Name: 201 - 50% Caustic Supply Tank

Function: Hold 10 day supply of 50% Caustic (Based upon 15% make-up)

Specifications:

Capacity: 150,000 gal

Material of construction: carbon steel

Operating Conditions:

Operating temperature: ambient

Operating Pressure: none

Estimated Cost:

Purchased cost: \$16,000

Installed cost 26,000

Unit Number and Name: 202 - NaOCl Supply

Function: Hold 10 day supply of NaOCl (15% Cl)

Specifications:

Capacity: 60,000 gal

Material of construction: fiber re-enforced polyester

Estimated Cost:

Purchased cost: \$16,000

Installed cost: 20,000

Unit Number and Name: 203 - Caustic Feed Pump

Function: Transfer caustic to mix tank

Specifications:

Type: centrifugal

Capacity: 15 gpm

Material of construction: carbon steel

Operating Conditions:

Operating temperature: ambient

Utilities:

Electricity: 2 Kw

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 204 - NaOCl Feed Pump

Function: Transfer NaOCl to mix tank

Specifications:

Type: centrifugal
Capacity: 15 gpm
Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: ambient

Utilities:

Electricity: 2 Kw

Estimated Cost:

Purchased cost: \$2,000
Installed cost: 4,000

Unit Number and Name: 205 - Polishing Filter

Function: Remove any suspended particles

Specifications:

Type: cartridge type

Capacity: 20 gpm

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: ambient

Operating pressure: 20 psi

Estimated Cost:

Purchased cost: \$ 600

Installed cost: 2,000

Unit Number and Name: 206 - Mixing Tank

Function: To mix NaOCl with NaOH at 0°C

Specifications:

Type: closed tank

Capacity: 500 gal

Agitation: yes

Jacketed: yes

Material of construction: glass-lined steel

Operating Conditions:

Operating temperature: 0°C

Operating pressure: atmospheric

Utilities:

Refrigeration: 25 tons/hr 250,000 + Btu/hr

Electricity: 40 Kw

Estimated Cost:

Purchased cost: \$18,000

Installed cost: 24,000

Unit Number and Name: 207 - Pump

Function: To pump the NaOCl/NaOH in unit for external cooling and to feed into next unit

Specifications:

Type: centrifugal
Capacity: 100 gpm, 35 ft head
Material of construction: glass-lined

Operating Conditions:

Operating temperature: 32°F
Operating pressure: 50 psi

Utilities:

Electricity: 30 Kw

Estimated Cost:

Purchased cost: \$ 8,000
Installed cost: 12,000

Unit Number and Name: 208 - Heat Exchanger

Function: Cool NaOH/NaOCl to 0°C

Specifications:

Type:

Capacity: 2,000 ft²

Material of construction: carbon steel and titanium

Operating Conditions:

Operating temperature: 0°C

Operating pressure: 25 psi

Utilities:

Refrigeration: 50 tons/hr (500,000 Btu/hr)

Estimated Cost:

Purchased cost: \$20,000

Installed cost: 28,000

Unit Number and Name: 209 - Chloramine Reactor

Function: To mix MMU with NaOCl and NaOH solution

Specifications:

Type: closed

Capacity: 500 gal

Agitation: yes

Jacketed: yes

Material of construction: glass-lined steel

Operating Conditions:

Operating temperature: -10° to 0°C

Operating pressure: atmospheric

Utilities:

Refrigeration: 25 tons/hr

Electricity: 45 Kw

Estimated Cost:

Purchased cost: \$18,000

Installed cost: 24,000

Unit Number and Name: 210 - Refrigeration System

Function: Cooling for mixing NaOH/NaOCl and the reaction with MMU

Specifications:

Capacity: 150 tons/hr

Utilities:

Cooling water: 50 gpm

Electricity: 100 hp

Estimated Cost:

Purchased cost: \$214,000

Installed cost: 286,000

Unit Number and Name: 211 - Pump

Function: To pump the solution in unit 209 for external cooling and to feed next reaction

Specifications:

Type: centrifugal
Capacity: 100 gpm, 35 ft head
Material of construction: glass-lined
Design temperature: -10°C

Operating Conditions:

Operating temperature: -10°C

Utilities:

Electricity: 30 Kw

Estimated Cost:

Purchased cost: \$ 8,000
Installed cost: 12,000

Unit Number and Name: 212 - Heat Exchanger

Function: To cool the solution in reactor to -10°C

Specifications:

Type: Fixed tubesheet

Capacity: 2,000 ft²

Material of construction: carbon steel and titanium

Operating Conditions:

Operating temperature: 0°C

Operating pressure: 50 psi

Utilities:

Refrigeration: 50 tons/hr

Estimated Cost:

Purchased cost: \$20,000

Installed cost: 28,000

Unit Number and Name: 213 - Heat Exchanger

Function: To heat chloramine solution to 90°C before entering reactor

Specifications:

Type: fixed tubesheet

Capacity: 100 ft²

Material of construction: carbon steel and titanium

Operating Conditions:

Operating temperature: 165°C/90°C

Operating pressure: 50 psi

Utilities:

Steam: 100 psi, 0.4 x 10⁶ Btu/hr

Estimated Cost:

Purchased cost: \$14,000

Installed cost: 19,000

Unit Number and Name: 214 - Reactor

Function: Reactor for bleach reaction at 90°C

Specifications:

Type: closed

Capacity: 2,000 gal

Agitation: yes

Jacketed: yes

Material of construction: glass-lined steel

Operating Conditions:

Operating temperature: 90°C

Operating pressure: atmospheric

Utilities:

Steam: 100,000 Btu/hr

Electricity: 20 hp

Estimated Cost:

Purchased cost: \$39,000

Installed cost: 65,000

Unit Number and Name: 215 - Pump

Function: To pump solution from unit 211 to unit 213

Specifications:

Type: centrifugal

Capacity: 60 gpm, 30 ft head

Material of construction: 304 stainless steel

Design temperature: 250°F

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 100°C

Utilities:

Electricity: 5 hp

Estimated Cost:

Purchased cost: \$ 6,000

Installed cost: 12,000

Unit Number and Name: 216 - Reactor

Function: For bleach reaction at high temperature

Specifications:

Type: closed

Capacity: 2,000 gal

Agitation: yes

Jacketed: yes

Material of construction: glass-lined steel

Operating Conditions:

Operating temperature: 100°C

Operating pressure: atmospheric

Utilities:

Steam: 100,000 Btu/hr

Electricity: 20 hp

Estimated Cost:

Purchased cost: \$39,000

Installed cost: 65,000

Unit Number and Name: 217 - Pump

Function: Transfer crude MMH product to hold tank

Specifications:

Type: centrifugal
Capacity: 60 gpm, 30 ft head
Material of construction: 304 stainless steel
Design temperature: 150°C
Design pressure: 150 psi

Operating Conditions:

Operating temperature: 100°C

Utilities:

Electricity: .5 hp

Estimated Cost:

Purchased cost: \$2,000
Installed cost: 4,000

Unit Number and Name: 218 - Holding Tank

Function: Feed tank for evaporator

Specifications:

Type: closed vertical

Capacity: 500 gal

Heating Coil - 200 ft 1 in. tube

Operating Conditions:

Operative temperature: 100 C

Estimated Cost:

Purchased cost: \$1,500

Installed cost: 3,000

Unit Number and Name: 219 - Pump

Function: Feed pump for evaporator

Specifications:

Type: centrifugal

Capacity: 60 gpm, 30 ft head

Material of constructions: 304 stainless steel

Design temperature: 250°F

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 100°C

Utilities:

Electricity: 5 hp

Estimated Cost:

Purchased cost: \$2,000

Installed cost: 4,000

Unit Number and Name: 220 - 1st Stage Evaporator

Function: Evaporate water to permit salt crystallization

Specifications:

Type: falling film

Capacity: feed 26,000 lbs/hr

Material of construction: 304 stainless steel

Utilities:

Steam: 10,000 lbs/hr

Estimated Cost:

Purchased cost: \$12,000

Installed cost: 17,000

Unit Number and Name: 221 - Pump

Function: Transfer from evaporator to cooling/crystallization tank

Specifications:

Type: positive displacement

Capacity: 40 gpm

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 100°C

Operating pressure: 50 mm Hg(a)

Utilities:

Electricity: 2 hp

Estimated Cost:

Purchased cost: \$3,500

Installed cost: 5,000

Unit Number and Name: 222 - Cooler/Crystallizer

Function: Cool and permit NaCl to crystallize

Specifications:

Type: vertical, conical bottom

Capacity: 1 hr hold-up, 20,000 lbs

Agitation: slow speed

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 100°C

Operating pressure: 50 mm Hg(a)

Utilities:

Cooling water: 30 gpm

Electricity: 2 hp

Estimated Cost:

Purchased cost: \$25,000

Installed cost: 35,000

Unit Number and Name: 223 - Continuous Discharge Centrifuge

Function: Separate salt cake

Specifications:

Type: horizontal basket

Capacity: 2,500 gal/hr 3,000 lbs salt/hr

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 25°C

Operating pressure: ambient

Utilities:

Electricity: 40 hp

Estimated Cost:

Purchased cost: \$63,000

Installed cost: 80,000

Unit Number and Name: 224 - Transfer Pump

Function: Transfer filtrate from centrifuge to second evaporator stage

Specifications:

Type: centrifugal

Capacity: 40 gpm 30 ft head

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 25°C

Operating pressure: ambient

Utilities:

Electricity: 2 hp

Estimated Cost:

Purchased cost: \$2,000

Installed cost: 4,000

Unit Number and Name: 225 - 2nd Stage Evaporator

Function: Evaporate water to permit salt crystallization

Specifications:

Type: falling film

Capacity: feed 26,000 lbs/hr

Material of construction: 304 stainless steel

Utilities:

Steam: 10,000 lbs/hr

Estimated Cost:

Purchased cost: \$12,000

Installed cost: 17,000

Unit Number and Name: 226 - Condenser

Function: Condense vapor from second stage evaporator

Specifications:

Capacity: 500 ft²

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 100°C

Utilities:

Cooling water: 150 gpm

Estimated Cost:

Purchased cost: \$26,800

Installed cost: 40,000

Unit Number and Name: 227 - Receiver Tank

Function: Hold crude MMH/water

Specifications:

Capacity: 500 gal

Material of construction: 304 stainless steel

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 228 - Pump

Function: Pump crude MMH/water out of vacuum receiver

Specifications:

Type: Positive displacement

Capacity: 40 gpm

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: ambient

Utilities:

Electricity: 3 hp

Estimated Cost:

Purchased cost: \$3,500

Installed cost: 5,000

Unit Number and Name: 229 - Pump

Function: Transfer from evaporator to cooling/crystallization tank

Specifications:

Type: positive displacement

Capacity: 40 gpm

Agitation: 40 gpm

Material of construction: 304 stainless steel

Operating Conditions:

Operating pressure: 50 mm Hg(a)

Utilities:

Electricity: 2 hp

Estimated Cost:

Purchased cost: \$3,500

Installed cost: 5,000

Unit Number and Name: 230 - Cooler Crystallizer

Function: Cool and permit NaCl to crystallize

Specifications:

Type: vertical, bottom

Capacity: 1 hr hold-up, 20,000 lbs

Agitation: slow speed

Material of constructions: 304 stainless steel

Operating Conditions:

Operating pressure: 50 mm Hg(a)

Utilities:

Cooling water: 30 gpm

Electricity: 2 hp

Estimated Cost:

Purchased cost: \$25,000

Installed cost: 35,000

Unit Number and Name: 231 - Centrifuge

Function: Separate salt cake

Specifications:

Type: Horizontal basket

Capacity: 2,500 gal/hr 3,000 lbs salt/hr

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 25°C

Operating pressure: ambient

Utilities:

Electricity

Estimated Cost:

Purchased cost: \$63,000

Installed cost: 80,000

Unit Number and Name: 232 - Transfer Pump

Function: Transfer filtrate from second evaporator to first evaporator

Specifications:

Type: centrifugal

Capacity: 40 gpm, 30 ft head

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 25°C

Operating pressure: ambient

Utilities:

Electricity: 2 hp

Estimated Cost:

Purchased cost: \$3,500

Installed cost: 5,000

APPENDIX A
SECTION III - MMH PURIFICATION

MMH PURIFICATION SYSTEM

Identification	Description	Purchased Cost	Installed Cost
300.	Holding tank for MMH solution from evaporator	\$ 2,700	\$ 3,700
301.	Azeotrope column to concentrate MMH to azeotropic	54,000	68,000
302.	Overhead condenser for azeotrope column	6,300	10,000
303.	Decanter for overhead condenser of azeotrope column	3,000	5,000
304.	Reflux pump for azeotrope column	10,000	14,000
305.	Reboiler for azeotrope column	1,000	2,000
306.	Feed pump of extractive distillation column	800	1,600
307.	Heat exchanger for heating	6,300	10,000
308.	Flash drum for light ends removal	10,000	14,000
309.	Single-stage flash with rectification column	12,000	20,000
310.	Pump to remove stripped water from flash drum for reuse	1,000	2,000
311.	Condenser, overhead, for low boiler removal flash	1,000	2,000
312.	Holding tank for overhead condenser of low boiler removal flash	2,000	3,500
313.	Reflux pump, light ends removal flash	500	1,000
314.	Extractive distillation column to purify MMH	10,000	14,000
315.	Overhead condenser for extractive distillation column	1,000	2,000
316.	Decanter for overhead condenser of extractive distillation column	2,000	3,500
317.	Reflux pump of extractive distillation column	800	1,600
318.	Reboiler of MMH extractive distillation column	1,000	2,000
319.	Feed pump of caustic evaporator	800	1,600
320.	Caustic evaporator	20,000	35,000
321.	Centrifugal pump for recovered caustic solution	800	1,600
322.	Fractionation column to concentrate N ₂ H ₄ to azeotropic	8,000	12,000
323.	Condenser of N ₂ H ₄ azeotrope column	1,000	2,000
324.	Decanter of N ₂ H ₄ azeotrope column	2,000	3,000
325.	Centrifugal pump for reflux in N ₂ H ₄ azeotrope column	1,000	2,000
326.	Centrifugal pump for transporting water to the storage tank for internal reuse	1,000	2,000
327.	Centrifugal pump for bottom stream of N ₂ H ₄ azeotrope column	1,000	2,000
328.	Reboiler of N ₂ H ₄ azeotrope column	1,000	2,000
329.	N ₂ H ₄ extractive column	8,000	12,000
330.	Reboiler	1,000	2,000
331.	Centrifugal pump for bottom stream of N ₂ H ₄ extractive column	1,000	2,000

MMH PURIFICATIONS SYSTEM (Continued)

<u>Identification</u>	<u>Description</u>	<u>Purchased Cost</u>	<u>Installed Cost</u>
332.	Condenser of N ₂ H ₄ , extractive column	\$ 1,000	\$ 2,000
333.	Decanter of N ₂ H ₄ , extractive column	2,000	3,000
334.	Centrifugal pump for reflux in N ₂ H ₄ , extractive column	1,000	2,000
335.	Fractionation column to separate MMH from N ₂ H ₄	8,000	14,000
336.	Centrifugal pump for bottom stream of N ₂ H ₄ , refining column	1,000	2,000
337.	Reboiler of N ₂ H ₄ , refining column	1,000	2,000
338.	Condenser of N ₂ H ₄ , refining column	1,000	2,000
339.	Decanter of N ₂ H ₄ , refining column	2,000	3,000
340.	Centrifugal pump for reflux of N ₂ H ₄ , refining column	<u>1,000</u>	<u>2,000</u>
	Total	\$191,000	\$291,000

Unit Number and Name: 300 - Holding Tank

Function: To hold MMH solution in vapor phase before feeding into
azeotropic distillation column

Specifications:

Capacity: 1000 gal

Material of Construction: 304 stainless steel

Operating Conditions:

Operating temperature: 95°C

Operating pressure: 710 mmHg

Estimated Cost:

Purchased cost: \$2,700

Installed cost: 3,700

Unit Number and Name: 301 - Azeotropic Distillation Column

Function: 1. Remove compounds lighter than MMH in the crude MMH stream
2. Reduce water concentration in the crude to approach the
MMH - H₂O azeotrope

Specifications:

Diameter: 5.0 ft
Number and type of trays: 30, bubble cap
Tray spacing: 18 in.
Height: 50 ft
Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 95°C
Operating pressure: 560 mmHg
Pressure drop: 200 mmHg
Reflux ratio (L/D): 0.5

Estimated Cost:

Purchased cost: \$54,000
Installed cost: 68,000

Unit Number and Name: 302 - Condenser

Function: Overhead condenser for azeotropic distillation column

Specifications:

Type: fixed tube sheet

Capacity: 100 ft²

Material of construction: carbon steel and 304 stainless steel

Design Pressure: 150 psi

Operating Conditions:

Operating temperature: 95°C

Operating pressure: 560 mmHg

Utilities:

Cooling water

Estimated Cost:

Purchased cost: \$ 6,300

Installed cost: 10,000

Unit Number and Name: 303 - Hold Tank

Function: For overhead condenser of azeotropic distillation column

Specifications:

Capacity: 150 gal

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 95°C

Operating pressure: 560 mmHg

Estimated Cost:

Purchased cost: \$3,000

Installed cost: 5,000

Unit Number and Name: 304 - Reflux Pump for Azeotrope Column

Function: Return reflux to azeotropic distillation column

Specifications:

Type: centrifugal

Capacity: 35 gpm

Material of construction: 304 stainless steel

Design temperatures: 250°F

Design pressure: 50 ft head

Operating Conditions:

Operating temperature: 95°C

Operating pressure: 560 mmHg

Utilities:

Electricity 8 Kw

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 305 - Reboiler, Azeotropic Distillation

Function: Heat input

Specifications:

Type: fixed tube sheet

Capacity: 200 ft²

Material of construction: carbon steel and 304 stainless steel

Design Pressure: 150 psi

Operating Conditions:

Operating temperature: 95°C

Operating pressure: 560 mmHg

Utilities:

Steam: 9000 lbs/hrs

Estimated Cost:

Purchased cost: \$10,000

Installed cost: 14,000

Unit Number and Name: 306 - Feed pump, Extractive Distillation Column

Function: Feed bottom stream from azeotropic distillation column into extractive distillation column

