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Quarterly Report No. 2

STUDY OF FUEL CELLS USING STORABLE ROCKET PROPELLANTS

18 May to 17 August 1965

by

R. F. Drake, L. F. Athearn, R. E. Chute,
J. C. Orth, and J. C. Smith

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS3-6476

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SUMMARY

This quarter the catalyst screening programs for Aerozine-50 reforming and N_2O_4 decomposition have continued. Four systems are presently contemplated for Aerozine reforming. These systems and the present hydrogen yield efficiencies for each are:

(1) Low temperature decomposition = 17.6%.

(2) Medium temperature decomposition = 1.4%.

(3) High temperature steam reforming-single catalyst = 29.2%.

(4) High temperature steam reforming followed by NH_3 decomposition and CO shift reaction = 55.0% (estimated).

Four more catalysts active for the decomposition of N_2O_4 have been uncovered. However, none showed much activity below 700°C. An accelerated screening program is outlined for this task.

Several catalysts active for the electro-oxidation of UDMH have been tested. However, Rh is still the best overall catalyst. Testing of this catalyst in a 3 x 3 in. cell definitely indicated that a diffusion barrier will be required to prevent excessive decomposition of the fuel on the electrode.

An MRC carbon electrode with a higher than normal carbon matrix density was tested with N_2O_4. The diffusion rate through this electrode was not substantially reduced by this method.

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I. INTRODUCTION

A. BACKGROUND

This is the second quarterly report in the third stage of an investigation whose objective is to develop a fuel cell operating on storable rocket propellants as primary or secondary reactants. Work on the previous contract (NAS3-4175) largely concerned the investigation of a number of possible systems and cell configurations and culminated in the construction and long-term testing of two cell types. One configuration used N_2H_4 dissolved in KOH electrolyte as the fuel and gaseous O_2 as the oxidizer. The other system used N_2H_4 dissolved in H_3PO_4 electrolyte as the fuel and gaseous N_2O_4 as the oxidizer. Both systems were developed to the point where System Designs were submitted to NASA specifications (ref. 1).

The present contract calls for the investigation and development of cells operating on gaseous N_2O_4 and Aerozine-50 as direct reactants, and for a reforming capability to use these reactants to produce O_2- and H_2-rich feedstreams for fuel cells. The construction and operation of working reformers and cells are the objectives of this work.

B. PROGRAM ORGANIZATION

The project consists of three phases, to be performed roughly in series. The overall work plan shown in Figure 1 illustrates the major tasks to be performed. Detailed working plans for Phase I have been developed and are illustrated in Figure 2. There are three major tasks in this phase: reforming of Aerozine-50, catalytic decomposition of N_2O_4, and electrode development for direct reactant use. Each task has been further broken down into subtasks which represent the actual work being done to complete the task successfully.

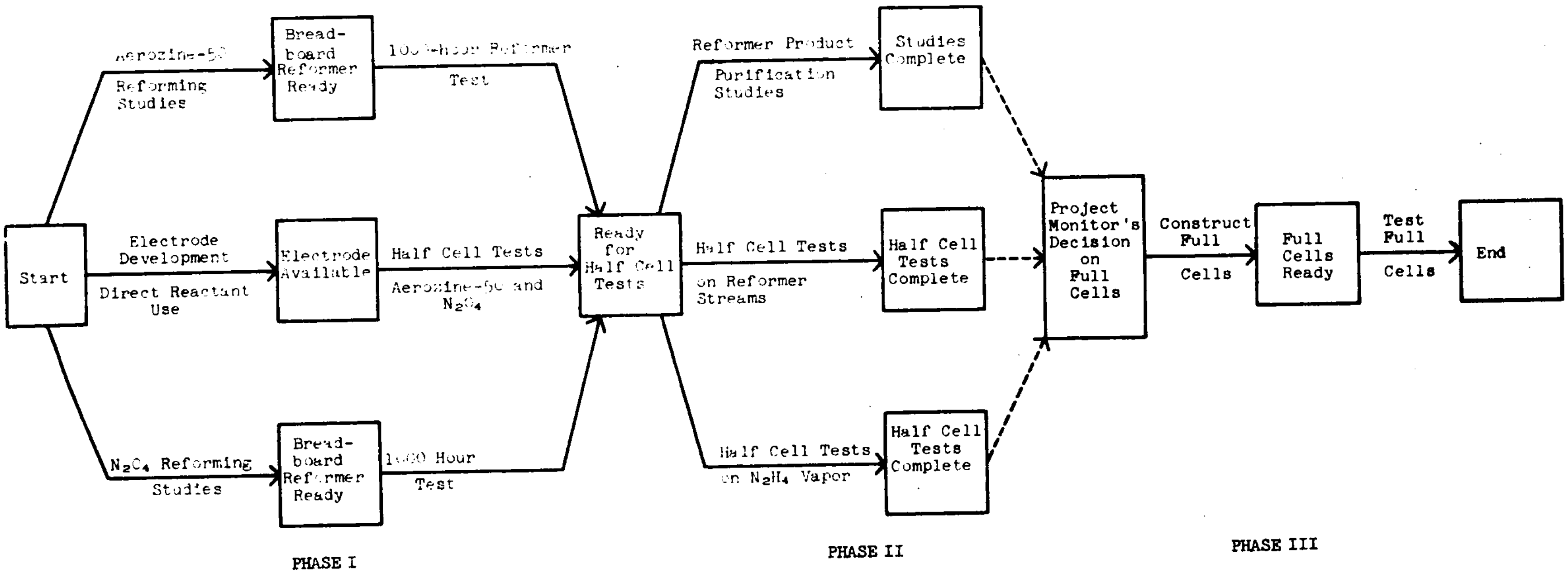
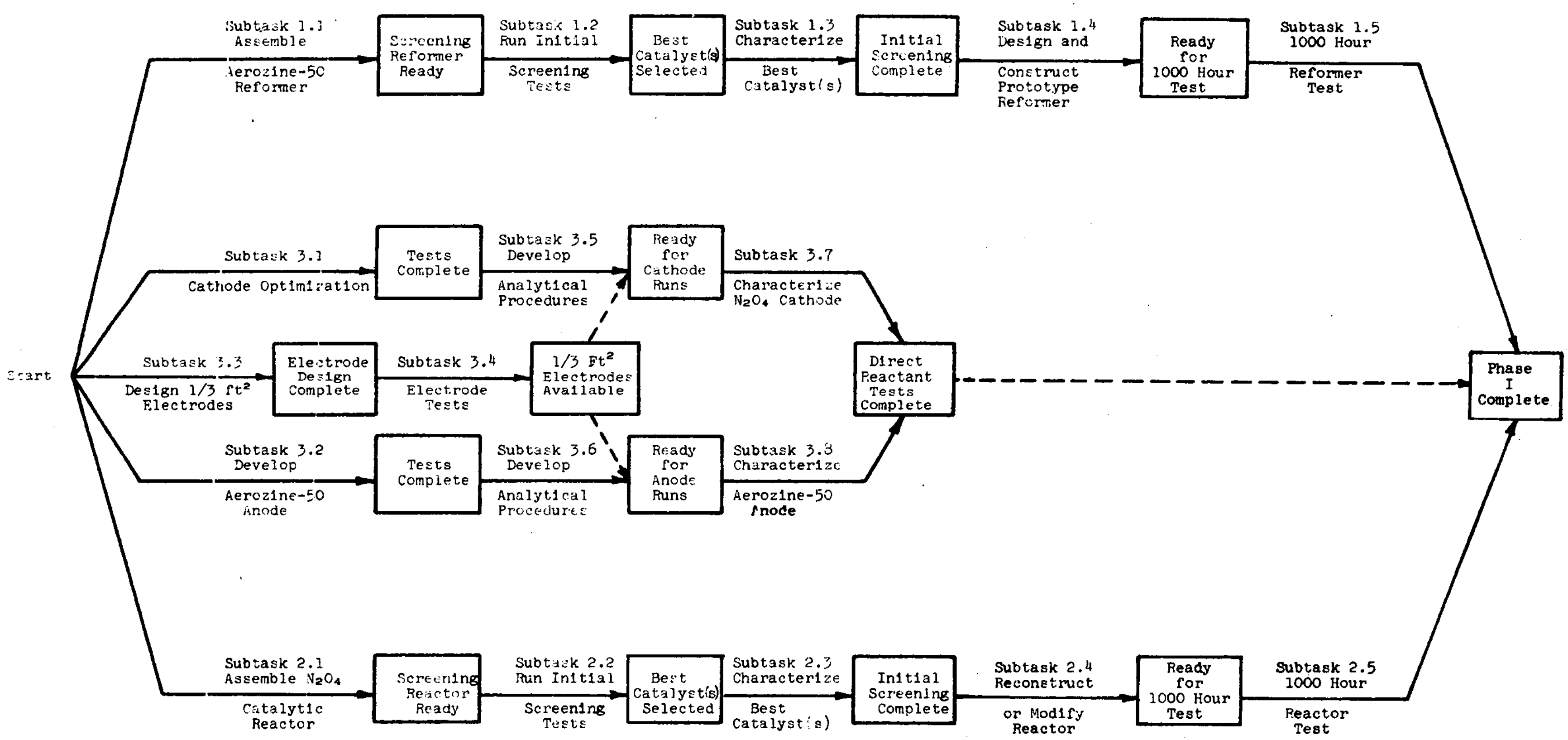


Figure 1. PROGRAM WORK PLAN AND EVENT CHART
NAS3-6476



PERT CHART

Figure 2. NAS3-6476 Phase I

C. SCOPE OF THIS REPORT

This report covers work done on the subtasks listed below.

Subtask Number	Description	Work Status
1.1	Assemble Aerozine-50 Reformer	complete
1.2	Run Initial Screening Tests	60% complete
2.1	Assemble N_2O_4 Catalytic Reactor	complete
2.2	Run Initial Screening Tests	40% complete
3.1	Cathode Optimization	50% complete
3.2	Develop Aerozine-50 Anode	50% complete
3.3	Design 1/3-ft^2 Electrodes	90% complete
3.4	1/3 ft^2 Electrode Tests	not started
3.5	Analytical Procedures (N_2O_4)	75% complete
3.6	Analytical Procedures (Aerozine-50)	50% complete

II. TASK I. AEROZINE-50 REFORMING STUDIES

A. BACKGROUND

The objective of the Aerozine-50 reforming studies is to produce a hydrogen-rich feed stream suitable for use in a fuel cell. The maximum amount of hydrogen will be produced from steam reforming the Aerozine-50. Theoretically, 9.8 moles of H_2 can be derived from 100 grams of fuel plus 60 grams of steam. In practice side reactions and incomplete reactant use reduce yields by various amounts depending on the catalyst and conditions.

The four systems listed below are under consideration at this time. Each has certain advantages with respect to heat inputs required, hydrogen yields and efficiency, complexity and reliability.

System 1: Low temperature decomposition of the fuel at 30 to 100°C in the liquid phase. Only the hydrazine component can be decomposed, and the maximum H_2 efficiency is 32%.

System 2: Medium temperature decomposition at 100 to 250°C in the vapor state where the reaction might proceed faster. The maximum efficiency is again 32%.

System 3: High temperature steam reforming from 300 to 500°C, using a single catalyst and reactor. Depending on side reactions, the possible efficiency is 100%.

System 4: High temperature steam reforming followed by reaction zones (or separate reactors) to decompose NH_3 and to convert additional CO to maximize the H_2 yield. The maximum efficiency is 100%.

The choice of system will depend not only on the actual H_2 efficiencies realized in the experimental work, but also on factors such as weight, volume, complexity, energy requirements, and the end use requirements. As a start on acquiring some of this information, heat balances have been worked out for each system and are included in Appendix I. The experimental work in support of each system is described in the following paragraphs.

B. LOW TEMPERATURE DECOMPOSITION

The work done to date (and the pertinent literature) bears out two facts:

(1) Only the N_2H_4 fraction is decomposable in the temperature range considered.

(2) N_2H_4 can decompose either to H_2 and N_2 or to NH_3 and N_2.

The extent of each reaction depends on the catalyst used. NH_3 formation can seriously limit the H_2 yields.

The reactor system used to evaluate catalysts in this work has been described in the First Quarterly Report (ref. 2). Briefly, it consists of a reaction flask and a gas analysis train. The fuel is added batchwise to the catalyst in the flask and gas volumes are measured and analyzed by VPC after scrubbing out NH_3.

All data on catalysts tested to date are included in Table 1. Two catalysts showed sufficient promise to warrant consideration: (1) a promoted Raney Ni-water slurry, and (2) Rh on various supports. Although the Ni catalyst gave the highest conversion to H_2 (88% compared to 55% for a typical Rh catalyst) the slurry form would be nearly impossible to use in a flow reactor system. The best choice, then, is the Rh catalyst supported on alumina, with which the H_2 efficiency obtained is 17.6% based on the total H_2 content of Aerozine-50, or 55% based on the decomposition of the N_2H_4 component alone.

C. MEDIUM TEMPERATURE DECOMPOSITION

The objective of this work is to improve the N_2H_4 decomposition rate and efficiency by operating at higher temperatures where the reactants are in the vapor phase. The tubular flow reactor described in the First Quarterly Report (for steam reforming) has been used to evaluate Pt, Pd, Rh, and Ni catalysts at 10 psig from 100°C to 250°C on pure Aerozine-50 feed. The results are presented in Table 2. No significant H_2 formation was found with any catalyst above 140°C where only the vapor phase exists in the reactor. At 100°C, where Aerozine-50 is only partially vaporized, some H_2 production was realized with a Pd catalyst. These results seem to indicate that the vapor phase reaction proceeds mainly to NH_3 on the catalysts tested. The H_2 conversion efficiency with the Pd catalyst was only 1.4%. Great improvement is necessary for this system to be useful.

D. HIGH TEMPERATURE STEAM REFORMING OF UDMH

Steam reforming of UDMH was the subject of the main investigation under this task during the last quarter. This process has the potential for the highest H_2 yields. However, in the temperature range considered (300° to 500°C), the thermodynamic equilibrium predicts mainly CH_4 and N_2 as reaction products. Thus, the reaction kinetics must be adjusted by the use of selective catalysts and proper conditions to promote the high H_2-yielding reactions.

There are a large number of possible reactions with this system. The most important now appear to be:

1. $(CH_3)_2NNH_2 \longrightarrow 2CH_4 + N_2$

2. $(CH_3)_2NNH_2 \longrightarrow 2C + 2NH_3 + H_2$

Table 1

LOW TEMPERATURE DECOMPOSITION OF UDMH, N_2H_4, AND AEROZINE-50

Catalyst Type	Weight, g	Fuel	Temp, °C	Gas Rate, ml/min	Specific Gas Rate, ml/min g *	Off Gas H_2/N_2 Ratio	% N_2H_4 Converted to H_2	% N_2H_4 Decomposed	Notes
Raney Nickel water slurry No. 28, Raney Nickel Corp.	-	UDMH	30	1.0	-	-	-	-	1 ml of slurry used
	-	UDMH	61	0.2	-	-	-	-	1 ml of slurry used
	-	N_2H_4	24	21.4	-	-	-	all	1 ml of slurry used
	-	N_2H_4	26	28.3	-	-	-	all	1 ml of slurry used
Raney Nickel water slurry with 0.3 g H_2PtCl_6	-	UDMH	61	0.2	-	-	-	-	1 ml of slurry used
	-	50/50	61	294	-	-	-	all	1 ml of slurry used
	-	UDMH	61	0.5	-	-	-	-	1 ml of slurry used
	-	25% N_2H_4			-				1 ml of slurry used
	-	75% UDMH	59	225	-	-	-	all	1 ml of slurry used
	-	N_2H_4	34	560	-	1.90	88	all	1 ml of slurry used
Girdler T-242 Ni + Cu Oxides	2.25	UDMH	30	0.9	0.4	-	-	-	1/8 in. tablets
	2.25	50/50	30	negligible	-		-	-	1/8 in. tablets
Baker 0.5% Pt on Alumina, 1/8 in. Tablets	1.80	UDMH	30	1.4	0.8	-	-	-	Rate decreasing with time
	1.80	50/50	30	0.6	0.3	-	-	-	Rate decreasing with time
Girdler T-308 0.05% Pd on Alumina	2.2	UDMH	30	0	-	-	-	-	1/8 in. tablets
	2.2	50/50	30	negligible	-	-	-	-	1/8 in. tablets
Girdler G-60 Promoted Nickel	2.8	UDMH	30	1.1	0.4	-	-	-	1/8 in. tablets
	2.8	50/50	30	negligible	-	-	-	-	1/8 in. tablets
Girdler T-325 reduced stabilized Nickel 1/8 in. tablets	2.3	N_2H_4	30	7.7	3.3	-	-	-	
	2.3	50/50	30	8.2	3.6	-	-	-	
	2.3	UDMH	30	0.6	0.3	-	-	-	Rate increasing
	2.3	50/50	30	6.7	2.9	-	-	-	

* Per gram of catalyst.

Table 1 (Continued)

Catalyst Type	Weight, g	Fuel	Temp, °C	Gas Rate, ml/min	Specific Gas Rate, ml/min g*	Off Gas H_2/N_2 Ratio	% N_2H_4 Converted to H_2	% N_2H_4 Decomposed	Noted
Girdler T-323 reduced stabilized cobalt 1/8 in. tablets	3.1	N_2H_4	30	explosive	-	-	-	-	Explosive decomposition
	1.0	UDMH	30	2.2	2.2	-	-	-	Stopped after 20 minutes
	1.0	50/50	30	49.7	49.7	0.05	0.9	all	Trace CH_4 in gas sample
Girdler G-52 reduced stabilized nickel on alumina	2.8	UDMH	30	1.1	0.4	-	-	-	Rate decreasing with time
	2.8	50/50	30	negligible	-	-	-	-	
Engelhard 5% Rh on Carbon Powder	0.7	N_2H_4	29.9	18.6	26.6	1.56	55	all	Rate decreasing with time
	0.7	UDMH	29.9	0.8	1.1	-	-		
	0.7	50/50	29.9	5.2	7.4	-	-	all	
	0.7	50/50	34.6	8.8	12.6	-	-	all	
	0.7	50/50	39.4	12.3	19.7	1.33	40	all	
Baker 0.5% Rh on Alumina	2.2	N_2H_4	29.9	2.8	1.3	1.56	55	all	1/8 in. tablets
Engelhard Rhodium Black	0.1	N_2H_4	49.7	24.3	243	1.6	57	all	
	0.2	50/50	50.0	27.2	136	1.65	61	all	
T-325 Reduced Nickel Catalyst	2.3	N_2H_4	49.5	-	-	0.96	24	all	Gas rate too fast to measure
	2.3	50/50	49.5	37.8	38.2	1.16	32	all	3 ml of catalyst was used
MRC Proprietary Catalyst 77604-4	0.1	UDMH	49.5	0	0	-	-	-	UDMH did not decompose
	0.1	50/50	49.5	12.3	123	1.37	42	all	
MRC Proprietary Catalyst 77604-5	0.1	UDMH	49.5	0	0	-	-	-	UDMH did not decompose
	0.1	50/50	49.5	76.8	768	0.70	15	all	
MRC Proprietary Catalyst 77604-1	0.1	UDMH	49.5	0	0	-	-	-	UDMH did not decompose
	0.1	50/50	49.8	36.8	368	0.89	21	all	

* Per gram of catalyst.

Table 1 (Continued)

Catalyst Type	Weight, g	Fuel	Temp, °C	Gas Rate, ml/min	Specific Gas Rate, ml/min g*	Off Gas H_2/N_2 Ratio	% N_2H_4 Converted to H_2	% N_2H_4 Decomposed	Notes
MRC Proprietary Catalyst 77604-2	0.1 0.1	UDMH 50/50	50.0 50.0	0 16.1	0 161	- 0.82	- 19	- all	UDMH did not decompose
Thorium	0.1 0.1	UDMH 50/50	50.0 50.0	0 0	0 0	- -	- 0	- 0	Heat treated in Ar 2 hr. [illegible] decomp. on UDMH or 50/50
Titanium	0.1 0.1	UDMH 50/50	50.0 50.0	0 0	0 0	- -	- 0	- 0	Heat treated in air 1 min. No decomp on UDMH or 50/50
MRC Proprietary Catalyst 73578-A	0.5 0.5	UDMH 50/50	50.0 50.0	0 204	0 408	- 0.69	- 15	- all	UDMH did not decompose
MRC Proprietary Catalyst 73578-B	0.5 0.5	UDMH 50/50	50.0 50.0	0 -	0 -	- 0.87	- 20	- all	UDMH did not decompose Decomp rate was very fast to explosive

* Per gram of catalyst.

Table 2

MEDIUM TEMPERATURE AEROZINE-50 DECOMPOSITION TESTS

Pressure: 10 psig

Catalyst	Temp, °C	Output Gas Composition H_2	N_2	CH_4	CO	Ethane	Input Aerozine g/hr	Moles N_2H_4 per hr	Moles H_2 per 100 g Aerozine	% of Maximum H_2 From N_2H_4	State of Aerozine In Reaction
Engelhard 0.5% Pt on Alumina	175	0	94.1	5.9	0	0	9.52	0.149	0	0	gas
	250	0.6	89.7	9.6	0	0.1	9.52	0.149	0.004	0.13	gas
Engelhard 0.5% Rh on Alumina	105	5.5	82.2	9.6	2.8	0	8.65	0.135	0.036	1.14	liquid
	170	0.2	90.1	9.7	0	0	9.09	0.142	0	0	gas
	250	2.3	76.8	20.0	0.6	0.2	9.09	0.142	0.018	0.6	gas
Engelhard 0.5% Pd on Alumina	100	52.1	47.9	0	0	0	9.01	0.141	0.07	2.3	liquid
	116	44.5	55.5	0	0	0	9.01	0.141	0.13	4.3	liquid
	134	5.6	84.8	9.6	0	0	9.01	0.141	0.04	1.1	
	178	0.5	81.6	17.3	0.6	0	9.01	0.141	0.005	0.1	gas
Girdler G-49A Nickel, reduced stabilized	105	7.1	83.5	8.7	0.7	0.1	9.46	0.148	0.05	1.5	liquid
	178	0	90.0	10.0	0	0	9.01	0.141	0	0	gas

NOTES

In all tests liquid outputs could not be obtained under equilibrium conditions. Therefore, the % decomposition of N_2H_4 and UDMH is not known. However, in general only a small amount of N_2H_4 was decomposed at 100 and 175°C. Most was decomposed at 250°C.

3. $(CH_3)_2NNH_2 \longrightarrow (CH_3)_2NH + 1/3N_2 + 1/3NH_3$

4. $(CH_3)_2NNH_2 \longrightarrow C_2H_6 + 2/3N_2 + 2/3NH_3$

5. $(CH_3)_2NNH_2 + 2H_2O \longrightarrow 2CO + 2NH_3 + 3H_2$

6. $(CH_3)_2NNH_2 + 4H_2O \longrightarrow 2CO_2 + 2NH_3 + 5H_2$

7. $(CH_3)_2NNH_2 + 4H_2O \longrightarrow 2CO_2 + N_2 + 8H_2$

Efficiencies in this section are reported as per cent of maximum H_2 available by reaction 7. Since only UDMH was fed to the reactor in these tests, the H_2 yield from N_2H_4 decomposition must be added to these results to extrapolate to Aerozine-50 yields. Actual reforming runs on Aerozine-50 are reported in a later section.

The tubular flow reactor, associated equipment, and operating procedure used in this testing were described in the First Quarterly Report. Data sheets on all runs made to date are included in Appendix II. Details on operating parameters, catalysts, analytical results, and calculated efficiencies and material balances are included for each run.

The following products are listed in the reactor output: UDMH, H_2O, NH_3, dimethyl amine (DMA), H_2, N_2, CH_4, CO, CO_2, and ethane. Where carbon deposition is present the amounts are indicated.

All components except H_2O, NH_3, DMA, and carbon were determined by direct analysis of the output, using gas chromatography. The water output was calculated from the difference between the input H_2O and the amount used to form CO, and CO_2. The NH_3, DMA, and carbon were determined by calculating mass balances (where possible) of each individual element entering the reactor. An example of the calculations for one of the runs is given in Table 3.

Using this method, complete mass balances have been obtained. The major criteria for determining the best catalyst and conditions are described below.

1. Hydrogen Output

Hydrogen output can be a maximum of 13.33 moles per 100 grams of UDMH input. This assumes that all the UDMH reacts to H_2, N_2, and CO_2. The best yield obtained thus far is 3.89 moles of H_2 per 100 grams of UDMH, with G-56B catalyst at 500°C and 50 psig, or 29.2% of maximum hydrogen output. The hydrogen efficiency should not be determined by total hydrogen input since the water is present in excess (50%). The water-to-carbon ratio will be varied in later tests.

Table 3

MATERIAL BALANCE EXAMPLE FOR UDMH STEAM REFORMING

Example:

G-56B Nickel Base Reforming Catalyst at 400°C, 50 psig

Input Conditions: 0.105 mole/hr UDMH, 0.823 mole/hr H_2O

Output Gas Composition (mole-%) after 1-1/2 hr: H_2, 50.8; N_2, 2.5; CH_4, 18.6; CO, 0.3; CO_2, 27.6; ethane, 0.2.

Output Gas (mole/hr): 0.319

% UDMH Reacted: 98.2

Elemental Balances:

1. Carbon Input = 0.210 g atoms
   Carbon Output = 0.150 from CH_4, CO_2, CO, and ethane
   + 0.004 from UDMH
   = 0.154 g atoms
   with 0.056 g atoms unaccounted for

2. Nitrogen Input = 0.210 g atoms
   Nitrogen Output = 0.016 from N_2
   + 0.004 from UDMH
   = 0.020 g atoms
   with 0.190 g atoms unaccounted for

3. Hydrogen Input = 0.840 g atoms from UDMH
   + 0.354 g atoms from H_2O to form CO and CO_2
   Hydrogen Output = 0.324 g atoms from H_2
   + 0.237 g atoms from CH_4
   + 0.004 g atoms from C_2H_6
   + 0.016 g atoms from UDMH
   = 0.581 g atoms
   with 0.613 g atoms unaccounted for

By trial and error, if 0.010 mole DMA and 0.180 mole NH_3 are formed:

Hydrogen Output = 1.191 g atoms or 99.7% of input

Nitrogen Output = 0.210 g atoms or 100% of input

Carbon Output = 0.174 g atoms, leaving 0.036 g atoms for carbon deposition on catalyst.

2. Amount of CO Formed

This factor is important since CO can be shifted to CO_2 easily at low temperatures, producing more H_2.

3. Amount of NH_3 Formed

This is important since NH_3 can be decomposed to N_2 and H_2 under the proper conditions.

4. Carbon Deposition

This process produces H_2 but is undesirable because the catalyst will eventually lose its activity. This can be reduced by higher water-to-carbon ratios and higher pressures.

We believe it will be possible to convert all materials except CH_4, ethane, and possibly dimethylamine to H_2 using two or three catalyst systems, thus greatly increasing the H_2 efficiency (System 4). However, this would add weight to the system and require different operating conditions (especially for NH_3 decomposition). For these reasons our preferred goal is the maximum H_2 output on a single pass through a single reactor (System 3). Table 4 lists the total H_2 efficiency for each test performed. Three values are shown corresponding to:

1. Actual experimental values of H_2 efficiency.

2. H_2 efficiency if CO is shifted to CO_2.

3. H_2 efficiency if CO is shifted to CO_2 and if NH_3 is decomposed.

The best actual efficiencies (26 to 30%) have been obtained at 500°C, 50 psig, with a Ni-base catalyst (Girdler G56B), a Ni oxide catalyst (Girdler T-1144), and a ZnO on alumina catalyst (Harshaw Zn0701). The best extrapolated efficiencies (45-55%) for the system combining steam reforming with NH_3 decomposition and CO conversion occur at 400°C with the following catalysts:

(1) Girdler T-310, 10% nickel oxide on activated alumina

(2) Girdler Ni-base reforming catalyst

(3) Girdler T-312 Ni and Cu oxides on alumina

(4) Girdler T-1144, 50% nickel oxide

Table 5 shows the fraction of UDMH consumed by each of the seven possible reaction paths (equations 1 through 7) for each catalyst, as calculated from the observed products. The following general conclusions can be drawn from these data:

Table 4

EXTRAPOLATION OF HYDROGEN EFFICIENCIES FOR HIGH TEMPERATURE STEAM REFORMING OF UDMH

(Total input of 19.0 to 21.0 g per hour)

Catalyst Data	Temp, °C	Pressure, psig	Hydrogen Efficiency Actual, %	Hydrogen Efficiency if CO Shifted to CO_2, %	Hydrogen Efficiency if CO Shifted and All NH_3 Decomposed, %	% Carbon Deposition
Girdler T-310 10% Nickel Oxide on Activated Alumina	300	50	2.4	2.5	16.8	5
	300	150	3.9	4.7	26.9	24
	400	50	20.9	21.2	36.8	none
	400	150	20.8	21.3	53.9	none
	500	50	18.7	19.1	32.3	none
	500	150	23.3	23.8	36.6	none
Girdler G-56B Nickel Base Reforming Catalyst	300	50	0.4	0.4	3.4	none
	300	150	8.8	10.1	36.1	25
	400	50	19.3	19.4	51.6	17
	400	150	19.1	19.1	50.9	none
	500	25	20.4	20.6	41.9	42
	500	50	31.9	32.4	42.4	6
	500	50	29.1	29.7	39.9	none
6-hour test	500	150	25.4	25.4	37.2	none
Girdler G-43 0.5% Platinum on Alumina	300	50	0.9	1.3	21.5	34
	300	150	-	-	-	
	400	50	3.0	4.2	27.6	20
	400	150	6.9	8.5	28.2	none
	500	50	11.0	13.1	29.8	6
	500	150	16.2	17.4	28.1	none
Harshaw Cu 2501 all CuO in Chip Form	300	50		no reaction		
	400	50	0.5	0.6	5.0	none
	500	50	2.9	3.5	9.3	9
Girdler T-309 Pt Oxide on Activated Alumina	400	50	2.8	6.6	30.7	23
	400	150	1.9	6.1	28.1	8
	500	50	10.5	13.6	43.1	59
	500	150	15.6	20.7	37.0	none

Table 4 (Continued)

Catalyst Data	Temp, °C	Pressure, psig	Hydrogen Efficiency Actual, %	Hydrogen Efficiency if CO Shifted to CO_2, %	Hydrogen Efficiency if CO Shifted and All NH_3 Decomposed, %	% Carbon Deposition
Girdler G-47 Promoted Iron Oxide	300	50	0.2	0.2	9.0	11
	300	150	-	-	-	
	400	50	1.9	2.1	13.5	11
	400	150	1.1	1.4	7.8	3
	500	50	13.0	13.6	22.7	none
	500	150	10.9	11.5	22.6	7
T-312 Girdler Nickel and Copper Oxides on Alumina	300	50	4.9	5.6	24.2	none
	300	150	1.1	1.2	14.1	none
	400	50	18.9	21.2	45.8	none
	400	150	18.9	21.0	45.4	none
	500	50	21.1	22.2	38.6	none
	500	150	15.1	15.4	28.3	none
Harshaw ZnO 308 Zinc Chromate	300	50	8.6	8.6	25.7	5
Girdler T-1144 50% Nickel as Oxide on Oxide Base	300	50	1.6	1.6	15.4	16
	400	50	22.6	23.8	52.9	14
	500	50	28.3	28.6	33.6	none
Girdler T-317 10% Cu Oxide on Alumina	300	50	15.1	15.2	40.2	43.5
	400	50		test invalid		
	500	50	17.8	22.7	38.0	none
Zn 0701 10% ZnO on Alumina	300	50	0	0	0	none
	400	50	16.7	16.9	43.2	<13
	500	50	26.0	26.7	40.9	none
Norton Zeolite Cation Acidic	300	50	-	-	-	-
	400	50	0.2	2.4	15.7	1
	500	50	3.0	4.7	11.5	2

Table 5

HIGH TEMPERATURE STEAM REFORMING OF UDMH

Moles of input UDMH reacting via equations 1 to 7.
Calculations based on 100 moles UDMH input.

Catalyst	Temp, °C	Pressure, psig	Moles UDMH Unreacted	Moles UDMH Reacting via Equation* 1	2	3	4	5	6	7
Girdler G-56B Nickel Base Steam Reforming Catalyst	300	50	66.7	4.3	0	26.7	0	0	2.2	0
	300	150	0.6	10.7	24.5	42.6	0	5.2	16.2	0
	400	50	1.8	28.1	17.1	10.0	0.6	0.5	41.9	0
	400	150	0	36.3	0	11.6	1.1	0	51.0	0
	500	25	0	31.6	42.5	5.7	0	1.0	13.2	6.1
	500	50	0	58.2	0	0	0	2.1	24.3	15.8
	500	150	0	63.7	0	0	0	0	31.6	4.8
T-310 Girdler 10% Nickel Oxide on Activated Alumina	300	50	18.8	2.6	5.2	62.8	0	0.5	10.0	0
	300	150	2.0	3.4	23.5	60.8	0	2.9	7.4	0
	400	50	1.5	2.6	0	50.3	0	1.7	44.0	0
	400	150	1.6	36.3	0	4.9	2.0	2.0	53.1	0
	500	50	0	61.8	0	3.1	3.1	2.1	29.9	0
	500	150	0	64.2	0	0	0	2.0	32.3	1.5
Girdler G-43 0.5% Platinum on Alumina	300	50	17.1	1.6	34.2	45.6	0	1.5	0	0
	300	150	37.0	Not enough gas produced for analysis.						
	400	50	2.3	2.3	21.1	61.4	0	4.5	8.4	0
	400	150	2.1	6.4	0.5	66.0	0	5.3	19.7	0
	500	50	0	39.8	5.9	27.4	1.8	8.1	17.0	0
	500	150	0	62.9	0	7.1	2.2	4.6	22.0	1.2
Harshaw Cu 2501 10% Copper Oxide	300	50	42.7	Not enough gas produced for analysis.						
	400	50	28.4	27.2	0	40.2	1.7	0.3	2.2	0
	500	50	2.5	67.5	8.8	16.5	1.3	2.3	1.1	0
Norton Zeolite Acidic Cation Type	300	50	60.6	Not enough gas produced for analysis.						
	400	50	13.0	16.0	0.5	54.8	4.1	8.9	2.5	0
	500	50	0.5	68.8	2.1	14.4	4.2	6.9	3.1	0

* See reactions 1-7 in Section II.D.

Table 5 (Continued)

Catalyst	Temp, °C	Pressure, psig	Moles UDMH Unreacted	Moles UDMH Reacting via Equation* 1	2	3	4	5	6	7
Girdler T-309	400	50	3.1	1.2	23.5	57.1	0	15.3	0	0
Pt Oxide on	400	150	2.1	2.0	8.3	68.0	0	16.7	3.0	0
Activated	500	50	0	13.0	59.0	15.0	0.3	12.5	0	0
Alumina	500	150	0	49.5	0	9.7	5.0	20.4	15.6	0
Girdler G-47	300	50	25.0	10.0	11.0	54.0	0	0	0	0
Promoted	300	150	95.5	-	-	-	-	-	-	-
Iron Oxide	400	50	12.4	31.3	12.0	38.4	1.0	1.0	4.0	0
	400	150	22.3	39.9	5.2	27.7	1.7	1.1	2.1	0
	500	50	0.5	55.0	0	18.8	4.0	2.5	16.9	2.4
	500	150	1.0	63.5	6.6	8.1	2.5	1.9	16.6	0
Girdler T-312	300	50	7.1	7.4	0	66.0	0	2.5	17.8	0
Nickel and Copper	300	150	3.2	5.3	0	79.8	0	0.5	11.2	0
Oxides on Alumina	400	50	0.7	5.6	0	50.8	0	9.1	33.8	0
	400	150	1.1	9.0	0	44.7	0	8.5	36.7	0
	500	50	0	50.3	0	8.2	2.4	4.6	34.5	0
	500	150	0	60.4	0	7.7	3.3	1.1	26.5	0
Harshaw Zn 0308 Zinc Chromite	300	50	12.6	5.2	5.2	57.6	0	0	19.4	0
Girdler T-1144	300	50	22.1	4.4	15.4	53.8	0	0	4.4	0
50% Nickel	400	50	1.0	17.5	14.0	22.3	0.6	4.9	39.7	0
as Oxide	500	50	0	58.3	0	7.7	0	1.3	11.1	21.4
T-317 Girdler	300	50	0.8	5.5	43.5	34.5	0	0.4	15.3	0
10% Copper Oxide	400	50	0	Data wrong due to high carbon deposition.						
on Alumina	500	50	0	50.2	0	8.6	3.1	19.5	18.6	0
Harshaw Zn 0701	300	50	98.9	Not enough reaction for analysis.						
10% Zn Oxide	400	50	3.9	1.9	12.6	47.9	0	1.1	32.8	0
on Alumina	500	50	0	48.5	0	7.0	2.3	2.5	33.5	6.1

* See reactions 1-7 in Section II.D.

(1) All the catalysts cause NH_3 formation at 300 and 400°C. The amount produced decreases as the temperature increases; in some cases none is formed at 500°C with the pressures used in this study.

(2) Methane production increases with temperature and pressure for most of the catalysts. The maximum found was 60 to 70% of the UDMH reacting by this path.

(3) Carbon deposition occurs with many of the catalysts at 300 and 400°C. This reaction produces H_2, but is undesirable because of eventual catalyst fouling.

(4) In some cases the direct formation of NH_3 from the elements appears to have occurred to some extent.

E. STEAM REFORMING OF AEROZINE-50 AT HIGH TEMPERATURE

The two best UDMH steam reforming catalysts, Girdler G56B and T-1144, were tested on Aerozine-50. The data sheets for these tests are included in Appendix II and the results are summarized in Table 6. Comparison of these results with the data acquired with UDMH alone indicates that the fraction of UDMH undergoing steam reforming is reduced (at 500°C), and the amount of CH_4 formed and carbon deposited at 400°C has also increased slightly. The net effect is a slightly reduced H_2 efficiency from the steam reforming reaction. However, a significant increase in NH_3 decomposition was found (24% for Girdler G56B and 56% for T-1144), which tended to increase H_2 yield. The overall H_2 efficiency (including the N_2H_4 component of the fuel) was 27.0% for T-1144 at 500°C, 50 psig.

We feel the overall efficiency of the system can be improved by optimization of the operating variables (temperature, pressure, input rates, and water excess amount used). A mixed catalyst system for both steam reforming and NH_3 dissociation would further improve H_2 production. However, a double zone reactor may be necessary if different temperature or pressure conditions are required for these two processes.

F. WORK PLANS

(1) Finish the screening runs.

(a) Test molecular sieve (Norton-Zeolite) with 1% Ni + 1% Rh for UDMH steam reforming.

(b) Test Harshaw Zn 0701 (10% ZnO on alumina) for Aerozine-50 steam reforming.

(c) Test 5-15% Pd on alumina and silica gel for low temperature decomposition.

Table 6

STEAM REFORMING OF AEROZINE-50

Input Composition, wt-%: 23.1 UDMH
23.1 N_2H_4
53.8 H_2O

Catalyst	Temp, °C	Pressure, psig	% NH_3 Dissociation	Actual H_2 Efficiency	H_2 Efficiency Assuming 90% Dissociation of NH_3 and CO Shift	% UDMH to Deposition of Carbon	% UDMH to CH_4 and N_2	% UDMH To Steam Reforming
G56B	300	25	0	3.2	43.5	24	3	8
	300	50	0	0.3	47.3	57	5	0.1
	400	25	0	14.2	60.3	29	27	36
	400	50	0	15.2	64.9	32	19	41
	500	50	24	22.8	50.4	0	68	33
T-1144	400	50	0.6	16.2	57.6	15	10	35
	500	50	56	27.1	41	1	67	15

(2) Optimize the low temperature system, and test the best catalyst under the following conditions:

(a) Flow rate varied by 3 g/hr from 7 to 16.

(b) Temperature varied by 15°C from the best temperature of screening.

(c) Pressure varied by 10 psig upward until performance deteriorates.

Conduct a five-day, long-term test of the best system.

(3) Optimize Aerozine-50 steam reforming. Test the best catalyst under the following conditions:

(a) Flow rate varied by 5 g/hr from 10 to 30.

(b) H_2O/C ratio varied from 2/1 to 6/1, or from stoichiometric to 200% excess.