Specifications:

Type: centrifugal

Capacity: 10 gpm

Material of construction: stainless steel

Design temperature: 250°F

Design pressure: 50 ft head

Operating Conditions:

Operating temperature: 95°C

Operating pressure: ambient

Utilities:

Electricity: 1 Kw

Estimated Cost:

Purchased cost: \$ 800

Installed cost: 1,600

Unit Number and Name: 307 - Heat Exchanger

Function: To superheat the overhead product of azeotropic distillation column

Specifications:

Type: Fixed tube sheet

Capacity: 100 ft²

Material of construction: carbon steel and 304 stainless steel

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 105°C

Operating pressure: 100 psi

Utilities:

Steam: 1200 lbs/hr at 150 psi

Estimated Cost:

Purchased cost: \$ 6,300

Installed cost: 10,000

Unit Number and Name: 308 - Flash Drum

Function: For light ends removal

Specifications:

Type: Horizontal

Capacity: 1000 gal, closed

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 105°C

Operating pressure: 950 mmHg

Estimated Cost:

Purchased cost: \$10,000

Installed cost: 14,000

Unit Number and Name: 309 - Single - Stage Flash with Rectification Column

Function: Remove compounds that boil under 100°C from water stream

Specifications:

Type: Drum with packed column

Diameter: 2 ft

Number and type of trays: 10 ft packed

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 100°C

Operating pressure: 750 mmHg

Reflux ratio (L/D): 3

Estimated Cost:

Purchased cost: \$12,000

Installed cost: 20,000

Unit Number and Name: 310 - Pump

Function: To pump stripped water from flash drum for reuse

Specifications:

Type: centrifugal

Capacity: 30 gpm

Material of construction: 304 stainless steel

Design temperature: 240°F

Design pressure: 50 ft head

Operating Conditions:

Operating temperature: 100°C

Operating pressure: 14.7 psi

Utilities:

Electricity: 1 Kw

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 311 - Condenser

Function: Light ends condenser

Specifications:

Type: fixed tube sheet

Capacity: 50 ft²

Material of construction: carbon steel and 304 stainless steel

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 65°C

Operating pressure: 810 mmHg

Utilities:

Cooling water: 50 gpm

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 312 - Hold tank

Function: Light ends Hold tank

Specifications:

Capacity: 50 gal, closed

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 105°C

Operating pressure: 898 mmHg

Estimated Cost:

Purchased cost: \$2,000

Installed cost: 3,500

Unit Number and Name: 313 - Reflux Pump, Lites Removal

Function: To pump reflux stream back to rectification column

Specifications:

Type: centrifugal
Capacity: 5 gpm
Material of construction: 304 stainless steel
Design temperature: 350°F
Design pressure: 50 ft head

Operating Conditions:

Operating temperature: 65°C
Operating pressure: atmospheric

Utilities:

Electricity: 1 Kw

Estimated Cost:

Purchased cost: \$ 500
Installed cost: 1,000

Unit Number and Name: 314 - Extractive Distillation Column

Function: Extractive fractionation MMH and water with sodium hydroxide

Specifications:

Type: plate column

Diameter: 1 ft

Number and type of trays: 20 bubble cap

Tray spacing: 18 in

Height: 33 ft

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 94°C

Operating pressure: 704 mmHg

Pressure drop: 138 mmHg

Reflux ratio (L/D): 4

Estimated Cost:

Purchased cost: \$10,000

Installed cost: 14,000

Unit Number and Name: 315 - Condenser

Function: To condense the overhead vapor of the extractive distillation column

Specifications:

Type: fixed tube sheet

Capacity: 50 ft²

Material of construction: carbon steel and stainless steel

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 94°C

Utilities:

Cooling water: 100 gpm (1.4 x 10⁵ Btu/hr)

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 316 - Decanter

Function: For overhead condenser of extractive distillation column.

Specifications:

Capacity: 50 gal

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 100°C

Operating pressure: 652 mmHg

Estimated Cost:

Purchased cost: \$2,000

Installed cost: 3,500

Unit Number and Name: 317 - Overhead Reflux Pump of Extractive Column

Function: To pump reflux stream back to extractive column

Specifications:

Type: centrifugal

Capacity: 10 gpm

Material of construction: stainless steel

Operating Conditions:

Operating temperature: 200°F

Utilities:

Electricity: 2 Kw

Estimated Cost:

Purchased cost: \$ 800

Installed cost: 1,600

Unit Number and Name: 318 - Reboiler

Function: Reboiler of MMH extractive column

Specifications:

Type: fixed tube sheet

Capacity: 10 ft²

Material of construction: carbon steel and stainless steel

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 120°C

Operating pressure: 704 mmHg

Utilities:

Steam: 100 psi, 386×10^5 Btu/hr

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 319 - Pump for Caustic Evaporator Feed

Function: To pump bottom product of extractive column to the caustic evaporator

Specifications:

Type: centrifugal

Capacity: 10 gpm

Material of construction: 304 stainless steel

Design temperature: 250°F

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 100°C

Utilities:

Electricity: 1 Kw

Estimated Cost:

Purchased cost: \$ 800

Installed cost: 1,600

Unit Number and Name: 320 - Caustic Evaporator

Function: Concentrate sodium hydroxide to 50% by weight for recirculation
to extraction column

Specifications:

Type: vertical tubes

Capacity: 100 ft²

Material of construction: 316 stainless steel

Operating Conditions:

Operating temperature: 120°C

Operating pressure: 760 mmHg

Utilities:

Steam: 100 psi, 300 lbs/hr

Estimated Cost:

Purchased cost: \$20,000

Installed cost: 35,000

Unit Number and Name: 321 - Pump

Function: To recycle 50% caustic to extractive column

Specifications:

Type: centrifugal

Capacity: 10 gpm

Material of construction: 304 stainless steel

Design temperature: 125°C

Design pressure: 50 ft head

Operating Conditions:

Operating temperature: 100°C

Utilities:

Electricity: 1 Kw

Estimated Cost:

Purchased cost: \$ 800

Installed cost: 1,600

Unit Number and Name: 322 - N_2H_4 , Azeotropic Column

Function: To concentrate N_2H_4 and MMH close to their azeotropic compositions

Specifications:

Type: vertical plate column
Diameter: 1 ft
Number and type of trays: 20 bubble cap
Tray spacing: 18 in
Height: 33 ft
Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: $94^{\circ}C$
Operating pressure: 700 mmHg
Pressure drop: 138 mmHg
Reflux ratio (R/D): .5

Estimated Cost:

Purchased cost: \$ 8,000
Installed cost: 12,000

Unit Number and Name: 323 - Condenser

Function: To condense overhead of N_2H_4 , azeotropic column

Specifications:

Type: fixed tube sheet

Capacity: 10 ft

Material of construction: carbon steel and stainless steel

Design pressure: 150 psi

Operating Conditions:

Operating temperature: $94^\circ C$

Operating pressure: 14.7 psi

Cooling required: 1.47×10^5 Btu/hr

Utilities:

Cooling water: 50 gpm

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 324 - Decanter

Function: For overhead of N_2H_4 Azeotropic column

Specifications:

Capacity: 35 gal

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 118°C

Operating pressure: 14.7 psig

Estimated Cost:

Purchased cost: \$2,000

Installed cost: 3,000

Unit Number and Name: 325 - Pump

Function: To pump recycle stream to N_2H_4 azeotrope column

Specifications:

Type: centrifugal

Capacity: 5 gpm

Material of construction: 304 stainless steel

Design temperature: 250°F

Operating Conditions:

Operating temperature: 240°F

Utilities:

Electricity: 1 hp

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 326 - Pump

Function: To pump water to storage tank

Specifications:

Type: centrifugal

Capacity: 10 gpm

Material of construction: 304 stainless steel

Design temperature: 250°F

Design pressure: 50 ft head

Operating Conditions:

Operating temperature: 100°C

Utilities:

Electricity: 1 hp

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 327 - Pump

Function: To pump the bottom stream of N_2H_4 Azeotropic column

Specifications:

Type: centrifugal

Capacity: 10 gpm

Material of construction: stainless steel

Design temperature: 250°F

Design pressure: 50 ft head

Operating Conditions:

Operating temperature: 100°C

Utilities:

Electricity: 1 Kw

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 328 - Reboiler

Function: Reboiler of N_2H_4 azeotropic column

Specifications:

Type: fixed tube sheet

Capacity: 10 ft²

Material of construction: carbon steel and stainless steel

Operating Conditions:

Operating temperature: 94°C

Operating pressure: 700 mmHg

Utilities:

Steam: 250 lbs/hr

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 329 - N₂H₄ Extractive Column

Function: Fractionate methylhydrazine and hydrazine from water

Specifications:

Type: plate column
Diameter: 1 ft
Number and type of trays: 20 bubble cap
Tray spacing: 18 in
Height: 33 ft
Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 94°C
Operating pressure: 700 mmHg
Pressure drop: 138 mmHg
Reflux ratio (R/D): 1.0

Estimated Cost:

Purchased cost: \$ 8,000
Installed cost: 12,000

Unit Number and Name: 330 - Reboiler

Function: To reboil bottom stream of N_2H_4 extractive column

Specifications:

Type: Fixed tube sheet

Capacity: 10 ft²

Material of construction: carbon steel and stainless steel

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 120°C

Operating pressure: 700 mmHg

Utilities:

Steam: 18,000 Btu/hr

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 331 - Pump

Function: To pump make-up caustic to extractive column

Specifications:

Type: centrifugal

Capacity: 10 gpm

Material of construction: 304 stainless steel

Design temperature: 250°F

Design pressure: 50 ft head

Operating Conditions:

Operating temperature: 100°C

Utilities:

Electricity: 1 Kw

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 332 - Condenser

Function: Condenser, Extractive Distillation Column

Specifications:

Type: fixed tube sheet

Capacity: 10 ft³

Material of construction: carbon steel and stainless steel

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 94°C

Operating pressure: 760 mmHg

Utilities:

Cooling water: 20 gpm

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 333 - Decanter

Function: To hold the overhead of the N_2H_4 extractive column

Specifications:

Capacity: 35 gal

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 91°C

Operating pressure: 88 mmHg

Estimated Cost:

Purchased cost: \$2,000

Installed cost: 3,000

Unit Number and Name: 334 - Reflux Pump of N_2H_4 Extractive Column

Function: To pump reflux stream back to N_2H_4 extractive column

Specifications:

Type: centrifugal

Capacity: 10 gpm

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 250°F

Operating pressure: 50 ft head

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 335 - N₂H₄ and MMH Refining Column

Function: Fractionate methylhydrazine and hydrazine

Specifications:

Type: plate column

Diameter: 1 ft

Number and type of trays: 20 bubble cap

Tray spacing: 18 in

Height: 33 ft

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 94°C

Operating pressure: 700 mmHg

Pressure drop: 138 mmHg

Estimated Cost:

Purchased cost: \$ 8,000

Installed cost: 14,000

Unit Number and Name: 336 - Pump

Function: To pump N_2H_4 to storage tank

Specifications:

Type: centrifugal

Capacity: 10 gpm

Material of construction: 304 stainless steel

Design temperature: 250°F

Design pressure: 50 ft head

Operating Conditions:

Operating temperature: 100°C

Utilities:

Electricity: 1 Kw

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 337 - Reboiler

Function: Reboiler of N_2H_4 refining column

Specifications:

Type: fixed tube sheet

Capacity: 10 ft²

Material of construction: 304 stainless steel

Design temperature: 250°F

Design pressure: 150 psi

Operating Conditions:

Operating temperature: 100°C

Utilities:

Steam: 25,000 Btu/hr

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 338 - Condenser

Function: Condenser, MMH/Hydrazine Column

Specifications:

Type: fixed tube sheet

Capacity: 20 ft²

Material of construction: 304 stainless steel

Design temperature: 250°F

Operating Conditions:

Operating temperature: 100°C

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

Unit Number and Name: 339 - Decanter

Function: To hold the overhead of MMH refining column

Specifications:

Capacity: 35 gal

Material of construction: 304 stainless steel

Operating Conditions:

Operating temperature: 100°C

Estimated Cost:

Purchased cost: \$2,000

Installed cost: 3,000

Unit Number and Name: 340 - Pump

Function: To pump MMH to storage tank

Specifications:

Type: centrifugal

Capacity: 10 gpm

Material of construction: 304 stainless steel

Design temperature: 250°F

Design pressure: 50 ft head

Operating Conditions:

Operating temperature: 100°C

Operating pressure: 14.7 psi

Utilities:

Electricity: 1 Kw

Estimated Cost:

Purchased cost: \$1,000

Installed cost: 2,000

APPENDIX B

Analytical Procedures

MMH, UDMH, and Hz by Solvent
Extraction and Capillary GC

THE ANALYSIS OF HYDRAZINE, MONOMETHYLHYDRAZINE, AND
UNSYMMETRICAL DIMETHYLHYDRAZINE USING GC TECHNIQUES

SUMMARY

The analysis of monomethylhydrazine (MMH), hydrazine (Hz), and unsymmetrical dimethylhydrazine (UDMH) by gas chromatographic (gc) procedures has been refined so that these materials can be assayed by a single analysis without organic solvent extractions, if quick sample turn around is desired. In this procedure, the hydrazine compound reacts with acetone to form a hydrazone derivative. Excess acetone does not interfere with the analysis. Acetone is miscible with the reaction mixture; it is also reactive over a wide pH range making solution pH control during the derivatization step, as in the case of 2, 4-pentanedione, unnecessary. The derivatization and recovery of MMH, UDMH, and Hz is quantitative and linear from trace levels to mg/ml concentrations. Once the derivative is formed, especially if extracted, it is stable up to 30 days. GC analysis using a 60 m OV - 101 glass capillary column and temperature programming from 105°C to 195°C provides good resolution of all the components and internal standards. A sample chromatogram is shown in Figure 1. The gc analysis time for all components is 12 minutes, the last peak being a standard. The use of the organic extraction step in the analysis procedure prolongs the column life and eliminates the need for cleaning the injection port. Over 300 gc analyses using the organic extraction procedures and the autosampler have been made without any machine maintenance.

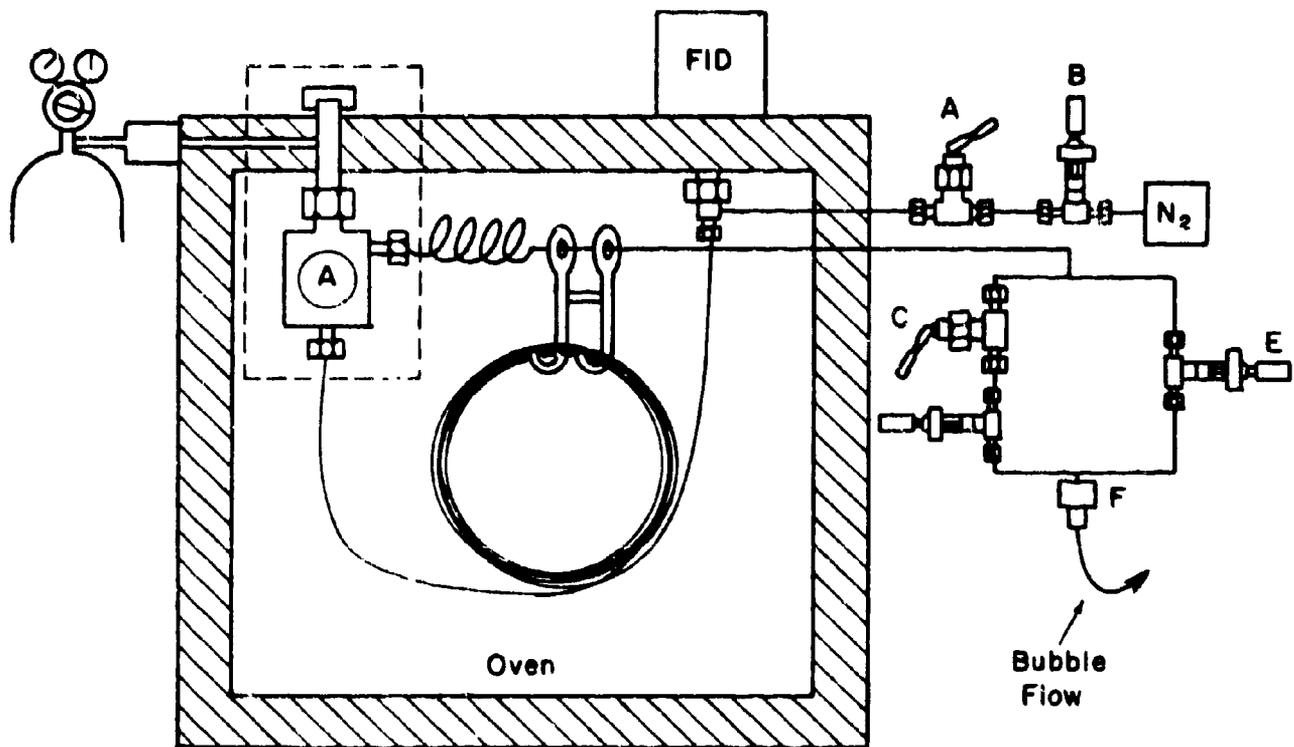


Fig. 1 INSTRUMENT CONFIGURATION FOR USE WITH
GLASS CAPILLARY COLUMN

INTRODUCTION

The quantitative analysis of hydrazine (Hz), and its methyl derivatives by gas chromatographic (gc) procedures have been previously reported by Dee and Webb (1), by Dee (2), and by other workers (3,4,5). While the procedures proposed by Dee offered improvements over previous analytical techniques in reducing the effect of interfering materials and decreasing analysis time, the procedure advanced was not without drawbacks.

The direct analysis procedure outlined by Dee and Webb did not provide sufficient sensitivity for many analytical problems, and column lifetimes were very short. In addition, sample stability prior to analysis and in the gc injection port was a problem. The use of 2,4-pentanedione advanced by Dee (2), to form pyrazole derivatives of Hz and monomethylhydrazine prior to gc analysis improved the sensitivity (3), reduced many of the interfering materials, and decreased problems of sample stability in the gc. But this analytical procedure could not be used to analyze two important methyl derivatives: symmetrical and unsymmetrical dimethylhydrazine (SDMH and UDMH). Furthermore, the sensitivity and recovery were dependent on reaction conditions such as pH and reaction time, while column lifetimes were reduced because reaction mixtures were directly injected into the gc column.