(c) Temperature varied by 15°C from the best screening result.

(d) Pressure varied by 10 psig from the best screening result.

Conduct a five-day test of optimized conditions.

(4) Investigate NH_3 decomposition systems.

(a) Select three or four NH_3 decomposition catalysts and try them (1) as intimate mixtures with reforming catalyst and (2) as a separate zone (same temperature and pressure).

(b) If results not good in (a), set up separate reactor and determine conditions required for decomposition, and calculate efficiencies.

(5) Run any further tests required to supply information needed in choosing final system (Project Monitor).

(6) Start breadboard reactor design.

III. TASK II. DECOMPOSITION OF N_2O_4

A. BACKGROUND

The objective of this task is to decompose nitrogen tetroxide to N_2 and O_2 by thermal and catalytic means to provide an oxygen-rich stream for a fuel cell. The reactions for this decomposition and the present state-of-the-art were discussed in the First Quarterly Report. The reactor system has been designed with this information in mind, and tests made to date indicate that the system performs satisfactorily for screening catalysts.

Each catalyst is packed in a 3/4 in. ID stainless steel tube to the depth of 12 in. The remainder of the tube is then filled with porcelain chips to provide preheating of the gas stream and support for the catalyst bed. The test consists of installing this packed tube in the system as shown in Figure 3, and heating to four temperatures (200, 400, 600, and 800°C) while passing N_2O_4. The time-delay tube operates at room temperature and permits the slow recombination reaction of undecomposed NO with oxygen to go to completion. The resulting NO_2 is frozen in the cold trap using Dry Ice and Triclene. Only oxygen, nitrogen and (in the case of some easily oxidized catalysts) nitric oxide pass through the cold trap to be measured and analyzed by gas chromatography.

The catalysts are held at each temperature for one hour while the gas evolution rate is determined. If, at the end of this period, the evolution rate is high enough to sweep out the sampling manifold of the gas chromatograph, three or more samples are analyzed. The tests on each catalyst usually require six to seven hours to complete.

B. RESULTS AND DISCUSSION

Twenty-two catalysts have been screened since the last Quarterly Report. Table 7 shows none of them has exhibited sufficient activity to be useful at temperatures below 750-800°C. Detailed data on all catalysts tested this quarter are included in Appendix III.

The screening tests have been performed using 20 grams per hour of N_2O_4 feed. At this feed rate, 100% decomposition of the N_2O_4 would yield 0.511 cu ft/hr of gas of the composition 66.6 mole % O_2, 33.3 mole % N_2. The highest gas evolution rate obtained to date is 0.32 cu ft/hr of a gas that approximates the 2:1-O_2:N_2 mole ratio (see Test 77457-1, Table 7) which represents a conversion efficiency of 62.6%. This was obtained using a 0.5% platinum catalyst at 800°C. Extending testing of this catalyst has not been performed since the operating temperature was quite high. With other catalysts having some activity at 800°C, the gas evolution rate is reduced by at least 50% when the temperature is lowered to 700°C.

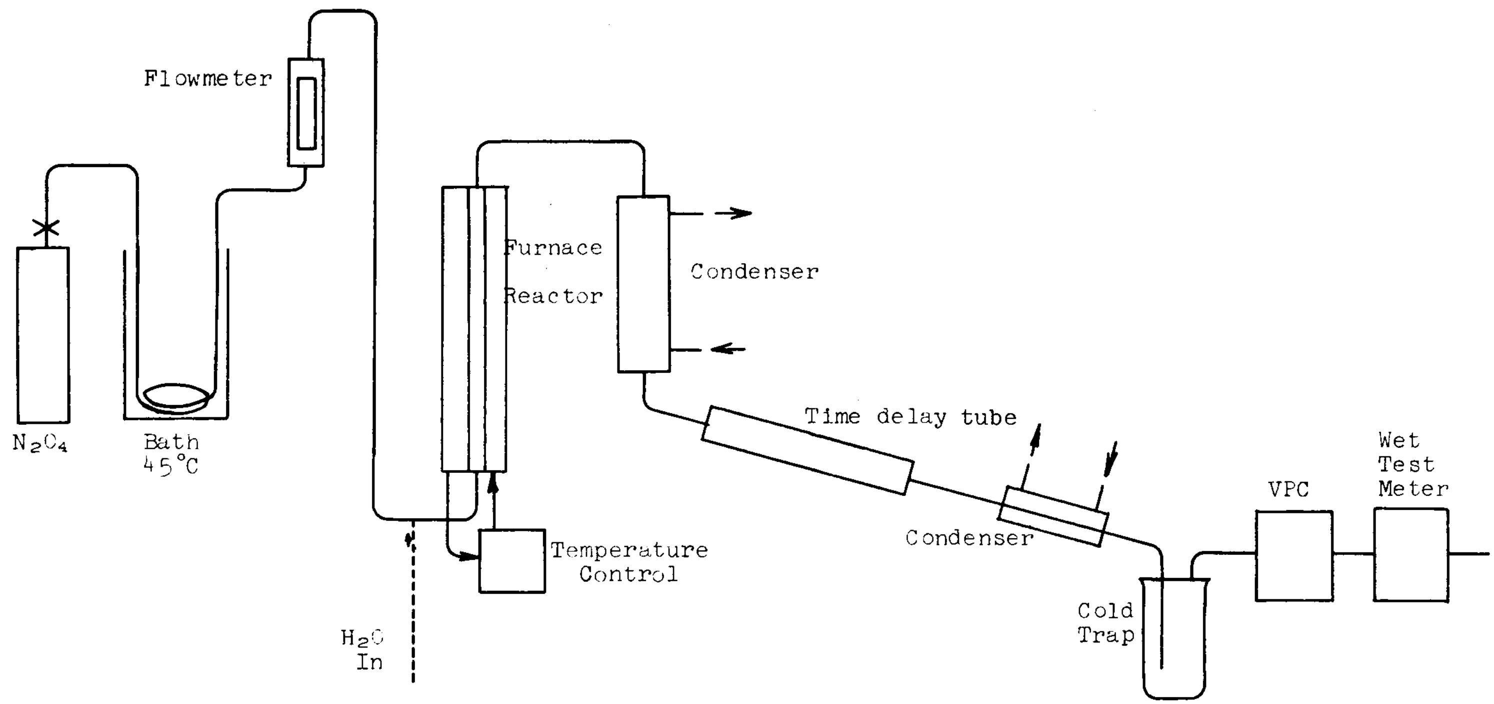


Figure 3. N_2O_4 Reactor Flow Diagram

Table 7

N_2O_4 REFORMING DATA

N_2O_4 Feed Rate: 20 g/hour

Run No.	Catalyst	Reactor Temp, °C	Gas Evolved, ft^3/hr	Run Duration, hours	Notes
72102-1	Baker 0.5%Pd lot 3107	198	0	0.75	Wet test meter reversed as volume reduced during run.
72102-2	Baker 0.5%Pd lot 3107	399	0	2.0	
72102-3	Baker 0.5%Pd lot 3107	600	0	1.0	
72102-4	Baker 0.5%Pd lot 3107	800	7.5 x 10^{-2}	1.50	Gas sample: O_2/N_2 = 1.5 mole/mole 100% decomposition yield = 0.511 ft^3/hr; N_2O_4 decomposition 14.7%**
72103-1	Baker 0.5%Pd lot 3107	800	13.2 x 10^{-2}	7.0	Gas sample: O_2/N_2 = 1.95 mole/mole
72106-1	Pt-Rh gauze	200	0.1 x 10^{-2}	1.0	Rate too low for VPC analysis
72106-2	Pt-Rh gauze	400	0.2 x 10^{-2}	2.0	
72106-3	Pt-Rh gauze	600	0	1.0	
72107-1	Pt-Rh gauze	800	0.45 x 10^{-2}	1.50	Rate too low for VPC analysis
77425-1	Norton Zeolon® H-BPS	200	0.18 x 10^{-2}	1.0	Rate too low for VPC analysis
77425-2	Norton Zeolon H-BPS	400	0.02 x 10^{-2}	1.0	
77425-3	Norton Zeolon H-BPS	600	0.25 x 10^{-2}	1.0	
77425-4	Norton Zeolon H-BPS	800	0.8 x 10^{-2}	1.0*	
77426-4	Norton Zeolon H-BPS	800	0.4 x 10^{-2}	0.75*	
77429-1	G-49A	202	31.2 x 10^{-2}	0.6	VPC analysis N_2 ~~+ NO~~
77429-2	G-49A	400	41.0 x 10^{-2}	0.9	VPC analysis N_2 + NO
77429-3	G-49A	600	1.2 x 10^{-2}	1.0	Thermocouple opened
77433-1	G-43 Pt	200	2.8 x 10^{-2}	1.0	
77433-2	G-43 Pt	400	0	1.0	
77433-3	G-43 Pt	600	0	1.0	
77433-4	G-43 Pt	800	9.4 x 10^{-2}	2.7	VPC analysis N_2 and trace O_2
77433-5	G-43 Pt	750	3.7 x 10^{-2}	1.25	
77433-6	G-43 Pt	700	1.4 x 10^{-2}	0.5	Rate too low for VPC analysis

* Gas was measured after the first hour and after the next 3/4 hour in run 77426-4.

** Not steady state conditions.

Table 7 (Continued)

Run No.	Catalyst	Reactor Temp, °C	Gas Evolved, ft^3/hr	Run Duration, hours	Notes
77436-1	T-309	200	1.0×10^{-2}	1.0	
77436-2	T-309	400	0	1.0	
77436-3	T-309	600	0	1.0	
77436-4	T-309	800	1.2×10^{-2}	1.0	Rate too low for VPC analysis
77437-1	Ag-Alumina	200	5.1×10^{-2}	1.0	Decreasing rate indicating oxidation of catalyst
77437-3	Ag-Alumina	300	0	1.0	
77437-4	Ag-Alumina	348	0.1×10^{-2}	1.0	
77437-5	Ag-Alumina	396	0	0.75	
77437-6	Ag-Alumina	600	0	1.0	
77438-1	Ag-Alumina	200-240	0	2.0	
77439-1	T-366	204			Reactor blocked
77440-1	G-47	200	2.7×10^{-2}	1.0	Flow stopped at 33 minutes
77440-2	G-47	400	2.5×10^{-2}	1.0	Flow stopped at 15 minutes
77440-3	G-47	600	0	1.0	
77440-4	G-47	800	0	1.0	
77441-1	0.5% Pd	200	3.7×10^{-2}	1.0	Flow stopped at 46 minutes
77441-2	0.5% Pd	400	0.7×10^{-2}	1.0	
77441-3	0.5% Pd	600	0	1.0	
77441-4	0.5% Pd	800	4.9×10^{-2}	1.0	No VPC analysis made
77441-5	0.5% Pd	750	0	0.5	
77442-1	0.5% Pd	700	3.2×10^{-2}	1.0	Rate falling after 23 minutes
77442-2	0.5% Pd	800	4.8×10^{-2}	1.0	
77442-3	0.5% Pd	750	28.0×10^{-2}	0.25	May be due to attempted temperature change and overshoot; no VPC analysis
77442-4	0.5% Pd	700	1.6×10^{-2}	1.0	
77442-5	0.5% Pd	650	0	0.75	
77443-1	CaO	200	0.7×10^{-2}	1.0	
77443-2	CaO	400	0.8×10^{-2}	1.0	
77443-3	CaO	600	0	1.0	Run terminated; trap's backed up
77444-1	0.5% Rh	200	0.4×10^{-2}	0.8	Flow stopped at 17 minutes
77444-2	0.5% Rh	400	0	0.75	
77444-3	0.5% Rh	600	0	1.0	
77444-4	0.5% Rh	800	3.2×10^{-2}	1.0	No VPC analysis made

Table 7 (Continued)

Run No.	Catalyst	Reactor Temp, °C	Gas Evolved, ft^3/hr	Run Duration, hours	Notes
77445-1	Ag-Hg	200	5.9 x 10^{-2}	0.92	Catalyst oxidizing
77445-2 thru 77445-12	Ag-Hg	400-490	2.0 x 10^{-2}	*	Flow stopped and traps backed up as temperature was raised
77445-13	Ag-Hg	500	0	0.5	
77445-14	Ag-Hg	550-600	0	*	
77445-15	Ag-Hg	800	0.2 x 10^{-2}	1.0	
77447-1	Pd-Hg	200	7.45 x 10^{-2}	1.0	Catalyst oxidizing
77447-2 thru 77447-9	Pd-Hg	400-500	0	*	
77447-10	Pd-Hg	600	0	0.25	
77447-11	Pd-Hg	800	0	0.57	
77457-1	II-077 (0.5% Pt)	800	32.0 x 10^{-2}	0.75	Nearly steady gas evolution rate for 45 minutes; 62% N_2O_4 decomposed
77457-2	II-077 (0.5% Pt)	800	18.0 x 10^{-2}	0.5	Argon saturated with H_2O added at 4 x 10^{-2} ft/hr rate
77457-3	II-077 (0.5% Pt)	800	24.0 x 10^{-2}	1.1	Nearly steady gas evolution rate for 68 minutes; 47% N_2O_4 decomposed
77457-4	II-077 (0.5% Pt)	800	8.0 x 10^{-2}	1.0	Helium saturated with H_2O added at 10 x 10^{-2} ft^3/hr
77460-1	Cu-2501	200	3.6 x 10^{-2}	1.0	Flow stopped at 32 minutes
77460-2	Cu-2501	400	0	1.0	
77460-3	Cu-2501	600	0	1.0	
77460-4	Cu-2501	800	0	1.0	
77461-1	Cu-0803	200	1.1 x 10^{-2}	1.0	Flow stopped at 30 minutes
77461-2	Cu-0803	400	0	1.0	
77461-3	Cu-0803	600	2.5 x 10^{-2}	0.9	
77461-4	Cu-0803	800	9.4 x 10^{-2}	1.0	
77461-5	Cu-0803	800	12.4 x 10^{-2}	1.0	VPC - 1.95 to 1 mole ratio $O_2:N_2$ 24% N_2O_4 decomposed**

* Temperature program approximately 10°C/hour.
**Not steady state conditions.

Table 7 (Continued)

Run No.	Catalyst	Reactor Temp, °C	Gas Evolved, ft^3/hr	Run Duration, hours	Notes
77462-2	Cu-0803	750	9.2×10^{-2}	1.0	18% N_2O_4 decomposed**
77462-3	Cu-0803	700	6.0×10^{-2}	0.25	11.8% N_2O_4 decomposed**
77450-1	MRC Pt-Hg	200	1.1×10^{-2}	0.75	Contained no O_2
77450-2 thru 77450-12	MRC Pt-Hg	400-600	0	4.75	Gradual temperature increase during run
77450-13	MRC Pt-Hg	800	4.3×10^{-2}	4.3	VPC - 1.9 to 1 mole ratio O_2:N_2 8.4% N_2O_4 decomposed**
77452-1	Ag-101E	200	3.4×10^{-2}	1.0	N_2 - flow stopped after 30 minutes
77452-2	Ag-101E	400	0	1.0	
77452-3	Ag-101E	600	2.1×10^{-2}	1.0	N_2 - flow stopped after 15 minutes
77452-4	Ag-101E	800	0	1.5	
77453-1	Cu-0402T	200	4.9×10^{-2}	1.0	N_2 - oxidizing catalyst
77453-2	Cu-0402T	400	2.4×10^{-2}	1.2	N_2 - oxidizing catalyst
77453-3	Cu-0402T	600	0.1×10^{-2}	0.8	Flow stopped
77453-4	Cu-0402T	800	0.3×10^{-2}	0.75	Too small for VPC
77454-1	Ni-4305E	200	3.9×10^{-2}	1.0	Flow stopped after 45 minutes
77454-2	Ni-4305E	400	0	1.0	Oxidizing catalyst
77454-3	Ni-4305E	600	0	1.0	
77454-4	Ni-4305E	800	0	1.0	
77455-1	II-077 (0.5% Pt)	200	3.7×10^{-2}	1.1	Oxidizing catalyst
77455-2	II-077 (0.5% Pt)	400	0	1.3	Flow stopped at 1 hour
77455-3	II-077 (0.5% Pt)	600	0.2×10^{-2}	1.0	
77455-4	II-077 (0.5% Pt)	800	23.0×10^{-2}	0.75	45% N_2O_4 decomposed**
77455-5	II-077 (0.5% Pt)	200-800	5.0×10^{-2}	7.0	Linear program approximately 100°C/hour rate given is maximum for 700-800° portion of test

** Not steady state conditions.

In many cases the gas evolution rates cannot be directly interpreted since the gas composition shifts during the test. More extended tests will be performed on the most promising catalysts after the screening program has been completed.

The noble metals have shown activity for decomposing N_2O_4. The extent of this activity appears to be related to the support used or the method of application to the support. Tests 77433 and 77455 illustrate this behavior. In both tests, the active material is platinum and the support is alumina. The catalysts were prepared by different suppliers and the performance difference at 800°C is obvious.

The palladium catalyst tested shows the same order of activity at 800°C as the best platinum catalyst. Test 77441 indicates the gas evolution rate change as the temperature is lowered. This catalyst is active in the 750-800°C range, and is only mildly active at 700°C. No activity is apparent at 650°C.

A test of the rhodium catalyst showed only mild activity at 800°C (see Test 77444).

The metals, nickel, copper, iron and silver, were tested. Where the reduced metal was the active material on the support, the metal was oxidized at 200 and 400°C by the N_2O_4 (see Tests 77429, 77437 and 77453). The gas evolved during this portion of the tests was mostly nitrogen. The composition shifted gradually to nitric oxide just before the flow stopped, indicating the oxidation of the catalyst was complete. Only trace amounts of oxygen were found. At higher temperatures these catalysts exhibited no activity for decomposing N_2O_4.

One of the catalysts, containing copper oxide on supported alumina, was active for N_2O_4 decomposition (see Test 77461). This catalyst, although not as active as platinum or palladium catalysts, does not appear to have the great absorption for oxygen that caused the delay in operation observed with the Pt and Pd catalysts. The catalyst does display the typical decrease of activity as the temperature is reduced from 800°C (see Tests 77462-2 and 77462-3).

The acid zeolite and base-type materials exhibited no activity (see Tests 77426 and 77443). Some further work will be done by incorporating metal cations with the zeolite type materials.

Special catalysts have been prepared and tested in an effort to determine the nature of the decomposition reaction. In several cases oxidation of the catalyst was experienced during the tests and it was felt that if these metal oxides could be decomposed to liberate oxygen and the oxides reformed from the N_2O_4 stream, an oxygen exchange system could be developed. With this in mind silver catalysts were prepared along with amalgams of silver, palladium, and platinum. It was hoped that the amalgams would reduce the decomposition temperature of the oxides of platinum and palladium. These special catalysts exhibited only limited activity for the decomposition of N_2O_4 (see Tests 77441, 77445, 77447 and 77437).

Several tests have been made using small additions of water to the feed stream to determine the effect on the activity of the catalyst. The method chosen to introduce the water has been to saturate a stream of inert gas, argon and helium, with water and inject this stream at the base of the reactor tube. Several difficulties were encountered because of the high solubility of N_2O_4 in water. After these were corrected, runs 77457-1 through 77457-4 were made. The reactor was operated with a catalyst that had measured activity (in this case catalyst II-077 was used) until a steady state gas evolution rate was obtained. At this time the stream of water-saturated argon or helium was started at a rate calculated to add 0.1 to 0.5% water to the N_2O_4 input. In both tests 77457-2 and 77457-4, the corrected gas evolution rate was lower than the measured rate taken just before the water was added. These results do not appear conclusive since the residence time for the system was changed considerably by adding the inert gases.

To check this technique more thoroughly, a microsyringe will be installed in the system, which will deliver 0.2 ml per hour of water to the input stream without adding the large volume of carrier gas used in previous experiments.

C. FUTURE PLANS

Since none of the catalysts tested to date have exhibited sufficient activity to be useful at lower temperatures, it was felt that a large number of new catalysts should be screened in the near future. A new four-reactor system has been designed (see Figure 4) and parts have been ordered to build it. When complete, the system will be operated on a 24-hour/day schedule using a temperature program from 200 to 800°C with automatic equipment to record the data. It is planned that four catalysts will be tested per day with enough time left during working hours to check the performance of the ones that exhibit the highest activity. Three weeks will be required to install this new system and check its operation.