The analysis procedure outlined here is basically a modification of Dee's procedure (2) in which the derivatizing reagent is changed, the derivative is extracted with organic solvents, and glass capillary columns are used for the chromatography. A variety of reagents, including benzaldehyde, cyclohexanone, and acetone, were studied. Several extraction solvents - hexane, benzene, pentane, CHCl_3 , and CH_2Cl_2 - were tried; and a variety of columns and column conditions were used. The analysis procedure outlined in this report was found to be the most satisfactory combination of conditions and reagents for the analysis of Hz, MMH, and UDMH. The analysis of SMDH was not possible by derivation and must be determined independently.

EXPERIMENTAL

Instrumentation. A Hewlett Packard 5840 series gc equipped with both FID and N-P detectors and modified for capillary columns was used to perform the analysis. Each detector has independent gas feeds and can be calibrated and operated independently from the gc console.

The FID was used for all analysis presented in the report unless otherwise indicated. The carrier gas was helium. Nitrogen was used for the make-up gas. A Hewlett Packard model 18824A auto injection system was used to perform all routine analyses.

The instrument modifications made to adapt the system for use with glass capillary (WCOT) columns are shown in Figure 1 and 2. The general instrument configuration is given in Figure 1. All seals between the column and injection liner are made with graphite ferrules. The split adjust configuration allows one fine metering valve to be used to balance the column at a low split ratio. The second valve (routed in parallel through an on/off valve) can be set to produce a second higher split ratio with the same column flow. The column flow and split ratios are dependent on column head pressure, so with a single-stage regulator and the splitter metering valves, the proper column flow and split can be achieved. The column flow was routed through the instrument's flow sensor, but the flow controller was bypassed. The makeup gas was plumbed through both the flow sensor and flow controller. This configuration allows both critical flows, the makeup gas and the splitter flow, to be monitored continuously at the console. The total carrier flow is the sum of the splitter flow in the 0.5 to 1.5 ml/min range. The flow sensor reading can be used to measure the splitter flow, which is at least a factor of 10 higher. This system also allows the instrument to be leak-tested, i.e., if the measured column flow and splitter flow do not equal the flow reading, the system has a leak. The splitter body shown in Figure 2 was obtained from J. & W. Scientific (Orangevale, Cal. 95662) and is based on the design reported by Jennings et al. (6). The splitter uses a $\frac{1}{4}$ in. O.D. glass liner. The I.D. of the liner and the liner packing used is dependent on the total splitter flow. For split ratios of less than 15:1 a 2-mm I.D. liner packed with coated

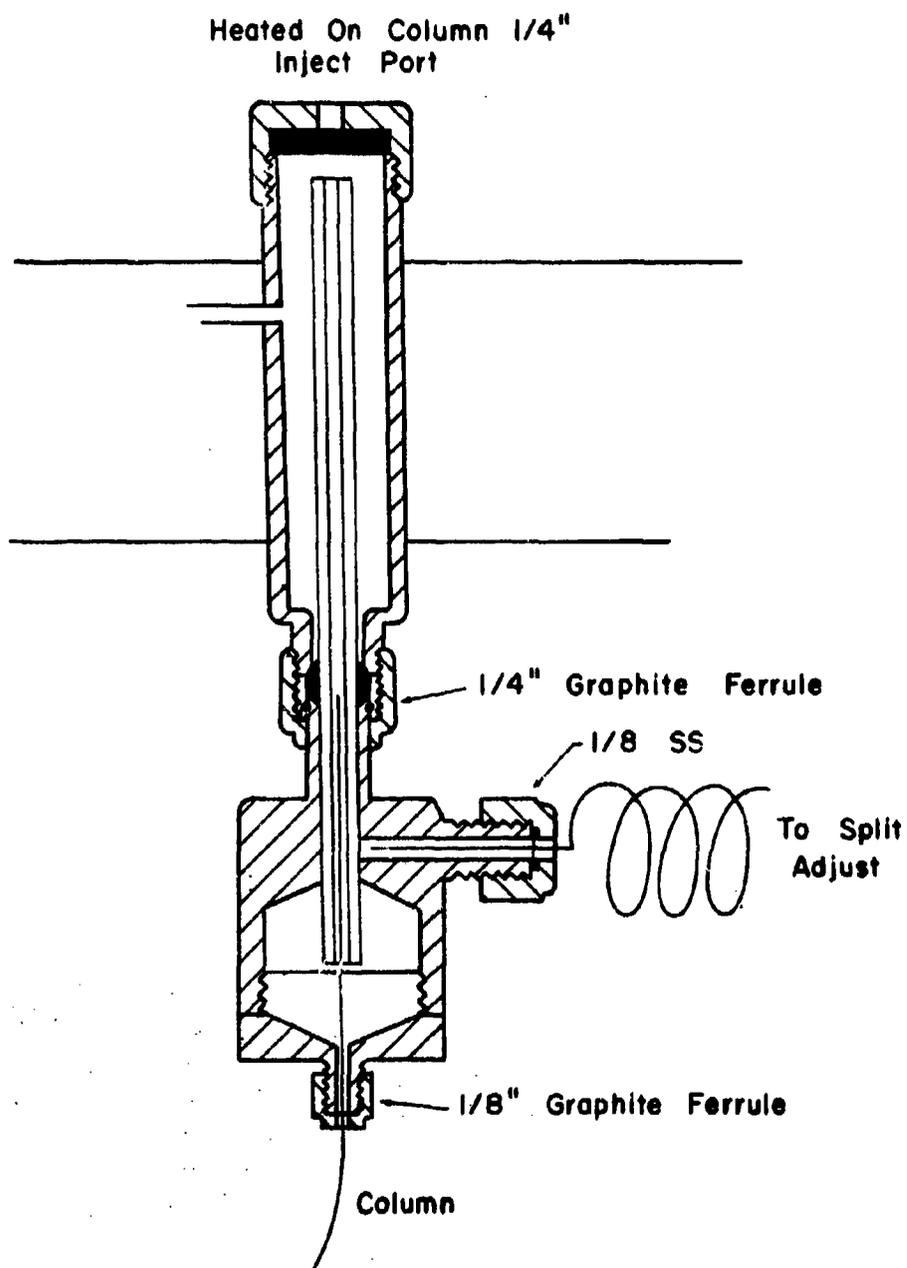


Fig. 2 INJECTION PORT CONFIGURATION FOR USE WITH GLASS CAPILLARY COLUMNS

glass beads is used. For higher split ratios a 4-mm liner packed with glass wool is used. The liners have a restriction at the point where the capillary column is placed to insure proper sample loading on the column. These liners can be obtained from A. A. Pesce Company.

The glass capillary columns were obtained from J. & W. Scientific (Orangevale, Cal. 95662). The reported analysis was performed on a 60-m OV-101 column (J. & W. number G100-OV-101, cost \$275.00). Analysis of the Hz and MMH acetone derivatives were also performed on a 18-m CW20M column obtained from the same source, but the UDMH derivative could not be resolved from the solvent peak.

Reagents. All solvents used were Burdick and Jackson high-purity solvents. The acetone was Baker reagent grade. The hydrocarbon standards were obtained from Poly Science Corporation (Kit No. 21A). The MMH and UDMH were obtained from Aldrich Chemical Company and the Hz from Baker Chemical Company.

Derivatization and Extraction Procedures. The hydrazone standards were prepared by reacting a known amount of each hydrazine (UDMH, MMH, and Hz) with a fivefold excess of acetone in methylene chloride. Completeness of reaction was checked at three concentration levels (100 $\mu\text{g/ml}$, 1000 $\mu\text{g/ml}$, and 10,000 $\mu\text{g/ml}$). Each solution was monitored by gc at 15, 30, 60, and 120 min and 4, 24, and 48 hr to determine completeness of reaction. The reaction product are stable for the 0.1 and 1.0 mg/ml concentrations at 15 min and for the 10 mg/ml concentration at 30 min. The area response for each hydrazine compound was based on the area response of the resulting hydrazone product from reaction. Extraction standards were prepared by adding known amounts of each hydrazine (UDMN, MMH, and Hz) to distilled water to simulate a reaction mixture. A threefold excess of acetone was added and the mixture was shaken on a wrist arm shaker for 15 min (30 min for concentration over 5.0 mg/ml). These samples were either assayed directly or extracted.

The extractions were performed following adjustment of the reaction solution to pH 9.0. A known amount of the reaction mixture (5 ml) was quantitatively transferred to a screw cap vial and twice this volume of CH_2Cl_2 was

added. The desired amount of internal standards was also added (octane and nonane for FID) and the mixture was shaken for 15 min. The organic layer was removed and the extraction repeated a second time without the addition of the standards. The extracts were combined and assayed on the gc. If the N-P detector was used, benzene or hexane were the extraction solvents and nicotine or pyrazol were the internal standards. The reaction mixtures were derivatized and extracted as described above, except water was added to make the acetone miscible when the mixture contained a very high salt content. For samples where the concentration levels of the products were not known 1 ml of acetone was added to every 2 ml of sample. This was extracted twice using an amount of solvent double the total volume of sample plus acetone.

Gas Chromatographic Analysis. The gc analysis conditions for use with the 60-m OV-101 column were as follows:

	<u>Maximum</u>	<u>Setting</u>	<u>Reading</u>
Temp 1	240	105**	105
Time	0.50		
Rate	5.00		
Temp 2	240*	195	
Time 2	10.00		
INJ Temp	350*	250	250
FID Temp	400*	300	300
AUX Temp	350*	300	300
CHT SPD	0.50		
ZERO	10.0		
ATTN 2	7		
FID SGNL	+B		
SLP SENS	1.00		
Area REJ		100	
Flow A	30.00	30.0	(make-up)
Flow B	38.1	38.9	(injector)
<u>Time Function</u>	<u>Value</u>		
3.00 Rate	25.00		
8.00 Attn 2	4		
12.00 Stop			

* Temperature Limits
 ** Temperature Set Points

(The hydrogen flow was 40 ml/min and the air flow was 240 ml/min).

The 5840A is processor-controlled and all major functions can be time-programmed. Therefore, the slope sensitivity (SLP SENS) and temperature programming rates were adjusted periodically to produce the best resolution and the most reproducible integration for each sample series.

The quantitative analysis of the components was accomplished using the 5840 integrator. Two internal standards (ISTDS), normally octane (Cn-8) and nonane (Cn-9), were used at all times. Slope sensitivities that yielded the most reproducible peak integrations were set using standard mixtures of all components. The relative area response factors for the hydrazone derivatives and the IDTDS were periodically recalculated and checked each day with the standard mixtures.

The primary quantitation was accomplished using the Cn-8 standard. Measurements of the Cn-9 standard provided a check on the standards and the analysis. The response of the standards and the sample extracts were found to be stable for up to 30 days without special handling and longer if kept cool and out of light.

RESULTS

Extraction Procedure. Chromatograms of standard mixtures and extracts of aqueous reaction standards of the UDMI, MMH, and Hz derivatives and the Cn-8 and Cn-9 internal standards are given in Figures 3A and 3B, while Figure 4 shows a chromatogram of a typical reaction sample. The column and analysis conditions used produced a $N_{eff} = 32,000$ at a partition ratio (k) = 2.3 for the Hz derivative and $N_{eff} = 18,000$ (k) = 2.5 for the Cn-8 standards. By optimizing analysis conditions, these can be increased by a factor of three. All peaks are symmetrical when the system is operating properly. Some tailing will occur following extensive use because of residue building up in the injection port liner. When tailing is observed, the liner should be cleaned. Some tailing is also found if the glass column ends that are straightened during mounting are not deactivated with a 5 percent CW20M/CH₂Cl₂ solution. In all cases, and analysis conditions produced adequate resolution for identification and quantitation of the components under investigation.

Figure 3. CHROMATOGRAMS OF HYDRAZONE PRODUCTS OF UDMH, MMH, AND HZ

3A. ACETONE DERIVATIVES OF UDMH, MMH, AND HZ IN CH_2Cl_2

3B. EXTRACT OF ACETONE DERIVATIZATION OF UDMH, MMH, AND HZ FROM SIMULATED REACTION MIXTURE

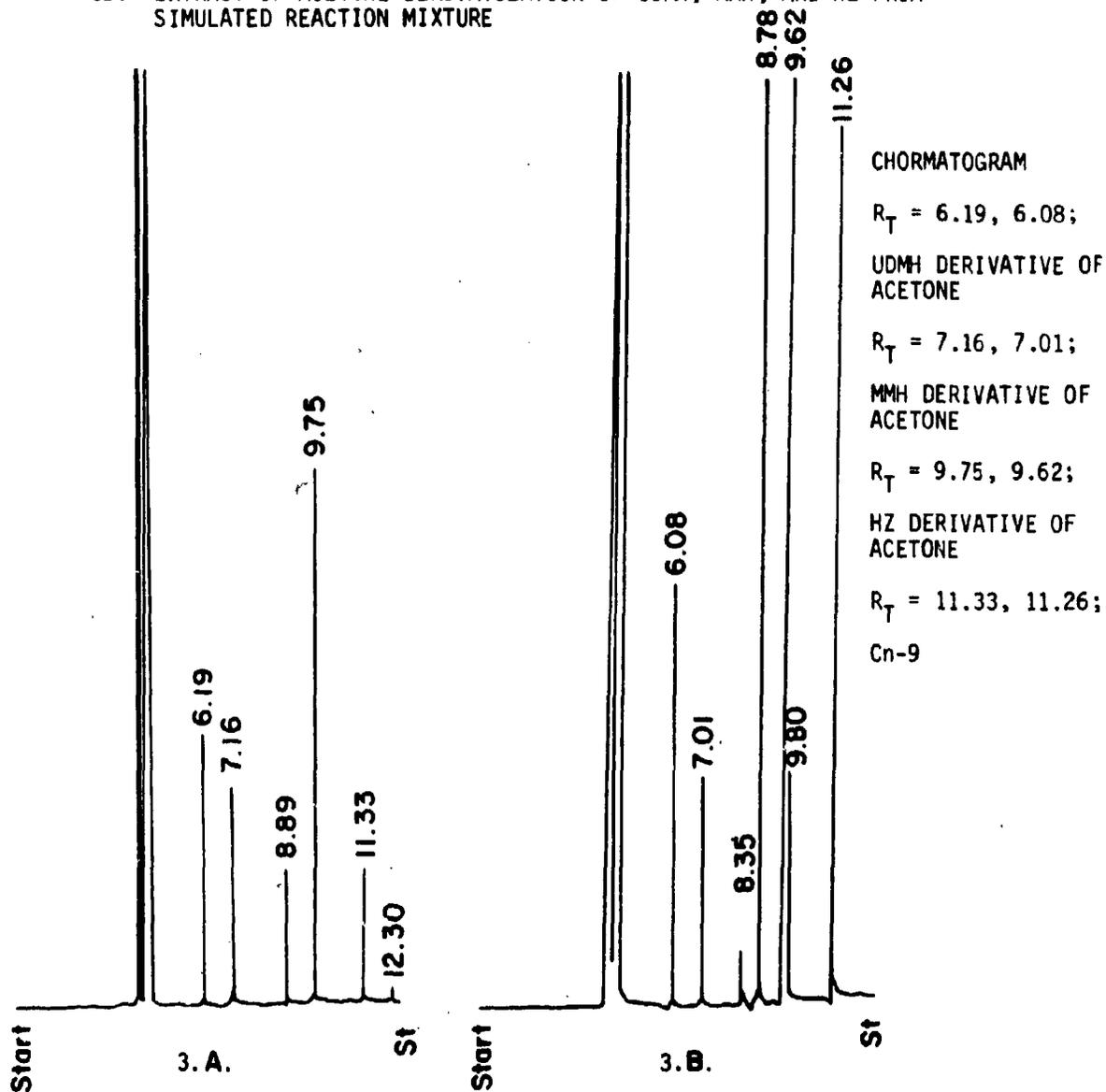
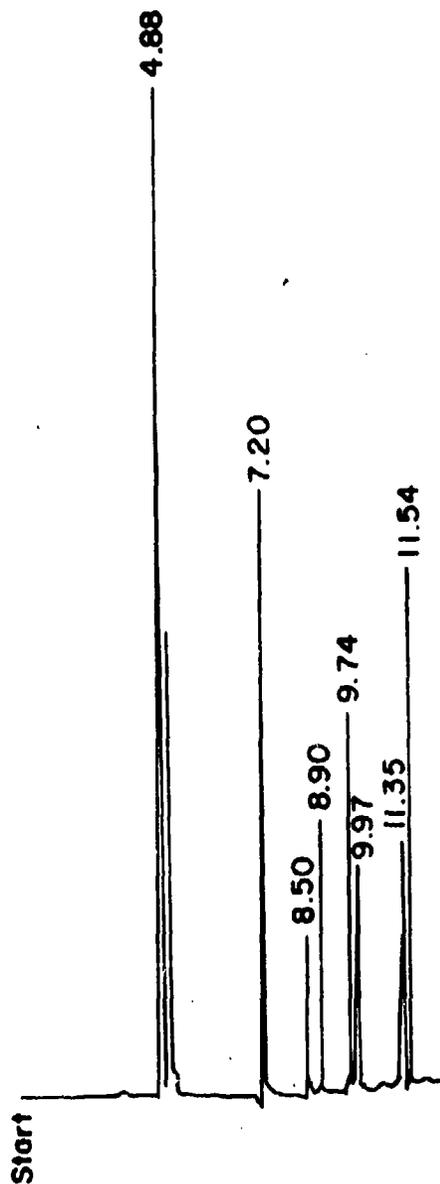


Figure 4. CHROMATOGRAM OF ACETONE DERIVATED
REACTION MIXTURE EXTRACT



SAMPLE

MMH REACTION MIXTURE

CHROMATOGRAM

$R_T = 7.20$; MMH DERIVATIVE

$R_T = 8.90$; Cn-8 STD

$R_T = 9.74$; H₂ DERIVATIVE

$R_T = 11.54$; Cn-9 STD

ALL OTHERS MAJOR PEAKS
ARE REACTION BY-PRODUCTS

The area response data for each component under investigations is given in Table 1. The maximum area that can be quantitatively measured (at signal to noise ratio of 3:1) is approximately 30 area units. The area responses are linear over the concentrations spanned by each split ratio. In practice, samples in similar concentration ranges are grouped and the split and analysis conditions are optimized for that concentration range. For mixtures where the individual components are in widely varying concentrations, the split is set to provide the necessary sensitivity for the lowest concentration component. The integration conditions are then adjusted to accommodate the overload tailing that results in the high concentration components. Standards reflecting this concentration variation are also used.