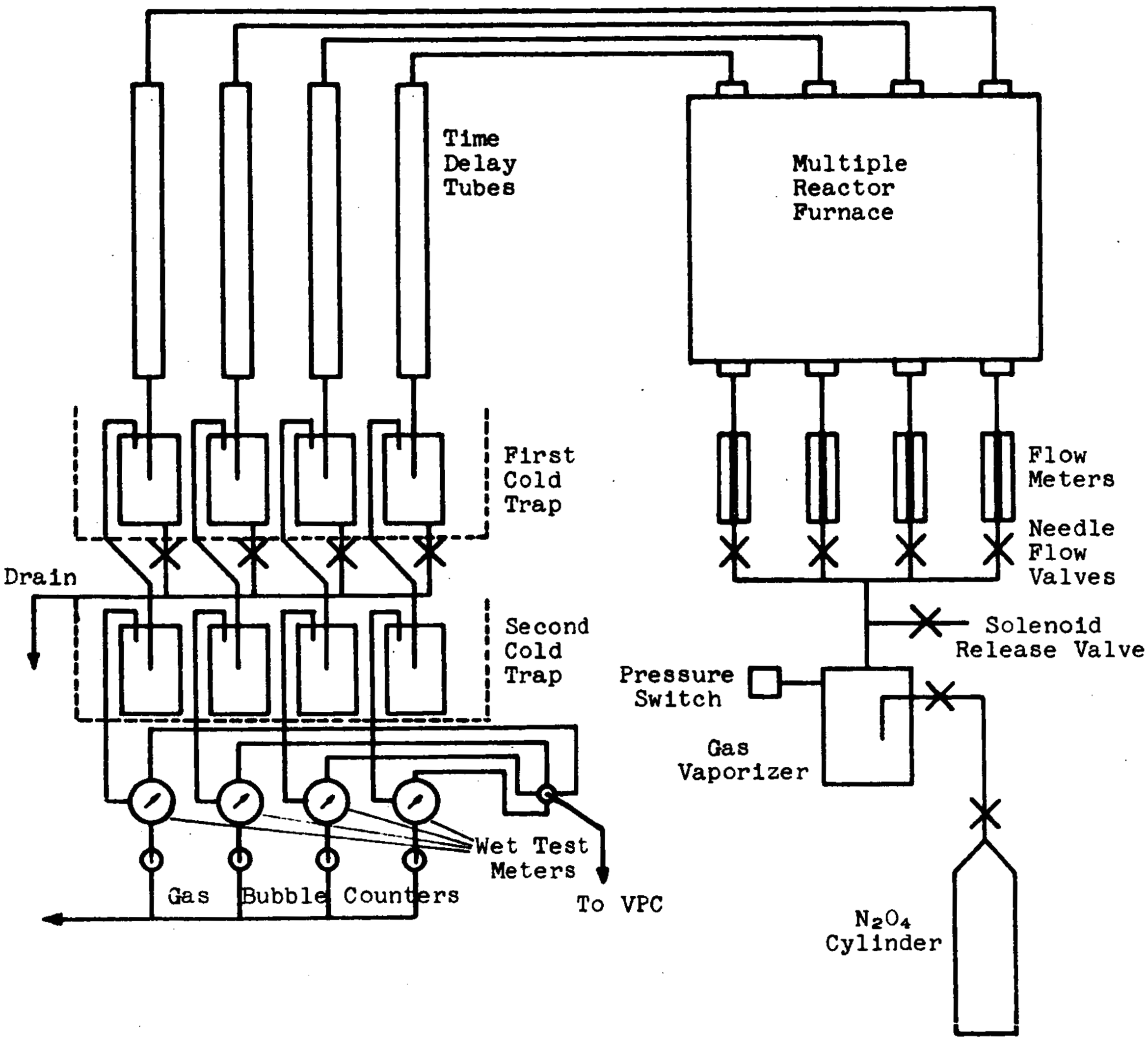


Figure 4. Multiple N_2O_4 Reactors Schematic

Several new catalysts have been prepared that have higher concentrations of the active materials found most satisfactory in the screening tests. Since 0.5% palladium-on-alumina has shown activity, two new catalysts have been prepared that have 5.0% palladium on both alumina and on silica. These were made by soaking the support materials in palladium chloride solution of known concentration, drying them, and then reducing them with hydrogen at elevated temperature for several hours. A catalyst containing 15% palladium-on-alumina is now being prepared in this manner. Catalysts with 5 and 15% platinum will also be made within the next week.

Catalysts will also be made up using Fe_2O_3, Bi_2O_3, MnO_2, CuO, $CaCO_3$, and activated carbon in various ratios as suggested by J. Zawadzki (ref. 3). These are ammonia oxidation catalysts that may also have activity for decomposing oxides of nitrogen at lower temperatures.

Several new catalysts will be made using precipitated silica gel to support reduced copper, copper-silver, and copper-gold alloys. These materials will also be deposited on alumina-silicate cracking catalyst support.

Another approach to testing basic type catalysts (CaO and MgO) will be made by heating the reactor to above the decomposition temperature of the nitrates of Ca and Mg. The temperature will then be reduced after the N_2O_4 feed is started.

IV. TASK III. DIRECT REACTANT USE

A. SUBTASK 3.1. CATHODE OPTIMIZATION

1. Background

The requirements for a good N_2O_4 cathode are as follows:

(a) High electrochemical activity at as high a potential as possible.

(b) Good coulombic efficiencies on a single pass of reactant through the electrode chamber.

(c) Reproducible and predictable diffusion rates of N_2O_4 through the electrode plus a method of controlling diffusion rates.

(d) A water back-diffusion rate less than or equal to stoichiometric water production.

Work on the previous contract (NAS3-4571) sufficiently covered the first requirement: the MRD carbon electrode has adequate polarization characteristics for this application. Work on the current contract has shown that coulombic efficiencies can be improved by proper manifold design aimed at reducing flow rates. This work is described in the First Quarterly Report. There is another area in which coulombic efficiencies can be improved. At present, the reaction product of the cathode reaction is NO:

$$N_2O_4 + 4H^+ + 4e^- = 2NO + 2H_2O$$

If the reaction can be made to proceed as:

$$N_2O_4 + 8H^+ + 8e^- = N_2 + 4H_2O$$

twice as many amp-hours/g of N_2O_4 are theoretically possible. This calls for a catalyst screening program with the objective of promoting the second reaction.

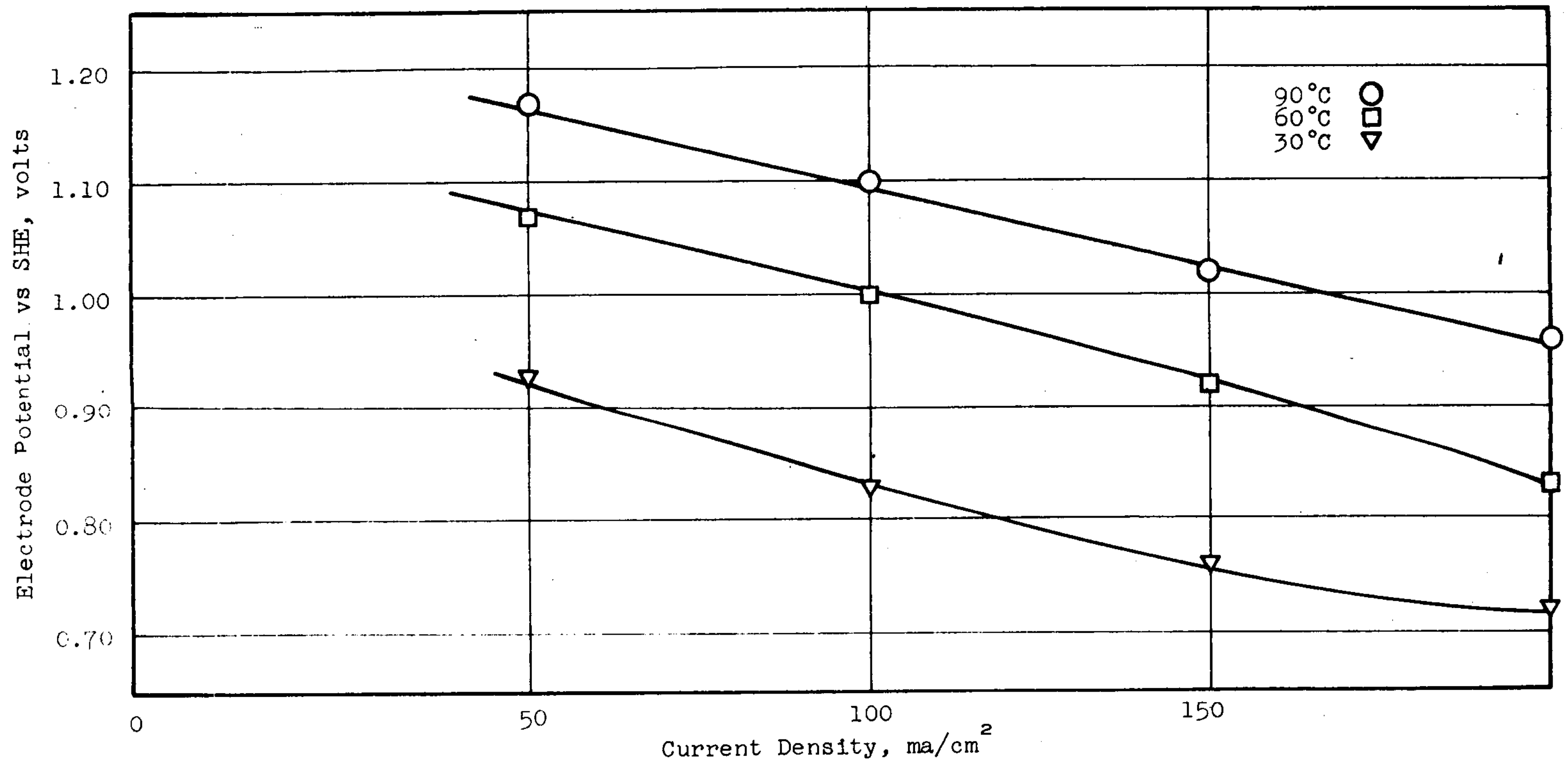
The N_2O_4 diffusion rate through the electrode is important because any excess N_2O_4 above the electrochemical requirements can dissolve in the electrolyte with deleterious effects on efficiency. Two approaches are possible. One method is to control the amount diffusing to that required to maintain the electrochemical reaction. This will require knowledge of the factors affecting diffusion through the electrode and a program has begun to acquire this knowledge. Both temperature and pressure are "external" parameters that can influence the diffusion rate. There are also the "internal" parameters of electrode porosity and composition. The objective of this work is to limit the diffusion of N_2O_4 through the electrode so that electrolyte contamination on open circuit is minimized and to match diffusion to cell current demand by metering the flow and controlling the N_2O_4 pressure. The equipment necessary to achieve this will have to be temperature compensated, since diffusion will be temperature dependent. Finally, since multicell modules will eventually be involved, and control of total N_2O_4 pressure to the module is certainly preferred over control of the supply to individual cells, the diffusion rate through individual electrodes must be reasonably reproducible from electrode to electrode. All these factors must be included in the program.

The second method of attack involves developing a hydrogen anode that can tolerate substantial quantities of nitric-nitrous acid in the electrolyte. A N_2H_4 anode would be less efficient because of the formation of hydrazine-nitrate salts. The H_2 would be produced from Aerozine-50 by steam reforming or low temperature decomposition. The cathode can operate either as a flow-through solution electrode with the N_2O_4 dissolved in the electrolyte (a free electrolyte cell) or as a gas electrode operating on N_2O_4 in a contained electrolyte cell. In either case, diffusion control is not necessary. This system is also attractive because contamination of electrolyte at the anode by UDMH or its reaction products is eliminated.

The back diffusion of H_2O vapor through the cathode is important in maintaining water balance in an operating module. In contained electrolyte cells operating on gaseous reactants, this is the only method that can be used. In other cell types, if all the water produced can be eliminated by this route, no auxiliaries (including phase separation devices) are required. Thus, the water transport properties of the electrode must be determined.

2. <u>Results</u>

Work during the last quarter centered on two aspects: (1) the analytical method used to determine nitrites and nitrates in the electrolyte, and (2) the effect of carbon density and screen mesh size on electrode performance. A new analytical method has been developed for this work and the details are presented in Appendix IV. A series of cathodes with thicknesses varying from 0.025 in. to 0.030 in. and carbon matrix densities from 0.59 to 0.70 g/cc were made using stainless steel screens of 30, 20, and 16 mesh. The higher density cathodes were cold rolled in the uncured (wet) state. Additional densification will be realized by cold pressing after curing. All electrodes will be screened in the diffusion cell described in the First Quarterly Report, and electrochemical performance will be determined in the H_2/N_2O_4 3 x 3 in. cell also described in the referenced report. One electrode has been so tested and the results are presented in Figure 5 and Table 8. This electrode



Electrolyte: 5M H_3PO_4 pumped through cell
N_2O_4: >400 ml/min STP at 5.4 in. H_2O pressure
Cathode: Double MRD-C carbon electrode, 0.048 in. thick, Cold pressed to a carbon matrix density of 0.71 g/cc supported on 16 mesh stainless steel screen.

Figure 5. Polarization Characteristics of Electrode 72493

Table 8

N_2O_4 DIFFUSION THROUGH ELECTRODE 72493

Electrolyte: 5M H_3PO_4
N_2O_4 Flow Rate Through Cell: 1.6-2.0 g/min

Temp, °C	N_2O_4 Pressure, in. H_2O gauge	Diffusion Rate, g N_2O_4/hr/cm^2
26	5.4	0.256
26	0	0.123
60	5.4	0.341
60	0	0.287
90	5.4	0.276
90	0	0.207

Stoichiometric Requirement:

100 ma/cm^2: 0.089 g N_2O_4/hr/cm^2

200 ma/cm^2: 0.178 g N_2O_4/hr/cm^2

had the highest carbon density, but even so, the diffusion rate was 2-3 times the stoichiometric requirement for 100 ma/sq cm over the temperature range of 30-90°C. The polarization characteristics are deemed adequate for this service.

3. <u>Work Plans</u>

(1) Fabricate test electrodes:

(a) Various densities and screen sizes (completed).

(b) Higher and lower carbon/Teflon ratios.

(c) Diffusion barriers: sprayed Teflon, precipited $MnPO_4 \cdot H_2O$, Kel-F oil.

(d) Four different carbon types.

(2) Determine N_2O_4 diffusion rates on above electrodes as a function of pressure and temperature. Check out and standardize ultraviolet absorption analytical method.

(3) Determine polarization characteristics of above electrodes in a 3 x 3 cell quick testing.

(4) Set up and test H_2/N_2O_4 contained electrolyte cell and H_2/HNO_3-HNO_2 (dissolved N_2O_4) free electrolyte cell using double MRD-Pt electrode for anode. Determine if H_2 anode will run for long periods without degradation, steady state coulombic efficiencies.

(5) Fabricate electrodes with different catalysts: Rh, Au, Ag, Ir, Ru, Pd, borides, silicides, NH_3 oxidation catalysts, Ag_2O-$AgSO_4$.

(6) Set up test apparatus to determine N_2O_4 reduction products from 3 x 3 cell. Check out and debug. Determine presence of N_2 and/or N_2O.

(7) Run electrodes made in (5) in apparatus (6). Check for reduction below NO by detecting N_2 or N_2O in product stream. Include evaluation of the effect of $FeSO_4$ in electrolyte (complex NO and hold for reaction).

(8) Run H_2O vapor back diffusion determinations on one or two of the most promising cathodes from above. Set up 3 x 3 cell with wet and dry bulb thermometers in outlet stream, run dry N_2 at a constant flow high enough to insure non-saturation.

B. SUBTASK 3.2. AEROZINE-50 ANODE DEVELOPMENT

1. Background

The objectives of this task are to develop an electrode that will operate on Aerozine-50 as a direct electrochemical fuel with:

(a) High electrochemical activity and little polarization.

(b) High coulombic efficiencies with a single pass of reactant through the electrode chamber.

(c) Little or no contamination of the electrolyte from unreacted fuel or from products of the reaction.

The first requirement dictated a catalyst selective for the reactions involved in the electro-oxidation of the components of the fuel. A catalyst screening program has been in progress to determine the activity of both UDMH and Aerozine-50 on a variety of prospective catalysts.

The achievement of the second objective hinges on two factors:

(a) Minimization of the catalytic decomposition of N_2H_4 on the electrode which causes a loss of fuel efficiency.

(b) Maximization of the ampere-hours output per gram of fuel.

The catalytic decomposition problem is susceptible to solution by electrode design; that is, by preventing direct contact of the catalytic surface of the electrode with large volumes of fuel. The coulombic capacity of the fuel can be greatly increased if some portion of the UDMH fraction can be utilized:

1.67 amp-hr/g of Aerozine-50 if only N_2H_4 is utilized

2.12 amp-hr/g of Aerozine-50 if N_2H_4 is utilized and UDMH is utilized in a $2e^-$ oxidation

3.00 amp-hr/g of Aerozine-50 if N_2H_4 is utilized and UDMH is utilized in a $6e^-$ oxidation

However, the desirability of promoting the electro-oxidation of UDMH depends on whether the reaction products are deleterious or difficult to accommodate in operating cells. Thus, the catalyst screening program has dual objectives:

(a) To find a catalyst that will electro-oxidize both UDMH and N_2H_4 at a reasonably good mixed potential.

(b) To find a catalyst that will electro-oxidize N_2H_4 efficiently but that is inert with respect to UDMH.

Promising catalysts uncovered in the screening program must be further characterized in larger cells in order to determine fuel coulombic efficiencies, long-term electrode performance, and the nature of the reaction products. In this testing various methods of reducing self decomposition of the fuel will be evaluated. Final definitive testing of the most promising electrodes developed will be accomplished in 1/3 sq ft cells in which fuel distribution and product removal systems, electrode support, and cell configuration parameters will be investigated.

2. Catalyst Screening Program

a. Experimental

The 1.3 sq cm cell and associated equipment used in this testing has been described in detail in our First Quarterly Report (ref. 2). Briefly, the fuel is dissolved in the electrolyte, which is pumped across the face of the electrode. This arrangement prevents the collection of gas bubbles on the electrode surface and reduces concentration polarization. IR-free potentials are determined with a Kordesch-Marko bridge. This method allows the true activity of the electrode to be determined free from diffusional effects and other physical limitations.

The catalyst powders are either commercially available or are made in-house by borohydride reduction of metal salts in solution. The latter process produces powders with very small particle size and high surface areas; they generally possess high catalytic activity. Test electrodes are made by incorporating the catalyst powders into MRD-type electrodes supported on Pt screen.

b. Results and Discussion

Thirteen catalysts were reported in the First Quarterly Report. The two that showed the best activity on UDMH fuel were Rh powder (Engelhard) and a proprietary MRC quaternary noble metal alloy catalyst (both gave 0.56 v vs. SHE at 100 ma/sq cm and 60°C). The best catalyst in short-term testing on Aerozine-50 fuel was the same Rh powder (0.13 v vs. SHE, 100 ma/sq cm, 60°C).