The recoveries for samples at 0.10 mg/ml and 1.00 mg/ml are 98.3 ± 0.5 percent ($n=10$) for MMH, 96.2 ± 1.2 percent for Hz, and 9.7 ± 1.2 percent for UDMH. The recoveries using two extractions for samples at 10.0 mg/ml are 96.3 ± 1.5 percent ($n=10$) for MMH, 93.0 ± 2.0 percent for Hz, and 91.8 ± 2.1 percent for UDMH. The use of a third extraction increases the recoveries for all components to 98 ± 1.0 percent. The recoveries of the components were the same for both water and the simulated reaction media. The data presented in Figure 5 illustrates the effect of the organic to aqueous ratios of the number of extractions on the recovery of the MMH and Hz derivatives from the simulated reaction media.

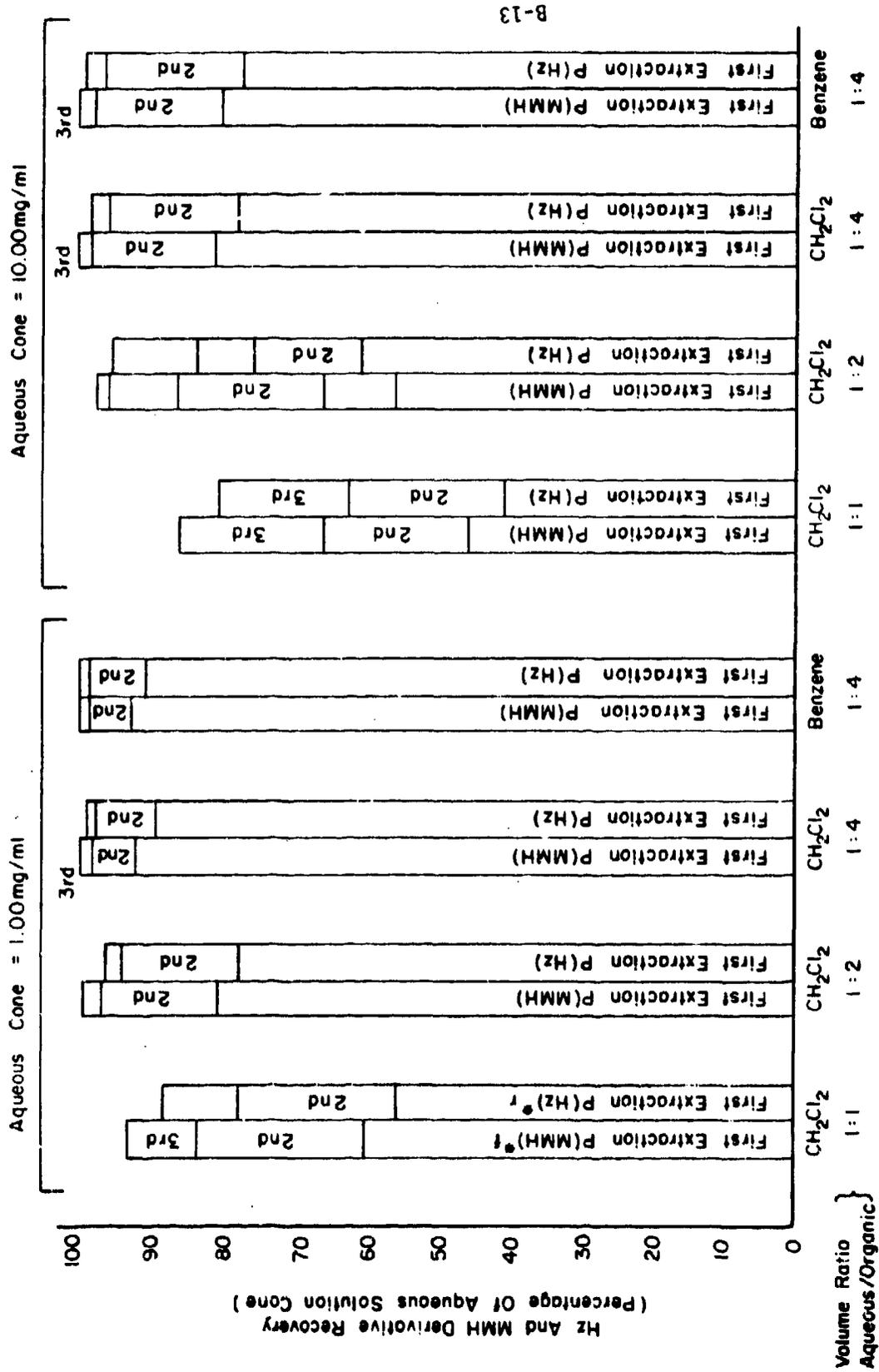
GC Analysis. The maximum sensitivity was achieved at a 5:1 split ratio with a 2 μ l injection using peak height for quantitation instead of integrated area. The lowest detectable concentration (a signal to noise ratio of 3) was approximately 0.5 μ g/ml for a MMH and 0.2 μ g/ml for Hz.

The integrator reproducibility for repeated (autosampler) injections of the sample was better than 1 percent. The reproducibility of the overall analysis procedure was better than 2.5 percent, on the analysis of 30 blind pairs of reaction samples and 10 pooled standards where sample component concentrations are greater than 100 μ g/ml. The error in the overall analysis procedure was the measurement of the total reaction mixture volume and the sample aliquot volume. These generally had a 5-10 percent factor. Thus the

Table 1

AREA RESPONSE FOR ACETONE DERIVATIVES OF
UDMH, MMH, AND HZ

Solution concentration of hydrazine compound ($\mu\text{g/ml}$)	Capillary splitter ratio (split flow column flow)	Area for UDMH hydrazine derivatives (area units) $n=5$	Area for MMH hydrazine derivatives (area units) $n=5$	Area for HZ hydrazine derivatives (area units) $n=5$
1.0	10:1	$7.8 \pm 1.6 \times 10^1$	$7.6 \pm 1.6 \times 10^1$	$1.8 \pm 0.5 \times 10^2$
5.0	10:1	$4.1 \pm 0.5 \times 10^2$	$4.0 \pm 0.5 \times 10^2$	$9.3 \pm 0.4 \times 10^2$
10.0	10:1	$8.3 \pm 0.6 \times 10^2$	$8.1 \pm 0.4 \times 10^2$	$18.8 \pm 0.4 \times 10^3$
50.0	10:1	$4.4 \pm 0.6 \times 10^3$	$4.5 \pm 0.3 \times 10^3$	$9.7 \pm 0.5 \times 10^3$
100.0	10:1	$9.1 \pm 0.5 \times 10^3$	$8.7 \pm 0.3 \times 10^3$	$20.0 \pm 0.4 \times 10^3$
500.0	30:1	$1.7 \pm 0.3 \times 10^4$	$1.5 \pm 0.1 \times 10^4$	$3.6 \pm 0.2 \times 10^4$
1000.0	30:1	$3.5 \pm 0.2 \times 10^4$	$3.2 \pm 0.2 \times 10^4$	$7.4 \pm 0.2 \times 10^4$
1500.0	30:1	$5.2 \pm 0.3 \times 10^4$	$4.9 \pm 0.2 \times 10^4$	$10.1 \pm 0.3 \times 10^4$
2500.0	30:1	$9.1 \pm 0.4 \times 10^4$	$8.9 \pm 0.2 \times 10^4$	$19.8 \pm 0.4 \times 10^4$
5000.0	30:1	$18.2 \pm 0.4 \times 10^4$	$17.7 \pm 0.3 \times 10^4$	$39.2 \pm 0.3 \times 10^4$
5000.0	60:1	$10.8 \pm 0.3 \times 10^4$	$9.4 \pm 0.1 \times 10^4$	$20.0 \pm 0.3 \times 10^4$
7500.0	60:1	$16.0 \pm 0.4 \times 10^4$	$14.5 \pm 0.2 \times 10^4$	$30.1 \pm 0.3 \times 10^4$
10,000.0	60:1	$21.7 \pm 0.3 \times 10^4$	$10.2 \pm 0.2 \times 10^4$	$39.2 \pm 0.2 \times 10^4$



• Methylene Chloride Was The Solvent And The Samples Were Shaken For 10 Min At Each Extraction

Fig. 5 ACETONE REACTION PRODUCT RECOVERIES
 ••P(MMH) = MMH ACETONE REACTION PRODUCT

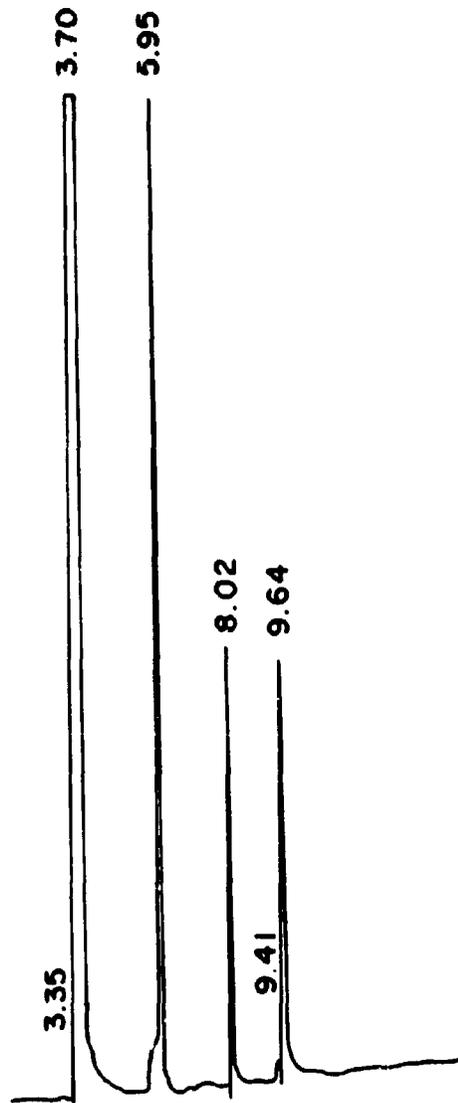
gc analysis procedure was not the limiting factor in the accuracy and reproducibility of the reaction mixture analysis.

The direct analysis of the reaction mixture or Hz solutions following derivatization with acetone was also accomplished using the OV-101 WCOT column (which is water stable). Figure 6 shows a chromatogram of a direct injection of a derivatized reaction mixture distillate sample. Peak tailing begins to occur following 8 to 10 injections. This can be corrected by changing the injector port liner and breaking off about 0.5 m of the column every 20 - 30 samples. The background is greater and the FID less sensitive for the direct analysis of aqueous samples. The lower detectable limit is about 5 ppm for each component. The area response for standard solutions (1.0 mg/ml) is stable 30 min after the addition of acetone. If mild heat is used 95 percent derivatization can be effected in 5 min and 98 percent in 10 min.

DISCUSSION

The gc glass capillary procedure utilizing the hydrazone derivatives of UDMH, MMH, and Hz provides a reliable analysis technique for use in situations that require large numbers of samples to be routinely assayed (the extraction procedure). It is also a useful procedure for analysis applications that require quick turnaround (the direct assay). The derivatization reaction utilizing acetone is quantitative and fast. Other reagents were tried and useable, chromatographable products were produced, but none provided as good an overall assay procedure as acetone for all components under consideration. The formation of pyrazoles using 2,4-pentanedione (AA), as outlined by Dee (2), has several disadvantages that can be overcome by using acetone to form the hydrazone products. Excess AA will produce some chromatographic interference with the product, making it necessary to hold the amount of AA added to a minimum. This is inconvenient for large-scale analysis of samples where the component concentrations are not known. Since the acetone peak is well-resolved from all of the hydrazone products, excess acetone does not present a problem. UDMH cannot be assayed using the AA procedure since a derivative is not formed. Acetone produces a hydrazone derivative with UDMH that is well-resolved from the MMH and Hz products, allowing a simple-standard procedure to be used for

Figure 6. CHROMATOGRAPH OF DIRECT INJECTION OF ACETONE DERIVATED REACTION MIXTURE



ANALYSIS CONDITIONS

TEMP 1 = 75°

TIME 1 = 6.00

RATE = 7.50°/MIN

TEMP 2 = 190°

TIME 2 = 5.0 MIN

STOP @ 15 MIN

SPLIT = 35:1

INJ = 1.2

SAMPLE

0.56 mg/ml HZ

0.83 mg/ml MMH

1.50 mg/ml UMDH

100 mg/ml ACETONE

SOLVENT - WATER

CHROMATOGRAM

R_T = 5.95; UDMH DERIVATIVE

R_T = 8.02; MMH DERIVATIVE

R_T = 9.64; HZ DERIVATIVE

all three compounds. The acetone reaction does not require pH control and the hydrazone products can be easily and quantitatively extracted from the aqueous reaction mixtures with a variety of solvents. The AA reaction is slower and extraction of pyrazoles requires larger solvent volumes, longer shaking time, and more careful pH control to obtain reproducible, quantitative recoveries. The advantages of using the acetone derivatives are restricted to the WCOT/GC technique in that the hydrazone products are very difficult to resolve using packed columns. Thus if WCOT columns are not available, the technique of Dee (2), modified by using organic extraction procedures to increase column life and decrease tailing, would still provide the best assay technique for MMH and Hz. The direct gc analysis of the derivatized aqueous reaction mixture or reaction mixture distillate can provide very quick sample turnaround time if that is desired, however, the salts deposited in the injections make injection port cleaning every 15 - 25 samples mandatory. Since less effort is expended performing the sample extraction than maintaining this instrument, the direct analysis does not produce an overall cost reduction. In addition, the FID response is better when organic solvents are used, and since N-P detectors cannot be used with direct water injections, the extraction procedure will allow increased sensitivity to be obtained where necessary by using the N-P detector system. The advantage of the direct injection system is that it can provide sample turnaround of less than 20 min. The sample can be derivatized in 5 min and the chromatogram can be compressed to as little as 3.5 min for MMH and UDMH and 6 min for Hz without compromising the analysis.

Because of the resolution power of the WCOT columns, reactive products other than UDMH, MMH, and Hz could also be monitored if desired. This would increase the gc analysis time, as many of the by-products are in the lower boiling ranges that require longer columns, lower temperatures, and slower temperature programming rates to achieve peak resolution. Some potential does exist for the direct analysis of the reactive mixture extracts using the N-P detector that would allow SDMH to be assayed also.

ANALYSIS PROCEDURE FOR UDMH, MMH AND HZ

I. Sample Preparation

1. Place 2.5 ml of sample (volumetrically) in a 20 ml screw cap vial, and add 1.0 ml of acetone. (If salt level is high, add H₂O until solution is miscible)
2. Let set for 20 min (5 min with mild heat).
3. Add 5.0 ml of CH₂Cl₂ (or benzene) and ISTD (1.0 mg of Cn-8 and Cn-9).
4. Add 0.5 ml of 3N NaOH (make pH 9.0).
5. Shake on a wrist are shaker for 10 min with sufficient agitation to make the solution homogeneous.
6. Allow the layers to separate and remove the organic layer to a pre-labeled vial.
7. Add 5.0 ml of CH₂Cl₂ (or benzene) and repeat steps 5 and 6.
8. Analyze on gc set up with 60-m OV-101 WCOT column. Base quantitation on Cn-8 STD. (Use Cn-9 STD as an internal check)

II. GC Procedures

1. The instrument analysis conditions are:

	<u>Maximum</u>	<u>Setting</u>	<u>Reading</u>
Temp 1	250	75	75
Time 1	6.00		
Rate	7.50		
Temp 2	250	240	
Time	20.00		
INJ Temp	350	200	200
FID Temp	400	300	300
AUX Temp	350	250	250
CHT SPT	0.50		
Zero	10.0		
ATTN 2	6		
FID SGNL	+8		
SLP SENS	40.00		
Area REJ			100
Flow A	30.0	30.0	(made up gas)
Flow B	78.3	74.3	(70 to 1 split)

<u>Time Function</u>	<u>Value</u>
6.00 SLP Sens	0.25
8.50 Rate	30.00
8.75 SLP Sens	0.10
9.50 SLP Sens	0.25
12.50 Stop	
13.60 IFN	
13.65 Si P Sens	10
15.00 Stop	1.00

2. For quantitation, the area response factors are calculated using the appropriate standards.

The absolute values for the area response are dependent on the split, but the relative response factors used to calculate sample values when ISTD's are used are not.

REFERENCES

1. DEE, L. A., and A. K. Webb. Gas Chromatographic Separation of Hydrazine Mixtures and Water Using a Stationary Phase That is Chemically Similar to Hydrazine. *Anal. Chem.*, 39:1165 (1967).
2. DEE, L. A. Gas Chromatographic Determination of Aqueous Trace Hydrazine and Methylhydrazine as Corresponding Pyrazoles. *Anal. Chem.*, 43:1416 (1971).
3. LIU, Yu-Ying, I., Schmelz, and D. Hoffman. Chemical Studies on Tobacco Smoke - Quantitative Analysis of Hydrazine in Tobacco and Cigarette Smoke. *Anal. Chem.*, 46:885 (1974).
4. SPIGARELLI, J. L. and C. E. Meloan. Rapid Analysis of Hydrazine-Methyl Substituted Hydrazine Mixtures by Reactive Column Gas Chromatography. *J. Chromatog. Sci.*, 8:40 (1970).
5. BIGHI, C. and G. Saliotto, The Effect of Alkalized Adsorbent on the Gas Chromatographic Separation of Hydrazine Derivatives. *J. Gas Chromatog* , 4:303 (1966).