This quarter, 17 new catalysts have been evaluated and several of the original 13 have been retested on Aerozine-50. The results of these tests are presented in Table 9. Two new catalysts that performed as well as Rh on UDMH fuel were Ru-Rh alloys (50-50 and 75-25% composition by weight); they yielded 0.54 v vs. SHE at 100 ma/sq cm, 60°C. These catalysts also were active on Aerozine-50 (0.06 v vs. SHE, 100 ma/sq cm, 60°C). Ru, Ir, Ni_2B, Ru-Rh (25-75), and a proprietary five-component alloy (electrode 77628) all showed relatively poor activity on UDMH, and fair to good activity on Aerozine-50, making them candidates for the second objective of the screening program discussed above. The

Table 9

AEROZINE-50 ELECTRODE CATALYST TEST RESULTS

Temperature: 60°C
Electrolyte: 5M H_3PO_4
Fuel: 3M in all cases, dissolved in electrolyte
Electrodes: Catalyst/Teflon mixtures cured on Pt Screen, MRC laboratory made catalysts made by borohydride reduction of salts

Electrode Code	Catalyst Description	Fuel	Electrode Potential (volts) vs SHE at Indicated Current Density, ma/cm² 0	50	100	150	200
50-67226	Rh (Engelhard) - Standard Catalyst	UDMH A-50	0.34 0.00	0.51 0.04	0.55 0.08	0.59 0.09	0.63 0.12
71221-1	Ru (MRC laboratory made)	UDMH A-50	0.39 0.05	0.59 0.08	0.69 0.11	0.77 0.13	0.7[illegible] 0.1[illegible]
71221-3	Rh (MRC laboratory made)	UDMH A-50	0.46 0.09	0.52 0.12	0.59 0.15	0.62 0.16	0.65 0.16
71221-6	Ru-Rh (25-75) Alloy Catalyst (MRC made)	UDMH A-50	0.51 0.09	0.57 0.11	0.64 0.12	0.72 0.13	0.77 0.14
71221-7	Ru-Rh (50-50) Alloy Catalyst (MRC made)	UDMH A-50	0.35 0.04	0.47 0.05	0.54 0.06	0.57 0.07	0.61 0.08
71221-8	Ru-Rh (75/25) Alloy Catalyst (MRC made)	UDMH A-50	0.33 0.04	0.47 0.05	0.54 0.06	0.60 0.06	0.64 0.07
71221-2	Ir (MRC laboratory made)	UDMH A-50	0.39 0.08	0.74 0.14	0.84 0.20	0.95 0.26	1.00 0.30
71221-4	Os (MRC laboratory made)	UDMH A-50	0.42 0.04		No Activity No Activity		
71221-5	Mo (MRC laboratory made)	UDMH A-50	0.41 0.11		No Activity No Activity		
71221-9	Au (MRC laboratory made)	UDMH A-50	0.19 0.11		No Activity No Activity		

Table 9 (Continued)

Electrode Code	Catalyst Description	Fuel	Electrode Potential (volts) vs SHE at Indicated Current Density, ma/cm^2 0	50	100	150	200
56838	MRC Chelate Catalyst on Carbon Substrate	UDMH			No Activity		
		A-50	0.33	0.57	0.65	-	-
68729-3	Raney Nickel on Carbon on SS Screen	UDMH	0.35		No Activity		
		A-50	0.13		No Activity		
73233-29	Ni_2B Catalyst	UDMH			No Activity		
		A-50	-0.02	0.25	0.29	0.30	0.30
73233-1a	Co_2B Catalyst	UDMH	0.36	0.58	0.87	-	-
		A-50	-0.05	0.46	0.50	0.58	0.66
77628	5-Component Precious Metal Alloy Proprietary Catalyst on Carbon	UDMH	0.53	0.69	0.78	-	-
		A-50	0.09	0.17	0.20	0.21	0.23
77605	Pt-1% Mo Alloy Catalyst (MRC made)	UDMH	0.53	0.75	0.84		
		A-50	0.25	0.33	0.40	0.44	0.49
70449-52	Pt-Rh (90-10) Alloy (MRC made)	UDMH	0.55	0.69	0.75		
		A-50	0.21	0.38	0.50	0.56	0.60
73354-9 and -10	5-Component Precious Metal Alloy Proprietary Catalyst	UDMH	0.47	0.55	0.61	0.65	0.66
		UDMH	0.43	0.61	0.64	0.65	0.64
73354-6 and -7 and -8	4-Component Precious Metal Alloy Proprietary catalyst	UDMH	0.45	0.63	0.64	0.65	0.64
		UDMH	0.41	0.62	0.63	0.62	0.63
		UDMH	0.41	0.62	0.67	0.69	0.71
73354-4	Pt -Ru (30-70) Alloy (MRC made)	UDMH	0.36	0.57	0.66	0.74	0.81
77604-1 and -2	5-Component Precious Metal Alloy Proprietary Catalysts	UDMH	0.41	0.58	0.61	[illegible]	0.65
		UDMH	0.45	0.61	0.62	0.63	0.64

best of these at this time appears to be Ru (0.69 v with UDMH, 0.11 v on Aerozine-50, both vs. SHE at 100 ma/sq cm, 60°C). All five catalysts are worth following up for this application.

3. Characterization of Rh Electrodes

a. Experimental

In order to characterize promising electrodes by determining fuel coulombic efficiencies and long-term electrode performance, a test stand and 3 x 3 in. cell configuration were designed, constructed, and tested this quarter. The object of these designs was to trap and measure off-gases from the electrode reactions. Analysis of these gases is a preferred method of determining fuel efficiency. The reactions that can occur with the hydrazine component are:

Catalytic decomposition: $$N_2H_4 \longrightarrow N_2 + 2H_2 \quad (8)$$

Electro-oxidation: $$N_2H_4 \longrightarrow N_2 + 4H^+ + 4e^- \quad (9)$$

The only likely reaction that might upset this analysis is the decomposition to ammonia:

$$3N_2H_4 \longrightarrow 4NH_3 + N_2 \quad (10)$$

The extent of this reaction can be determined by checking H_2/N_2 ratios in the off-gases from open circuit testing; substantial excursions from a 2:1 ratio will indicate that reaction 10 is a significant factor.

The reactions of UDMH are more complex, with many more products involved (ref. 4). However, N_2 is the only gaseous product likely to be formed. In addition, our work on low-temperature decomposition of Aerozine-50 shows UDMH self-decomposition is nonexistent at temperatures of interest in this work. Thus, the participation of UDMH in the anodic reaction will be indicated by the volume of N_2 produced per ampere-hour of cell electrical output.

Calculation details on the effect of UDMH on the volume of N_2 produced per Ampere-hour are included in Appendix V. In general this factor will be a maximum at 7.4×10^{-3} ft^3 of N_2/Ampere-hour. This will occur only when N_2H_4 is the sole reactant at the electrode (UDMH an inert diluent), oxidizing as indicated by reaction 9. The participation of UDMH in the electrooxidation in any mode will decrease this factor. Thus values substantially below 7.4×10^{-3} are a strong indication of UDMH reaction. In practice it is necessary to account for N_2 produced by catalytic decomposition of N_2H_4 in calculating the factor. This can be accomplished by analyzing the off gases for H_2 and back calculating and subtracting the corresponding amount of N_2 using equation (8).

The Aerozine-50/O_2 acid electrolyte cell design used to conduct these tests is shown in Figure 6. This is a free electrolyte cell with the electrolyte pumped across the anode surface. An ion exchange membrane (Ionics Inc. cation exchange membrane 61AZL-183) is used to prevent O_2 from the cathode entering the electrolyte, and to prevent exit of anode gases through the cathode.

The test stand used with this cell is shown in Figure 7. Provision is made for trapping anode off-gases whether from the fuel side of the electrode or from the electrolyte itself. The gas volume can be measured accurately with a Wet Test meter and analytical samples taken for VPC analysis. A controlled power supply and associated equipment is used to determine electrode performance and ampere-hour output.

b. <u>Results and Discussion</u>

Two electrodes containing Rh catalysts (Engelhard) have been tested to date. The first was a standard MRD Rh/Teflon electrode supported on a Pt screen. Catalyst loading was 0.3 g of Rh/in.^{2}, and no provision was made to limit the contact of fuel with the catalytic surface. Pure Aerozine-50 was pumped to the anode chamber at a rate of 19 g/min. The self-decomposition rate of this electrode (measured on open circuit) was extremely high; at 40°C the gas evolution rate was 2.5 ft^3/hour. The reaction is exothermic, and enough heat was generated in this test to raise the cell temperature sharply. The electrode was apparently damaged by the high temperature and subsequently leaked electrolyte badly. Thus, the electrochemical performance could not be determined on pure Aerozine-50. The catalytic activity of the electrode was reduced as shown by the results with the fuel dissolved in the electrolyte (0.43 v vs. SHE at 100 ma/sq cm, 60°C). This test decisively demonstrated the necessity of limiting the gross contact of the fuel with the catalytic surface by incorporation of suitable diffusion barriers.

The second anode tested consisted of an MRD Rh electrode, with the same catalyst loading as the electrode previously described, in conjunction with a MRD carbon electrode, 0.020 in. thick, with the carbon side toward the fuel and the catalytic side toward the electrolyte. The MRD carbon electrodes have been shown to be capillary membranes (passing vapors only). Thus, this electrode served as a vapor diffusion membrane in this test. The self-decomposition rate of Aerozine-50 on this electrode was determined as function of temperature as shown in Figure 8. At 40°C, the gas evolution rate on open circuit measured 4.4×10^{-2} ft^3/hour, nearly two orders-of-magnitude below the rate found with the unprotected electrode. Duplicate VPC analysis on gas samples (taken during the 55°C test) showed a H_2/N_2 ratio of 1.8/1, close enough to the theoretical 2.0 to indicate little NH_3 formation.

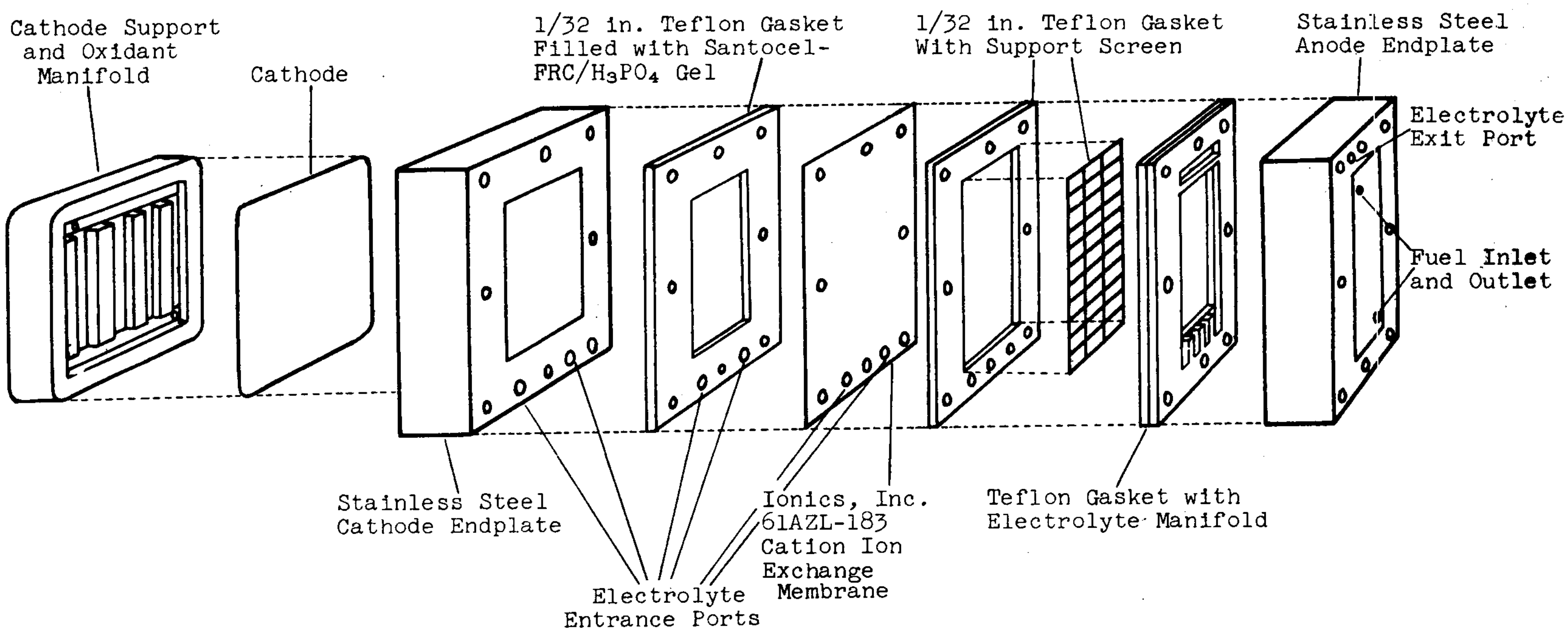


Figure 6. Aerozine-50 Anode Test Cell Construction

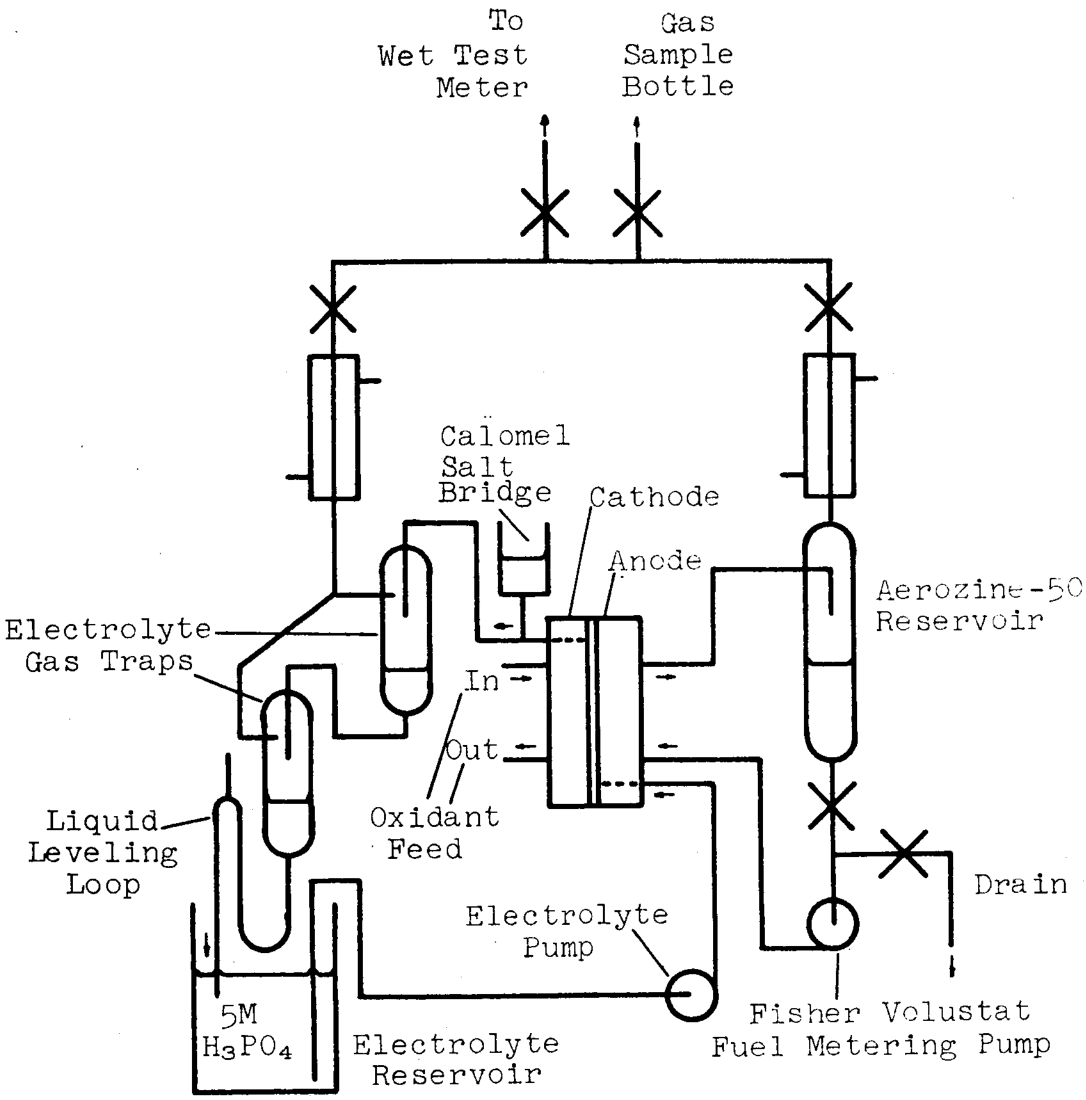


Figure 7. Aerozine-50/O_2 Cell Test Stand

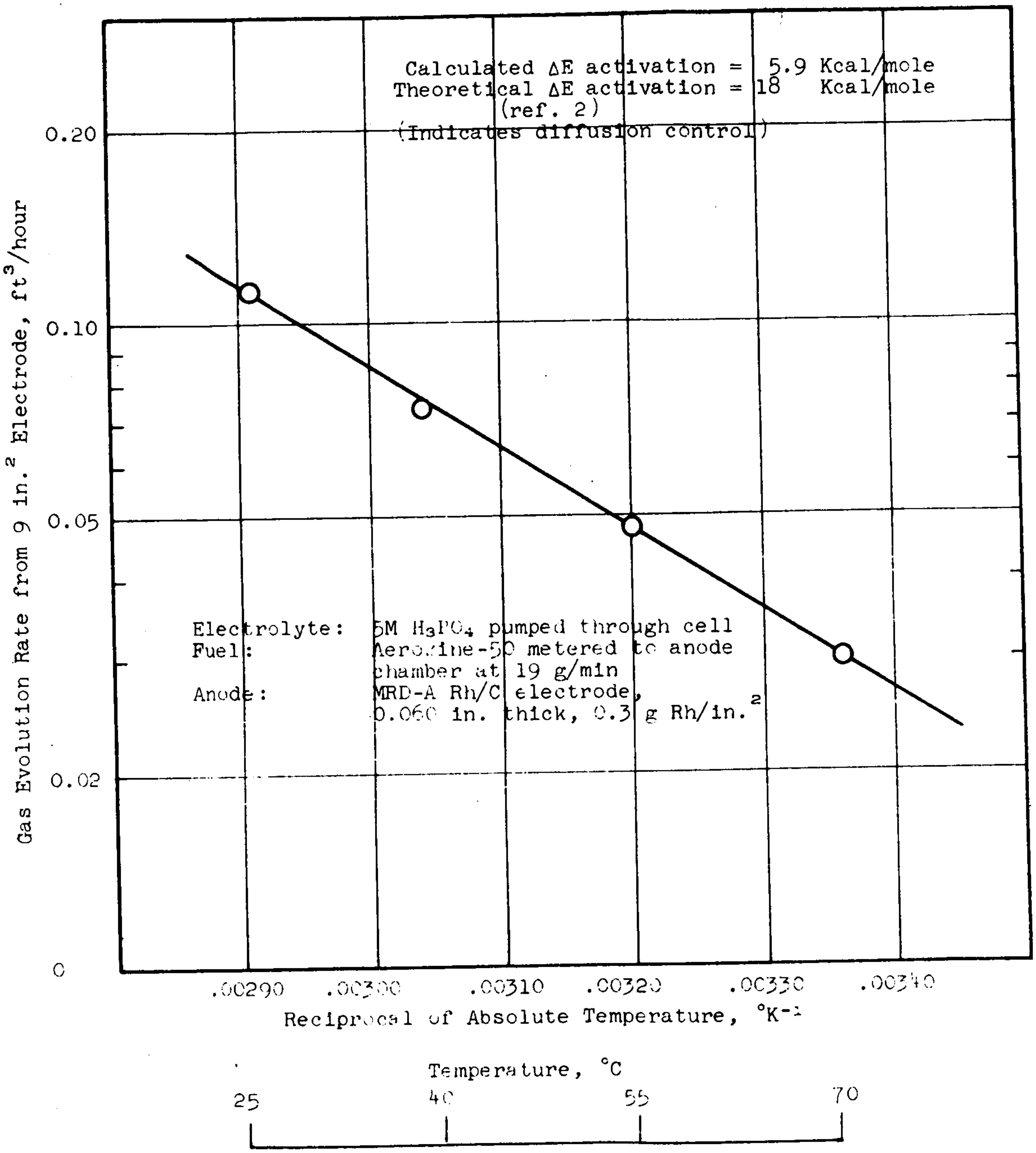


Figure 8. Self Decomposition of Aerozine-50 on Electrode 72468-A

Polarization characteristics were determined as a function of temperature as shown in Figure 9. The results are generally indicative of diffusion limitations. Tests at 55°C indicated the limiting current density with this electrode is 10 to 15 ma/sq cm. The results of a two-hour run at 55°C, 50 ma/sq cm, are given in Table 10. Several conclusions can be drawn from these test results:

(1) The fuel diffusion rate through the carbon electrode is not sufficient to support 50 ma/sq cm. Future electrodes must provide more diffusion, but this will probably cause some increase in the self-decomposition rate.

(2) The self-decomposition rate was greatly reduced during this test. This is most likely due to the low concentration of N_2H_4 at the electrode surface because of limited diffusion and the competing electrochemical reaction.

(3) The change in N_2 volume per ampere-hour factor from the first hour of test to the second hour indicates a change in the dominant reaction at the electrode. This conclusion is supported by the change also observed in the electrode potential. However, the possible deleterious effects of reaction products has not been established in this test because of the poor diffusion characteristics.

4. Future Plans

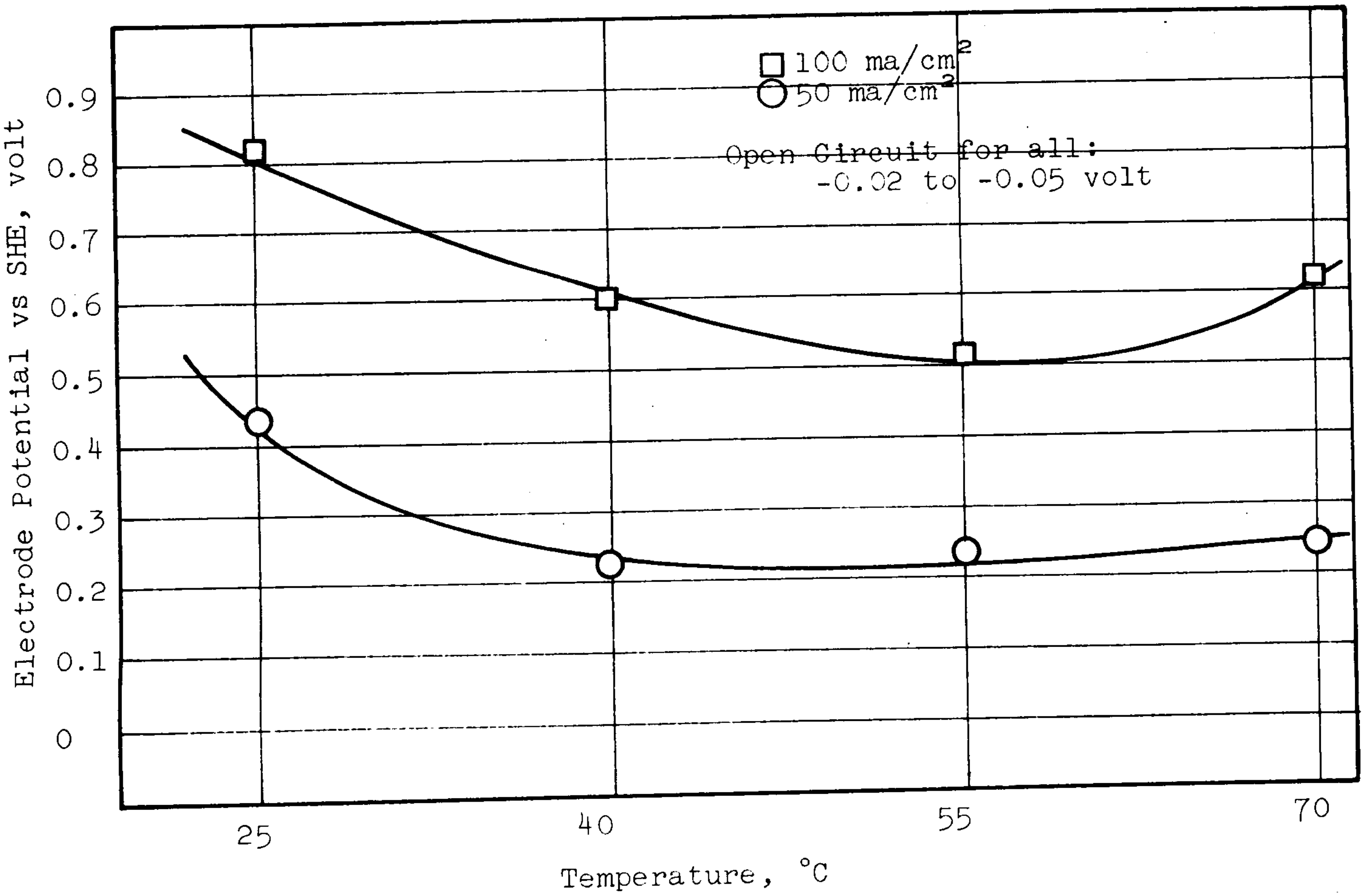
(1) Test different diffusion barriers with Rh electrodes: more porous carbon, stainless steel plaque, silica-gel/Teflon membranes.

(2) Run long-term test on Rh: determine if UDMH active and if products can be tolerated.

(3) Fabricate and test electrodes made with catalysts not active on UDMH but which worked well with Aerozine-50.

(4) Evaluate results after above tests complete: if not satisfactory, start catalyst screening program again to discover new catalysts worthy of test, retest same in 3 x 3 cell.

(5) Select best 1 or 2 electrodes, fabricate 7" x 7" electrodes and run tests in 1/3 ft^2 cells. Check efficiency and performance, determine proper fuel manifold geometry, test both contained and free electrolyte cell configuration.



Electrolyte: 5M H_3PO_4 pumped through cell
Fuel: Aerozine-50 metered to anode chamber at 19 g/min
Anode: MRD-A Rh/C electrode, 0.060 in. thick, 0.3 g Rh/in.^{2}

Figure 9. Polarization Characteristics of Electrode 72468-A

Table 10

TWO-HOUR RUN OF Rh/C ANODE

Fuel:	Aerozine-50 pumped to electrode at 19 g/min
Electrolyte:	5M H_3PO_4, pumped through cell
Current Drain:	50 ma/cm^2
Temperature:	55°C

Time, hours	Potential vs SHE, volt	Cumulative Gas Volume, ft^3
0	-0.02	0
0.25	0.37	0.0072
0.5	0.35	0.0118
1.0	0.37	0.0185
1.5	0.47	0.0258
2.0	0.53	0.0280

Gas Sample VPC Analysis: H_2, 3.7%
N_2, 96.3%

Calculated N_2 Volume Factor:

First hour of test, 5.9×10^{-3} ft^3/amp-hour
Second hour of test, 3.2×10^{-3} ft^3/amp-hour

C. SUBTASK 3.2 DESIGN AND TEST 1/3-FT^2 ELECTRODES

1. Background

The contract work statement requires definitive electrode testing to be performed in 1/3-ft^2 half cells, with ultimate testing of all reactants of interest (including reformer products) in this size cell. Initial screening programs are being carried out in smaller cell sizes, but final testing of all promising developments will be performed in the larger cells. The cell frames and holders have been designed and four sets ordered. The manifold geometry has been approved by the Project Monitor and three flow plate thicknesses have been ordered. The first work with these cells will be to determine the effect of flow plate geometry and thickness on the coulombic efficiency of the N_2O_4 electrode. Previous work has shown the importance of gas Reynolds number on performance of these electrodes. Similar studies will be carried out with Aerozine-50. Finally, half cells operating on all reactants of interest will be demonstrated in this configuration.

2. Work Plan

(a) Design and construct test stands including control and analytical equipment.

(b) Fabricate N_2O_4 electrodes to be tested (2 or 3 most promising from initial program) and determine optimum operating parameters:

Reactant flow rate
Temperature (40-100°C)
Reactant pressures
Three manifold plates

Measure:
Coulombic efficiencies at 100 ma/cm^2
Polarization characteristic 50-200 ma/cm^2
Electrolyte contamination

In addition, measure H_2O back diffusion at temperatures 40-100°C with N_{Re} equivalent to flow rates used.

(c) Fabricate Aerozine-50 anodes to be tested (2 or 3 most promising); determine optimum operating parameters (flow rates, temperature, pressure, manifold plates).

(d) Fabricate electrodes and run initial tests for following reactants:

(1) $O_2 + N_2$ in 2:1 mole ratio (simulated N_2O_4 reformer stream) on Pt MRD laminar electrode.

(2) $H_2 + CO_2 + CO$ in ratios as determined from steam reforming data, on best catalyst found in dirty hydrogen work on another contract (ref. 5).

(3) H_2 from decomposition of Aerozine-50 ($H_2 + N_2$ in 2:1 mole ratio + UDMH at partial pressure = vapor pressure of UDMH at decomposition temperature), on Pt MRD electrode.

(e) Depending on results in 3 x 3 cell testing: construct one full cell (either contained or free electrolyte) operating on H_2 and N_2O_4 (gas or dissolved in electrolyte). Determine coulombic efficiency over long-term run. Determine optimum operating parameters.

V. REFERENCES

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3. J. Zawadski, Disc Faraday Soc., 8, 140 (1950).

4. D. M. King and A. J. Bard, "The Electrochemistry of the Methylhydrazines", J. Am. Chem. Soc., 87:3, 419 (1965).

5. J. C. Orth, "Research to Improve Electrochemical Catalysts", Final Report, Contract DA-49-186-AMC-166(X), USAERDL, Fort Belvoir, Va., to be published.

APPENDIX I

HEAT BALANCES FOR AEROZINE-50 REFORMING SYSTEMS

In the following discussion and tables heats of reaction and heats for raising and lowering the temperature of reactants and products are given in kilocalories (Kcal). A positive sign indicates that external heat is needed to maintain the temperature of the system, and a negative sign indicates the system must reject waste heat.

SYSTEM 1

Only N_2H_4 decomposes to H_2, N_2 and NH_3. Table 1 shows the total heat balance at 25°C for N_2H_4 decomposing in various ratios of NH_3 and H_2 formation for 100 g Aerozine-50 input.

Table A-1

HEAT BALANCE FOR SYSTEM 1 AT 25°C, BASIS 100 G AEROZINE-50

% N_2H_4 Decomposing to NH_3	% N_2H_4 Decomposing to H_2	Total System Heat Balance, Kcal
70	30	-35.71
40	60	-28.48
10	90	-21.33

Reactions: a. $N_2H_4(\ell) \longrightarrow N_2(g) + 2H_2(g)$

$\Delta H = -12.05$ Kcal

b. $N_2H_4(\ell) \longrightarrow 4/3\ NH_3(g) + 1/3\ N_2(g)$

$\Delta H = -27.50$ Kcal

This indicates that effective cooling is needed to maintain temperature. Higher temperatures such as 60°C may be preferable since the fuel cell would probably operate at this temperature and the UDMH portion of the fuel could be used as a heat absorber.

SYSTEM 2

At temperatures of 100°C to 250°C, significant decomposition of UDMH to CH_4 and N_2 takes place. This adds more exothermic heat, which must be rejected. The reactions are:

		ΔH at 100°C as Liquid, Kcal	ΔH at 175°C as Vapor, Kcal	ΔH at 250°C as Vapor, Kcal
a.	$N_2H_4(\ell) \rightarrow N_2 + 2H_2$	-12.79		
b.	$N_2H_4(g) \rightarrow N_2 + 2H_2$		-21.79	-21.31
c.	$N_2H_4(\ell) \rightarrow 4/3\ NH_3 + 1/3\ N_2$	-28.63		
d.	$N_2H_4(g) \rightarrow 4/3\ NH_3 + 1/3\ N_2$		-37.92	-37.67
e.	$UDMH(\ell) \rightarrow 2CH_4 + N_2$	-48.53		
f.	$UDMH(g) \rightarrow 2CH_4 + N_2$		-54.91	-54.16

Table A-2 shows the overall heat balance for this system, assuming reactants are heated to operating temperature and products are cooled to 100°C. The basis is 100 g of Aerozine-50.

Table A-2

HEAT BALANCE FOR SYSTEM 2 AT 100°C, 175°C, AND 250°C FOR 100 G AEROZINE-50 INPUT

Temp, °C	% N_2H_4 to $4/3\ NH_3 + 1/3\ N_2$	% N_2H_4 to $2H_2 + N_2$	% UDMH to $2CH_4 + N_2$	Total Heat Balance, Kcal
100	70	30	5	-33.95
	40	60	5	-26.53
	10	90	5	-19.11
175	70	30	20	-39.02
	40	60	20	-31.70
	10	90	20	-24.41
250	70	30	50	-50.29
	40	60	50	-43.09
	10	90	50	-35.85

SYSTEMS 3 AND 4

Systems 3 and 4 include a variety of reactions. Those easiest to work from and having a basis in experimental fact are:

		ΔH at 400°C, Kcal	ΔH at 500°C, Kcal
a.	$UDMH(g) \rightarrow 2CH_4 + N_2$	-52.40	-50.82
b.	$UDMH(g) \rightarrow (CH_3)_2NH + 1/3\ N_2 + 1/3\ NH_3$	-29.66	-29.12
3.	$UDMH(g) + 2H_2O \rightarrow 2CO + 2NH_3 + 3H_2$	24.56	26.06
d.	$UDMH(g) + 4H_2O \rightarrow 2CO_2 + 2NH_3 + 5H_2$	9.88	13.52
e.	$N_2H_4(g) \rightarrow 4/3\ NH_3 + 1/3\ N_2$	-36.87	-36.36
f.	$CO + H_2O \rightarrow CO_2 + H_2$	- 7.34	- 6.27
g.	$NH_3 \rightarrow 3/2\ H_2 + 1/2\ N_2$	12.46	12.47

Table A-3 gives the heat balances under different conditions for Systems 3 and 4. System 4 converts all CO and NH_3 from System 1 to H_2 and N_2.

All reactants are heated from 25°C to operating temperature, and products are cooled to 100°C, including the heat of condensation of unreacted H_2O.

Table A-3

HEAT BALANCES FOR SYSTEMS 3 AND 4 AT 400°C and 500°C ASSUMING 100 G AEROZINE-50 AND 50% H_2O EXCESS

Temp, °C	% N_2H_4 to NH_3	% N_2H_4 to H_2	% UDMH by reactions					Heat Balance System 3, Kcal	Heat Balance System 4, Kcal
			a	b	c	d	d+e		
400	100	0	5	50	5	40	0	-22.68	10.48
400	50	50	5	50	5	40	0	- 9.71	10.48
500	100	50	60	0	2	20	18	-31.13	- 4.41
500	50	50	60	0	2	20	18	-18.16	- 4.41

Thus, under reaction conditions assumed for System 3 at 400°C and 500°C, significant excess heat is present when N_2H_4 produces NH_3 only. About 50% less heat is present when 50% of N_2H_4 is producing H_2. This heat would probably be needed to maintain temperature from heat radiation losses.

System 4 will need external heating at 400°C, but will be close to a balance at 500°C. Thus, a much higher H_2 efficiency must be realized from this system to supplant needed external power.

APPENDIX IIA

UDMH STEAM REFORMING DATA

UDMH STEAM REFORMING DATA SHEET

Catalyst Norton Zeolite (cation type) Temperature, °C 300

Pressure, psig 50 Gas Volume Rate, l/hr ______

Moles Gas Produced/Hr ______ % UDMH Used 39.4

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.465	15.08	21.55
Feed Composition, mole/hr	0.1078	0.838	0.946

Total Output Composition, mole-%: UDMH ______ H_2O ______

N_2H_4 ______ NH_3 ______ Dimethylamine ______ H_2 ______

N_2 ______ CH_4 ______ CO ______ CO_2 ______

Ethane ______ Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:						

% H_2O Used: ______ % Reforming to CO_2: ______ % to CO: ______

Moles NH_3 Formed/hr: ______

Moles Dimethylamine Formed/hr: ______

g atom Carbon Deposition/hr: ______

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: ______

Moles H_2 per 100 g total input: ______

Hydrogen efficiency =

Note: Not enough gas produced for analysis.

UDMH STEAM REFORMING DATA SHEET

Catalyst: Norton Zeolite — Temperature, °C: 400

Pressure, psig: 50 — Gas Volume Rate, l/hr: 2.20

Moles Gas Produced/Hr: 0.089 — % UDMH Used: 87.0

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.243	14.57	20.81
Feed Composition, mole/hr	0.104	0.809	0.913

Total Output Composition, mole-%: UDMH 1.4 — H_2O 77.1

N_2H_4 ____ — NH_3 7.3 — Dimethylamine 5.6 — H_2 0.1

N_2 2.5 — CH_4 3.3 — CO 1.8 — CO_2 0.5

Ethane 0.4 — Other ____

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:	3.0	28.3	37.4	20.8	5.8	4.8

% H_2O Used: 3.6 — % Reforming to CO_2: 2.5 — % to CO: 8.9

Moles NH_3 Formed/hr: 0.074 }
Moles Dimethylamine Formed/hr: 0.057 } calculated to complete mass balance
g atom Carbon Deposition/hr: 0.001 }

Moles H_2 per 100 g UDMH input: 0.02

Moles H_2 per 100 g total input: 0.006

Hydrogen efficiency = 0.2%

Note: Output liquid highly colored indicating other compounds besides amines present

UDMH STEAM REFORMING DATA SHEET

Catalyst Norton Zeolite   Temperature, °C 500

Pressure, psig 50   Gas Volume Rate, l/hr 6.460

Moles Gas Produced/Hr 0.263   % UDMH Used 99.5

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.923	13.83	19.75
Feed Composition, mole/hr	0.0987	0.768	0.867

Total Output Composition, mole-%: UDMH 0.05 H_2O 70.5

N_2H_4 ____ NH_3 3.3   Dimethylamine 1.3 H_2 2.2

N_2 6.9 CH_4 13.4   CO 1.3 CO_2 0.6

Ethane 0.4   Other ____

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:	9.0	27.9	53.9	5.2	2.3	1.6

% H_2O Used: 3.4   % Reforming to CO_2: 3.0   % to CO: 6.9

Moles NH_3 Formed/hr: 0.037

Moles Dimethylamine Formed/hr: 0.014

g atom Carbon Deposition/hr: 0.004

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 0.40

Moles H_2 per 100 g total input: 0.12

Hydrogen efficiency = 3.0%

UDMH STEAM REFORMING DATA SHEET

Catalyst ZnO701   Temperature, °C 300

Pressure, psig 50   Gas Volume Rate, l/hr 0.14

Moles Gas Produced/Hr 0.006   % UDMH Used 6.1

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.402	14.94	21.34
Feed Composition, mole/hr	0.1065	0.830	0.937

Total Output Composition, mole-%: UDMH ______ H_2O ______

N_2H_4 ______ NH_3 ______ Dimethylamine ______ H_2 ______

N_2 ______ CH_4 ______ CO ______ CO_2 ______

Ethane ______ Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:						

% H_2O Used: ______ % Reforming to CO_2: ______ % to CO: ______

Moles NH_3 Formed/hr: ______

Moles Dimethylamine Formed/hr: ______

g atom Carbon Deposition/hr: ______

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: ______

Moles H_2 per 100 g total input: ______

Hydrogen efficiency =

Note: Not enough gas produced for analysis.

UDMH STEAM REFORMING DATA SHEET

Catalyst ZnO701 Temperature, °C 400

Pressure, psig 50 Gas Volume Rate, l/hr 5.438

Moles Gas Produced/Hr 0.221 % UDMH Used 96.1

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.402	14.94	21.34
Feed Composition, mole/hr	0.1065	0.830	0.937

Total Output Composition, mole-%: UDMH 0.4 H_2O 61.8

N_2H_4 ____ NH_3 13.4 Dimethylamine 4.6 H_2 12.8

N_2 0.2 CH_4 0.4 CO 0.2 CO_2 6.3

Ethane 0 Other ____

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	57.6	1.1	1.7	1.0	38.7	none
1-1/2 hour:	64.3	1.2	1.8	1.1	31.6	none

% H_2O Used: 17.1 % Reforming to CO_2: 32.8 % to CO: 1.1

Moles NH_3 Formed/hr: 0.149
Moles Dimethylamine Formed/hr: 0.051
g atom Carbon Deposition/hr: 0.027
} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 2.22

Moles H_2 per 100 g total input: 0.67

Hydrogen efficiency = 16.7

UDMH STEAM REFORMING DATA SHEET

Catalyst Zn0701 Temperature, °C 500

Pressure, psig 50 Gas Volume Rate, l/hr 11.79

Moles Gas Produced/Hr 0.479 % UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.402	14.94	21.34
Feed Composition, mole/hr	0.1065	0.830	0.937

Total Output Composition, mole-%: UDMH 0 H_2O 53.6

N_2H_4 ____ NH_3 6.6 Dimethylamine 0.6 H_2 18.1

N_2 5.1 CH_4 8.5 CO 0.4 CO_2 6.9

Ethane 0.2 Other ____

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	43.3	11.8	20.2	1.0	23.4	0.5
1-1/2 hour:	46.3	13.0	21.6	1.1	17.6	0.5

% H_2O Used: 21.0 % Reforming to CO_2: 39.6 % to CO: 2.5%

Moles NH_3 Formed/hr: 0.081

Moles Dimethylamine Formed/hr: 0.0075

g atom Carbon Deposition/hr: 0

} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 3.47

Moles H_2 per 100 g total input: 1.04

Hydrogen efficiency = 26.0

UDMH STEAM REFORMING DATA SHEET

Catalyst T-317 Cu oxide on Alumina
Temperature, °C 300

Pressure, psig 50
Gas Volume Rate, l/hr 4.431

Moles Gas Produced/Hr 0.180
% UDMH Used 99.2

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.264	14.62	20.88
Feed Composition, mole/hr	0.1045	0.8122	0.9167

Total Output Composition, mole-%: UDMH 0.1 H_2O 67.4

N_2H_4 ____ NH_3 12.5 Dimethylamine 3.2 H_2 11.3

N_2 1.5 CH_4 1.0 CO 0.1 CO_2 2.8

Ethane 0 Other ____

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:	66.8	9.0	6.4	0.5	17.3	none

% H_2O Used: 7.8 % Reforming to CO_2: 14.9 % to CO: 0.4

Moles NH_3 Formed/hr: 0.139 }
Moles Dimethylamine Formed/hr: 0.036 } calculated to complete mass balance
g atom Carbon Deposition/hr: 0.091 }

Moles H_2 per 100 g UDMH input: 2.0

Moles H_2 per 100 g total input: 0.60

Hydrogen efficiency = 15.1%

Note: Gas rate slowing down with time.

UDMH STEAM REFORMING DATA SHEET

Catalyst T-317 Temperature, °C 400

Pressure, psig 50 Gas Volume Rate, l/hr 3.016

Moles Gas Produced/Hr 0.123 % UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.264	14.62	20.88
Feed Composition, mole/hr	0.1045	0.812	0.917

Total Output Composition, mole-%: UDMH ______ H_2O ______

N_2H_4 ______ NH_3 ______ Dimethylamine ______ H_2 ______

N_2 ______ CH_4 ______ CO ______ CO_2 ______

Ethane ______ Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	37.8	7.1	8.4	24.0	22.7	none
1-1/2 hour:	45.5	9.1	10.1	31.0	4.3	none

% H_2O Used: ______ % Reforming to CO_2: ______ % to CO: ______

Moles NH_3 Formed/hr: ______

Moles Dimethylamine Formed/hr: ______

g atom Carbon Deposition/hr: ______

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: ______

Moles H_2 per 100 g total input: ______

Hydrogen efficiency =

Note: Test invalid due to large carbon deposition at 300°C which affected this test.

UDMH STEAM REFORMING DATA SHEET

Catalyst T-317 Temperature, °C 500

Pressure, psig 50 Gas Volume Rate, l/hr 9.740

Moles Gas Produced/Hr 0.396 % UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.264	14.62	20.88
Feed Composition, mole/hr	0.1045	0.812	0.917

Total Output Composition, mole-%: UDMH 0 H_2O 58.6

N_2H_4 ______ NH_3 7.2 Dimethylamine 0.8 H_2 12.6

N_2 4.9 CH_4 8.9 CO 3.5 CO_2 3.4

Ethane 0.3 Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:	37.6	14.5	26.5	10.3	10.2	0.8

% H_2O Used: 15.0 % Reforming to CO_2: 19.3 % to CO: 19.5

Moles NH_3 Formed/hr: 0.085

Moles Dimethylamine Formed/hr: .009

g atom Carbon Deposition/hr: 0

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 2.37

Moles H_2 per 100 g total input: 0.71

Hydrogen efficiency = 17.8

UDMH STEAM REFORMING DATA SHEET

Catalyst Girdler T-1144 Temperature, °C 300

Pressure, psig 50 Gas Volume Rate, l/hr 1.148

Moles Gas Produced/Hr 0.047 % UDMH Used 77.9

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.234	14.55	20.78
Feed Composition, mole/hr	0.104	0.808	0.912

Total Output Composition, mole-%: UDMH 2.3 H_2O 79.6

N_2H_4 ______ NH_3 7.6 Dimethylamine 5.8 H_2 1.4

N_2 1.5 CH_4 0.9 CO 0 CO_2 0.9

Ethane 0 Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:	28.6	32.4	19.5	none	19.4	none

% H_2O Used: 2.2 % Reforming to CO_2: 4.3 % to CO: 0

Moles NH_3 Formed/hr: 0.076

Moles Dimethylamine Formed/hr: 0.056

g atom Carbon Deposition/hr: 0.032

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 0.22

Moles H_2 per 100 g total input: 0.06

Hydrogen efficiency = 1.6

UDMH STEAM REFORMING DATA SHEET

Catalyst Girdler T-1144 | Temperature, °C 400

Pressure, psig 50 | Gas Volume Rate, l/hr 7.660

Moles Gas Produced/Hr 0.311 | % UDMH Used 98.9

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.916	13.80	19.72
Feed Composition, mole/hr	0.0985	0.767	0.866

Total Output Composition, mole-%: UDMH 0.1 H_2O 55.2

N_2H_4 ____ NH_3 14.1 Dimethylamine 2.0 H_2 16.4

N_2 0.9 CH_4 3.2 CO 0.9 CO_2 7.2

Ethane 0.1 Other ____

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	59.1	3.5	6.8	5.1	25.5	none
1-1/2 hour:	54.9	2.9	15.2	1.0	25.6	0.3
one	57.3	3.2	11.1	3.1	25.1	0.2

% H_2O Used: 21.6 % Reforming to CO_2: 39.6 % to CO: 4.9

Moles NH_3 Formed/hr: 0.153

Moles Dimethylamine Formed/hr: 0.022

g atom Carbon Deposition/hr: 0.028

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 3.02

Moles H_2 per 100 g total input: 0.90

Hydrogen efficiency = 22.6%

UDMH STEAM REFORMING DATA SHEET

Catalyst Girdler T-1144 Temperature, °C 500

Pressure, psig 50 Gas Volume Rate, l/hr 11.77

Moles Gas Produced/Hr 0.4784 % UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.820	13.58	19.40
Feed Composition, mole/hr	0.097	0.754	0.851

Total Output Composition, mole-%: UDMH 0 H_2O 55.0

N_2H_4 ______ NH_3 2.3 Dimethylamine 0.7 H_2 19.3

N_2 7.0 CH_4 9.9 CO 0.2 CO_2 5.5

Ethane none Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	38.4	13.5	18.5	1.1	28.5	none
1-1/2 hour:	45.9	16.7	23.7	0.5	13.2	none

% H_2O Used: 17.1 % Reforming to CO_2: 32.5 % to CO: 1.2

Moles NH_3 Formed/hr: 0.026

Moles Dimethylamine Formed/hr: 0.008

g atom Carbon Deposition/hr: none

} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 3.77

Moles H_2 per 100 g total input: 1.13

Hydrogen efficiency = 28.3

UDMH STEAM REFORMING DATA SHEET

Catalyst Zn0308 | Temperature, °C 300

Pressure, psig 50 | Gas Volume Rate, l/hr 3.417

Moles Gas Produced/Hr 0.139 | % UDMH Used 87.5

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.354	14.83	21.18
Feed Composition, mole/hr	0.106	0.824	0.930

Total Output Composition, mole-%: UDMH 1.3 H_2O 70.5

N_2H_4 ______ NH_3 9.2 Dimethylamine 5.8 H_2 6.9

N_2 1.3 CH_4 1.1 CO 0 CO_2 3.9

Ethane 0 Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:	52.6	9.8	8.0	none	29.6	none

% H_2O Used: 10.0 % Reforming to CO_2: 19.4 % to CO: 0

Moles NH_3 Formed/hr: 0.097

Moles Dimethylamine Formed/hr: 0.061

g atom Carbon Deposition/hr: 0.011

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 1.15

Moles H_2 per 100 g total input: 0.34

Hydrogen efficiency = 8.6

Note: Zinc chromite catalyst was attacked and prevented further testing at higher temperatures.

UDMH STEAM REFORMING DATA SHEET

Catalyst Cu2501 — Temperature, °C 300

Pressure, psig 50 — Gas Volume Rate, l/hr ______

Moles Gas Produced/Hr ______ — % UDMH Used 57.3

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.402	14.94	21.34
Feed Composition, mole/hr	0.1065	0.830	0.937

Total Output Composition, mole-%: UDMH ______ H_2O ______

N_2H_4 ______ NH_3 ______ Dimethylamine ______ H_2 ______

N_2 ______ CH_4 ______ CO ______ CO_2 ______

Ethane ______ Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:						

% H_2O Used: ______ % Reforming to CO_2: ______ % to CO: ______

Moles NH_3 Formed/hr: ______
Moles Dimethylamine Formed/hr: ______
g atom Carbon Deposition/hr: ______
} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: ______

Moles H_2 per 100 g total input: ______

Hydrogen efficiency =

Note: Not enough gas production for measurement. Catalyst attacked at higher temperatures.

UDMH STEAM REFORMING DATA SHEET

Catalyst T-310 NiO — Temperature, °C 300

Pressure, psig 50 — Gas Volume Rate, l/hr 1.32

Moles Gas Produced/Hr 0.054 — % UDMH Used 81.3

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.73	13.37	19.10
Feed Composition, mole/hr	0.0955	0.743	0.839

Total Output Composition, mole-%: UDMH 2.0 H_2O 77.4

N_2H_4 - NH_3 8.0 Dimethylamine 6.6 H_2 2.0

N_2 1.2 CH_4 0.6 CO 0.1 CO_2 2.1

Ethane none Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:	33.0	20.7	9.6	1.0	35.7	none

% H_2O Used: 5.3 % Reforming to CO_2: 10.1 % to CO: 10.3

Moles NH_3 Formed/hr: 0.073
Moles Dimethylamine Formed/hr: 0.060
g atom Carbon Deposition/hr: 0.010
} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 0.31

Moles H_2 per 100 g total input: 0.09

Hydrogen efficiency = 2.3%

UDMH STEAM REFORMING DATA SHEET

Catalyst T-310 NiO

Temperature, °C 400

Pressure, psig 50

Gas Volume Rate, l/hr 6.31

Moles Gas Produced/Hr 0.257

% UDMH Used 98.5

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.73	13.37	19.10
Feed Composition, mole/hr	0.0955	0.743	0.839

Total Output Composition, mole-%: UDMH 0.1 H_2O 56.9

N_2H_4 - NH_3 12.7 Dimethylamine 4.8 H_2 56.9

N_2 0.6 CH_4 0.5 CO 0.3 CO_2 8.3

Ethane 0 Other ____

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:	61.8	2.3	2.0	1.3	32.6	none

% H_2O Used: 23.0 % Reforming to CO_2: 44.0 % to CO: 1.7

Moles NH_3 Formed/hr: 0.128

Moles Dimethylamine Formed/hr: 0.048

g atom Carbon Deposition/hr: ____

} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 2.79

Moles H_2 per 100 g total input: 0.83

Hydrogen efficiency = 20.9%

UDMH STEAM REFORMING DATA SHEET

Catalyst T-310 NiO

Temperature, °C 500

Pressure, psig 50

Gas Volume Rate, l/hr 9.55

Moles Gas Produced/Hr 0.388

% UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.73	13.37	19.10
Feed Composition, mole/hr	0.0955	0.743	0.839

Total Output Composition, mole-%: UDMH 0 H_2O 57.4

N_2H_4 - NH_3 6.2 Dimethylamine 0.3 H_2 13.2

N_2 5.7 CH_4 11.0 CO 0.4 CO_2 5.7

Ethane 0.3 Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	33.9	13.4	26.9	1.3	24.1	0.6
1-1/2 hour:	36.6	15.6	30.3	1.1	15.6	0.7

% H_2O Used: 16.8 % Reforming to CO_2: 31.9 % to CO: 2.1

Moles NH_3 Formed/hr: 0.067

Moles Dimethylamine Formed/hr: 0.003

g atom Carbon Deposition/hr: ______

} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 2.49

Moles H_2 per 100 g total input: 0.74

Hydrogen efficiency = 18.5%

UDMH STEAM REFORMING DATA SHEET

Catalyst T-310 | Temperature, °C 300

Pressure, psig 150 | Gas Volume Rate, l/hr 1.83

Moles Gas Produced/Hr 0.074 | % UDMH Used 97.6

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.11	14.26	20.37
Feed Composition, mole/hr	0.102	0.792	0.894

Total Output Composition, mole-%: UDMH 0.2 H_2O 74.3

N_2H_4 - NH_3 12.1 Dimethylamine 6.2 H_2 3.2

N_2 0.8 CH_4 0.7 CO 0.6 CO_2 2.1

Ethane 0 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	43.2	11.0	9.4	8.6	27.8	none
1-1/2 hour:						

% H_2O Used: 6.1 % Reforming to CO_2: 10.3 % to CO: 2.9

Moles NH_3 Formed/hr: 0.121

Moles Dimethylamine Formed/hr: 0.062

g atom Carbon Deposition/hr: 0.048

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 0.52

Moles H_2 per 100 g total input: 0.16

Hydrogen efficiency = 3.9%

UDMH STEAM REFORMING DATA SHEET

Catalyst T-310 — Temperature, °C 400

Pressure, psig 150 — Gas Volume Rate, l/hr 9.19

Moles Gas Produced/Hr 0.374 — % UDMH Used 98.4

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.11	14.26	20.37
Feed Composition, mole/hr	0.102	0.792	0.894

Total Output Composition, mole-%: UDMH 0.1 H_2O 49.5

N_2H_4 -- NH_3 15.6 Dimethylamine 0.4 H_2 15.0

N_2 0.9 CH_4 6.5 CO 0.4 CO_2 10.1

Ethane 0.2 Other ____

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	48.7	2.5	19.1	1.5	27.6	0.5
1-1/2 hour:	45.4	2.6	19.8	1.0	30.6	0.5

% H_2O Used: 29.3 % Reforming to CO_2: 55.9 % to CO: 2.0

Moles NH_3 Formed/hr: 0.177 }

Moles Dimethylamine Formed/hr: 0.005 } calculated to complete mass balance

g atom Carbon Deposition/hr: ____ }

Moles H_2 per 100 g UDMH input: 2.79

Moles H_2 per 100 g total input: 0.83

Hydrogen efficiency = 20.8%

UDMH STEAM REFORMING DATA SHEET

Catalyst T-310 NiO

Temperature, °C 500

Pressure, psig 150

Gas Volume Rate, l/hr 11.53

Moles Gas Produced/Hr 0.469

% UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.11	14.26	20.37
Feed Composition, mole/hr	0.102	0.792	0.894

Total Output Composition, mole-%: UDMH 0 H_2O 54.0

N_2H_4 - NH_3 6.0 Dimethylamine 0 H_2 16.2

N_2 5.7 CH_4 11.2 CO 0.3 CO_2 6.6

Ethane 0 Other ____

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	37.7	13.9	28.2	1.0	19.2	none
1-1/2 hour:	40.5	14.3	28.0	0.8	16.4	none

% H_2O Used: 19.9 % Reforming to CO_2: 37.7 % to CO: 2.0

Moles NH_3 Formed/hr: 0.070
Moles Dimethylamine Formed/hr: 0
g atom Carbon Deposition/hr: ____
} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 3.11

Moles H_2 per 100 g total input: 0.93

Hydrogen efficiency = 23.3%

UDMH STEAM REFORMING DATA SHEET

Catalyst G-56B | Temperature, °C 500

Pressure, psig 25 | Gas Volume Rate, l/hr 8.02

Moles Gas Produced/Hr 0.326 | % UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.36	14.84	21.20
Feed Composition, mole/hr	0.106	0.824	0.930

Total Output Composition, mole-%: UDMH 0 H_2O 62.1

N_2H_4 - NH_3 10.1 Dimethylamine 0.5 H_2 14.5

N_2 3.6 CH_4 5.6 CO 0.2 CO_2 3.4

Ethane 0 Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:	53.2	13.2	20.5	0.6	12.6	none

% H_2O Used: 10.2 % Reforming to CO_2: 19.3 % to CO: 0.9

Moles NH_3 Formed/hr: 0.120
Moles Dimethylamine Formed/hr: 0.006
g atom Carbon Deposition/hr: 0.090
} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 2.70

Moles H_2 per 100 g total input: 0.82

Hydrogen efficiency = 20.4

UDMH STEAM REFORMING DATA SHEET

Catalyst G-56B Ni base reforming catalyst — Temperature, °C 300

Pressure, psig 50 — Gas Volume Rate, l/hr 0.73

Moles Gas Produced/Hr 0.030 — % UDMH Used 33.3

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.31	14.61	21.02
Feed Composition, mole/hr	0.105	0.823	0.928

Total Output Composition, mole-%: UDMH 7.3 H_2O 84.7

N_2H_4 ______ NH_3 1.8 Dimethylamine 2.9 H_2 0.3

N_2 1.4 CH_4 0.9 CO none CO_2 0.6

Ethane none Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	9.0	42.3	28.6	none	20.0	none
1-1/2 hour:						

% H_2O Used: 1.5 % Reforming to CO_2: 2.9 % to CO: none

Moles NH_3 Formed/hr: 0.017
Moles Dimethylamine Formed/hr: 0.028
g atom Carbon Deposition/hr: ______
} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 0.05

Moles H_2 per 100 g total input: 0.014

Hydrogen efficiency = 0.4%

UDMH STEAM REFORMING DATA SHEET

Catalyst G-56B Temperature, °C 400

Pressure, psig 50 Gas Volume Rate, l/hr 7.84

Moles Gas Produced/Hr 0.319 % UDMH Used 98.2

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.31	14.61	21.02
Feed Composition, mole/hr	0.105	0.823	0.928

Total Output Composition, mole-%: UDMH 0.2 H_2O 55.8

N_2H_4 - NH_3 15.6 Dimethylamine 0.9 H_2 14.0

N_2 0.7 CH_4 5.1 CO 0.1 CO_2 7.6

Ethane 0.1 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	52.0	2.2	17.4	0.6	27.7	none
1-1/2 hour:	50.8	2.5	18.6	0.3	27.6	0.2

% H_2O Used: 21.5 % Reforming to CO_2: 41.9 % to CO: 0.5

Moles NH_3 Formed/hr: 0.180

Moles Dimethylamine Formed/hr: 0.010

g atom Carbon Deposition/hr: 0.036

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 2.57

Moles H_2 per 100 g total input: 0.77

Hydrogen efficiency = 19.3%

UDMH STEAM REFORMING DATA SHEET

Catalyst G-56B Ni base steam reforming catalyst　　Temperature, °C 500

Pressure, psig 50　　Gas Volume Rate, l/hr 11.93

Moles Gas Produced/Hr 0.485　　% UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	
Feed Composition, g/hr	5.72	13.35	19.07
Feed Composition, mole/hr	0.0953	0.7416	0.8369

Total Output Composition, mole-%: UDMH 0　　H_2O 51.3

N_2H_4 -　　NH_3 4.7　　Dimethylamine 0　　H_2 20.1

N_2 6.4　　CH_4 10.1　　CO 0.4　　CO_2 7.1

Ethane 0　　Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
~~45 minutes~~:						
~~1-1/2 hour~~:	40.35	15.78	25.13	1.00	17.75	none
4-hr average	45.77	14.35	22.85	0.9	16.14	none

% H_2O Used: 21.7　　% Reforming to CO_2: 40.8　　% to CO: 2.1

Moles NH_3 Formed/hr: 0.052

Moles Dimethylamine Formed/hr: none

g atom Carbon Deposition/hr:

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 3.89

Moles H_2 per 100 g total input: 1.16

Hydrogen efficiency = 29.1

NOTE: Repeat of previous test over a 6-hour period.

UDMH STEAM REFORMING DATA SHEET

Catalyst G-56B — Temperature, °C 500

Pressure, psig 50 — Gas Volume Rate, l/hr 13.30

Moles Gas Produced/Hr 0.541 — % UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	80.6	
Feed Composition, g/hr	6.31	14.61	21.02
Feed Composition, mole/hr	0.105	0.823	0.928

Total Output Composition, mole-%: UDMH 0 — H_2O 51.3

N_2H_4 - — NH_3 4.7 — Dimethylamine 0 — H_2 20.1

N_2 6.4 — CH_4 10.1 — CO 0.4 — CO_2 7.1

Ethane 0 — Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	48.2	12.5	17.7	0.9	20.6	none
1-1/2 hour:	49.5	14.2	21.5	0.7	14.2	none

% H_2O Used: 19.2 — % Reforming to CO_2: 36.7 — % to CO: 1.9

Moles NH_3 Formed/hr: 0.056 }

Moles Dimethylamine Formed/hr: 0 } calculated to complete mass balance

g atom Carbon Deposition/hr: 0.013 }

Moles H_2 per 100 g UDMH input: 4.25

Moles H_2 per 100 g total input: 1.28

Hydrogen efficiency = 31.9%

UDMH STEAM REFORMING DATA SHEET

Catalyst G-56B — Temperature, °C 300

Pressure, psig 150 — Gas Volume Rate, l/hr 3.81

Moles Gas Produced/Hr 0.155 — % UDMH Used 99.4

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.465	15.085	21.55
Feed Composition, mole/hr	0.108	0.839	0.947

Total Output Composition, mole-%: UDMH 0.1 H_2O 68.3

N_2H_4 - NH_3 13.5 Dimethylamine 4.2 H_2 6.9

N_2 0.8 CH_4 2.1 CO 1.0 CO_2 3.2

Ethane 0 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	49.4	7.1	14.5	8.6	20.3	none
1-1/2 hour:	49.0	6.0	14.7	7.2	22.5	0.5

% H_2O Used: 9.7 % Reforming to CO_2: 16.2 % to CO: 5.1

Moles NH_3 Formed/hr: 0.150

Moles Dimethylamine Formed/hr: 0.046

g atom Carbon Deposition/hr: 0.053

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 1.17

Moles H_2 per 100 g total input: 0.35

Hydrogen efficiency = 8.8%

UDMH STEAM REFORMING DATA SHEET

Catalyst G-65B Ni base reforming catalyst Temperature, °C 400

Pressure, psig 150 Gas Volume Rate, l/hr 7.72

Moles Gas Produced/Hr 0.314 % UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.41	12.63	18.04
Feed Composition, mole/hr	0.0902	0.702	0.792

Total Output Composition, mole-%: UDMH 0 H_2O 51.6

N_2H_4 - NH_3 15.6 Dimethylamine 1.1 H_2 14.0

N_2 0.8 CH_4 7.0 CO 0 CO_2 9.8

Ethane 0.1 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	42.6	2.5	24.0	none	30.4	0.5
1-1/2 hour:	43.91	2.5	22.1	none	30.9	0.4

% H_2O Used: 27.6 % Reforming to CO_2: 53.9 % to CO: 0

Moles NH_3 Formed/hr: 0.153

Moles Dimethylamine Formed/hr: 0.011

g atom Carbon Deposition/hr:

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 2.56

Moles H_2 per 100 g total input: 0.77

Hydrogen efficiency = 19.1%

UDMH STEAM REFORMING DATA SHEET

Catalyst G-56B — Temperature, °C 500

Pressure, psig 150 — Gas Volume Rate, l/hr 11.03

Moles Gas Produced/Hr 0.448 — % UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.70	13.31	19.01
Feed Composition, mole/hr	0.0950	0.739	0.834

Total Output Composition, mole-%: UDMH 0 — H_2O 54.2

N_2H_4 -- — NH_3 5.4 — Dimethylamine 0 — H_2 17.4

N_2 5.9 — CH_4 10.9 — CO 0 — CO_2 6.2

Ethane 0 — Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	38.0	13.0	26.3	none	22.6	none
1-1/2 hour: average	43.0	14.5	27.1	none	15.4	none

% H_2O Used: 18.7 — % Reforming to CO_2: 36.3 — % to CO: 0

Moles NH_3 Formed/hr: 0.060

Moles Dimethylamine Formed/hr: none

g atom Carbon Deposition/hr: ______

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 3.39

Moles H_2 per 100 g total input: 1.02

Hydrogen efficiency = 25.4%

UDMH STEAM REFORMING DATA SHEET

Catalyst G-43 | Temperature, °C 300

Pressure, psig 50 | Gas Volume Rate, l/hr 0.495

Moles Gas Produced/Hr 0.020 | % UDMH Used 83.3

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.97	13.92	19.89
Feed Composition, mole/hr	0.0995	0.773	0.873

Total Output Composition, mole-%: UDMH 1.8 H_2O 80.2

N_2H_4 - NH_3 11.1 Dimethylamine 4.8 H_2 0.8

N_2 0.7 CH_4 0.3 CO 0.3 CO_2 0

Ethane 0 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:	37.2	31.8	16.4	14.5	none	none

% H_2O Used: 0.4 % Reforming to CO_2: 0 % to CO: 1.5

Moles NH_3 Formed/hr: 0.107

Moles Dimethylamine Formed/hr: 0.046

g atom Carbon Deposition/hr: 0.068

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 0.13

Moles H_2 per 100 g total input: 0.04

Hydrogen efficiency = 0.9%

UDMH STEAM REFORMING DATA SHEET

Catalyst G-43 Temperature, °C 400

Pressure, psig 50 Gas Volume Rate, l/hr 1.48

Moles Gas Produced/Hr 0.060 % UDMH Used 97.7

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.05	14.13	20.18
Feed Composition, mole/hr	0.101	0.785	0.886

Total Output Composition, mole-%: UDMH 0.2 H_2O 74.7

N_2H_4 - NH_3 12.8 Dimethylamine 6.3 H_2 2.4

N_2 0.5 CH_4 0.5 CO 1.0 CO_2 1.7

Ethane 0 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	42.6	9.9	9.2	17.0	20.6	0.7
1-1/2 hour:	39.7	7.5	7.6	16.5	28.7	

% H_2O Used: 5.6 % Reforming to CO_2: 8.4 % to CO: 5.0

Moles NH_3 Formed/hr: 0.126
Moles Dimethylamine Formed/hr: 0.062
g atom Carbon Deposition/hr: 0.041
} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 0.40

Moles H_2 per 100 g total input: 0.12

Hydrogen efficiency = 3.0%

UDMH STEAM REFORMING DATA SHEET

Catalyst G-43 — Temperature, °C 500

Pressure, psig 50 — Gas Volume Rate, l/hr 6.35

Moles Gas Produced/Hr 0.258 — % UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.91	13.79	19.70
Feed Composition, mole/hr	0.0985	0.766	0.865

Total Output Composition, mole-%: UDMH 0 — H_2O 64.7

N_2H_4 - — NH_3 8.3 — Dimethylamine 2.6 — H_2 8.2

N_2 3.9 — CH_4 7.4 — CO 1.5 — CO_2 3.2

Ethane 0.2 — Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	33.7	17.4	26.1	6.1	16.6	-
1-1/2 hour:	33.8	15.9	30.5	6.1	13.0	0.7

% H_2O Used: 10.8 — % Reforming to CO_2: 17.0 — % to CO: 8.1

Moles NH_3 Formed/hr: 0.088
Moles Dimethylamine Formed/hr: 0.027
g atom Carbon Deposition/hr: 0.011
} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 1.47

Moles H_2 per 100 g total input: 0.44

Hydrogen efficiency = 11.0%

UDMH STEAM REFORMING DATA SHEET

Catalyst G-43 | Temperature, °C 300

Pressure, psig 150 | Gas Volume Rate, l/hr 0.57

Moles Gas Produced/Hr ______ | % UDMH Used 63.0

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.59	13.03	18.62
Feed Composition, mole/hr	0.093	0.724	0.817

Total Output Composition, mole-%: UDMH ______ H_2O ______

N_2H_4 ______ NH_3 ______ Dimethylamine ______ H_2 ______

N_2 ______ CH_4 ______ CO ______ CO_2 ______

Ethane ______ Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:						

% H_2O Used: ______ % Reforming to CO_2: ______ % to CO: ______

Moles NH_3 Formed/hr: ______
Moles Dimethylamine Formed/hr: ______
g atom Carbon Deposition/hr: ______

} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: ______

Moles H_2 per 100 g total input: ______

Hydrogen efficiency =

Not enough gas produced for valid gas analysis.

UDMH STEAM REFORMING DATA SHEET

Catalyst G-43 Temperature, °C 400

Pressure, psig 150 Gas Volume Rate, l/hr 3.02

Moles Gas Produced/Hr 0.123 % UDMH Used 98.0

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.63	13.12	18.75
Feed Composition, mole/hr	0.094	0.729	0.823

Total Output Composition, mole-%: UDMH 0.2 H_2O 69.2

N_2H_4 - NH_3 10.8 Dimethylamine 6.7 H_2 5.6

N_2 1.2 CH_4 1.3 CO 1.1 CO_2 4.0

Ethane 0 Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:	42.2	8.8	10.0	8.5	30.4	0

% H_2O Used: 11.7 % Reforming to CO_2: 19.7 % to CO: 5.3

Moles NH_3 Formed/hr: 0.100

Moles Dimethylamine Formed/hr: 0.062

g atom Carbon Deposition/hr: ______

} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 0.93

Moles H_2 per 100 g total input: 0.28

Hydrogen efficiency = 6.9

UDMH STEAM REFORMING DATA SHEET

Catalyst G-43 Pt

Temperature, °C 500

Pressure, psig 150

Gas Volume Rate, l/hr 9.02

Moles Gas Produced/Hr 0.367

% UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.91	13.79	19.70
Feed Composition, mole/hr	0.0985	0.766	0.865

Total Output Composition, mole-%: UDMH 0 H_2O 60.1

N_2H_4 - NH_3 5.1 Dimethylamine 0.6 H_2 11.6

N_2 6.1 CH_4 11.2 CO 0.8 CO_2 4.3

Ethane 0.2 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:	32.2	18.3	33.9	2.4	12.7	0.6

% H_2O Used: 13.3 % Reforming to CO_2: 23.9 % to CO: 4.6

Moles NH_3 Formed/hr: 0.056

Moles Dimethylamine Formed/hr: 0.007

g atom Carbon Deposition/hr:

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 2.17

Moles H_2 per 100 g total input: 0.65

Hydrogen efficiency = 16.2%

UDMH STEAM REFORMING DATA SHEET

Catalyst Pt oxide in alumina   Temperature, ° 400

Pressure, psig 50   Gas Volume Rate, l/hr 1.41

Moles Gas Produced/Hr 0.057   % UDMH Used 96.9

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	
Feed Composition, g/hr	5.88	13.71	19.59
Feed Composition, mole/hr	0.098	0.762	0.860

Total Output Composition, mole-%: UDMH 0.3 H_2O 75.1

N_2H_4 - NH_3 12.9   Dimethylamine 5.7 H_2 2.2

N_2 0.4 CH_4 0.2   CO 3.1 CO_2 0

Ethane 0   Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	36.0	7.2	3.9	52.9	none	none
1-1/2 hour:	36.1	7.2	4.1	52.6	none	none

% H_2O Used: 3.9   % Reforming to CO_2: 0   % to CO: 15.3

Moles NH_3 Formed/hr: .126

Moles Dimethylamine Formed/hr: .056

g atom Carbon Deposition/hr: 0.046

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 0.37

Moles H_2 per 100 g total input 0.11

Hydrogen efficiency = 2.870

UDMH STEAM REFORMING DATA SHEET

Catalyst Pt oxide in alumina Temperature, °C 500

Pressure, psig 50 Gas Volume Rate, l/hr 3.66

Moles Gas Produced/Hr 0.149 % UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.01	14.03	20.04
Feed Composition, mole/hr	0.100	0.779	0.879

Total Output Composition, mole-%: UDMH 0 H_2O 70.11

N_2H_4 - NH_3 14.6 Dimethylamine 1.4 H_2 7.8

N_2 1.3 CH_4 2.4 CO 2.3 CO_2 0

Ethane 0 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	49.6	7.9	14.6	26.0	1.6	0.2
1-1/2 hour:	56.1	9.2	17.4	17.1	none	0.2

% H_2O Used: 3.3 % Reforming to CO_2: 0 % to CO: 12.5

Moles NH_3 Formed/hr: 0.157

Moles Dimethylamine Formed/hr: 0.015

g atom Carbon Deposition/hr: 0.118

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 1.40

Moles H_2 per 100 g total input: 0.42

Hydrogen efficiency = 10.5

UDMH STEAM REFORMING DATA SHEET

Catalyst Pt Oxide   Temperature, °C 400

Pressure, psig 150   Gas Volume Rate, l/hr 1.52

Moles Gas Produced/Hr 0.062   % UDMH Used 97.9

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.82	13.58	19.40
Feed Composition, mole/hr	0.097	0.754	0.851

Total Output Composition, mole-%: UDMH 0.2 H_2O 74.4

N_2H_4 -- NH_3 11.9   Dimethylamine 6.9 H_2 1.6

N_2 0.5 CH_4 0.4   CO 3.4 CO_2 0.6

Ethane 0   Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	22.8	6.3	7.2	54.1	9.5	0
1-1/2 hour:	24.3	8.3	6.1	52.1	9.3	0

% H_2O Used: 5.8   % Reforming to CO_2: 3.0   % to CO: 17.0

Moles NH_3 Formed/hr: 0.114

Moles Dimethylamine Formed/hr: 0.066

g atom Carbon Deposition/hr: 0.016

} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 0.26

Moles H_2 per 100 g total input: 0.08

Hydrogen efficiency = 1.9%

UDMH STEAM REFORMING DATA SHEET

Catalyst Pt oxide on alumina   Temperature, °C 500

Pressure, psig 150   Gas Volume Rate, l/hr 8.07

Moles Gas Produced/Hr 0.328   % UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.58	13.02	18.60
Feed Composition, mole/hr	0.093	0.723	0.816

Total Output Composition, mole-%: UDMH 0 H_2O 60.0

N_2H_4 - NH_3 7.8   Dimethylamine 0.9 H_2 60.0

N_2 4.6 CH_4 8.8   CO 3.6 CO_2 2.8

Ethane 0.4   Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	34.0	17.6	30.0	10.8	7.6	
1-1/2 hour:	35.5	14.7	28.1	11.6	8.8	1.4

% H_2O Used: 13.3   % Reforming to CO_2: 15.6   % to CO: 20.4

Moles NH_3 Formed/hr: .081
Moles Dimethylamine Formed/hr: .009
g atom Carbon Deposition/hr: ______
} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 2.07

Moles H_2 per 100 g total input: 0.62

Hydrogen efficiency = 15.6%

UDMH STEAM REFORMING DATA SHEET

Catalyst T-312 | Temperature, °C 300

Pressure, psig 50 | Gas Volume Rate, l/hr 2.34

Moles Gas Produced/Hr 0.095 | % UDMH Used 92.9

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.91	13.79	19.70
Feed Composition, mole/hr	0.0985	0.766	0.865

Total Output Composition, mole-%: UDMH 0.7 H_2O 72.4

N_2H_4 - NH_3 10.3 Dimethylamine 6.8 H_2 4.1

N_2 1.0 CH_4 0.5 CO 0.5 CO_2 3.7

Ethane 0 Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	48.3	10.1	5.8	6.5	29.3	none
1-1/2 hour:	41.4	10.6	5.7	5.6	36.8	none

% H_2O Used: 9.8 % Reforming to CO_2: 17.8 % to CO: 2.5

Moles NH_3 Formed/hr: 0.098

Moles Dimethylamine Formed/hr: 0.065

g atom Carbon Deposition/hr: —

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 0.66

Moles H_2 per 100 g total input: 0.20

Hydrogen efficiency = 4.9

UDMH STEAM REFORMING DATA SHEET

Catalyst T312 Temperature, °C 400

Pressure, psig 50 Gas Volume Rate, l/hr 6.27

Moles Gas Produced/Hr 0.255 % UDMH Used 99.3

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.91	13.79	19.70
Feed Composition, mole/hr	0.0985	0.766	0.865

Total Output Composition, mole-%: UDMH 0.1 H_2O 58.5

N_2H_4 - NH_3 12.3 Dimethylamine 4.8 H_2 14.2

N_2 0.8 CH_4 1.1 CO 1.7 CO_2 6.5

Ethane 0 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	53.2	2.9	3.8	6.6	33.4	none
1-1/2 hour:	58.4	3.4	4.4	7.1	26.6	none

% H_2O Used: 20.1 % Reforming to CO_2: 34.5 % to CO: 9.1

Moles NH_3 Formed/hr: 0.129

Moles Dimethylamine Formed/hr: 0.050

g atom Carbon Deposition/hr: -

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 2.53

Moles H_2 per 100 g total input: 0.76

Hydrogen efficiency = 18.9

UDMH STEAM REFORMING DATA SHEET

Catalyst T312 | Temperature, °C 500

Pressure, psig 50 | Gas Volume Rate, l/hr 9.73

Moles Gas Produced/Hr 0.396 | % UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.91	13.79	19.70
Feed Composition, mole/hr	0.0985	0.766	0.865

Total Output Composition, mole-%: UDMH 0 H_2O 55.8

N_2H_4 - NH_3 7.7 Dimethylamine 0.7 H_2 14.9

N_2 4.9 CH_4 8.9 CO 0.8 CO_2 6.1

Ethane 0.2 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	39.5	11.7	22.6	2.0	24.3	0.7
1-1/2 hour:	42.0	13.0	25.0	2.3	17.2	0.6

% H_2O Used: 18.9 % Reforming to CO_2: 34.5 % to CO: 4.6

Moles NH_3 Formed/hr: .086

Moles Dimethylamine Formed/hr: 0.008

g atom Carbon Deposition/hr: ______

} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 2.81

Moles H_2 per 100 g total input: 0.84

Hydrogen efficiency = 21.1

UDMH STEAM REFORMING DATA SHEET

Catalyst T-312 Cu+Ni Oxides on Alumina Temperature, °C 300

Pressure, psig 150 Gas Volume Rate, l/hr 1.37

Moles Gas Produced/Hr 0.056 % UDMH Used 96.5

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	
Feed Composition, g/hr	5.65	13.17	18.82
Feed Composition, mole/hr	0.0942	0.732	0.826

Total Output Composition, mole-%: UDMH 0.3 H_2O 76.6

N_2H_4 - NH_3 8.3 Dimethylamine 8.4 H_2 0.9

N_2 1.8 CH_4 1.1 CO 0.1 CO_2 2.4

Ethane - Other -

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	14.1	28.3	18.2	1.3	38.0	-
1-1/2 hour:						

% H_2O Used: ______ % Reforming to CO_2: ______ % to CO: ______

Moles NH_3 Formed/hr: ______

Moles Dimethylamine Formed/hr: ______

g atom Carbon Deposition/hr: ______

} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: ______

Moles H_2 per 100 g total input: ______

Hydrogen efficiency =

UDMH STEAM REFORMING DATA SHEET

Catalyst T312 Ni + Cu Oxides Temperature, °C 400

Pressure, psig 150 Gas Volume Rate, l/hr 6.29

Moles Gas Produced/Hr 0.256 % UDMH Used 99.0

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.65	13.17	18.82
Feed Composition, mole/hr	0.094	0.732	0.826

Total Output Composition, mole-%: UDMH 0.1 H_2O 57.7

N_2H_4 - NH_3 12.3 Dimethylamine 4.2 H_2 14.3

N_2 1.1 CH_4 1.7 CO 1.6 CO_2 7.2

Ethane 0 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	51.9	3.6	6.2	4.9	33.4	none
1-1/2 hour:	55.3	4.4	6.5	6.2	27.7	none

% H_2O Used: 21.6 % Reforming to CO_2: 37.8 % to CO: 8.5

Moles NH_3 Formed/hr: 0.122
Moles Dimethylamine Formed/hr: 0.042
g atom Carbon Deposition/hr:
} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 2.51

Moles H_2 per 100 g total input: 0.76

Hydrogen efficiency = 18.9

UDMH STEAM REFORMING DATA SHEET

Catalyst T312 Ni + Cu Oxides on Alumina

Temperature, °C 500

Pressure, psig 150

Gas Volume Rate, l/hr 8.46

Moles Gas Produced/Hr 0.344

% UDMH Used 100

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.65	13.17	18.82
Feed Composition, mole/hr	0.094	0.732	0.826

Total Output Composition, mole-%: UDMH 0 H_2O 60.1

N_2H_4 - NH_3 6.3 Dimethylamine 0.7 H_2 11.0

N_2 5.6 CH_4 11.0 CO 0.2 CO_2 5.0

Ethane 0.3 Other other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	31.6	16.3	28.3	0.5	22.4	0.9
1-1/2 hour:	33.2	16.9	33.1	0.7	15.2	0.8

% H_2O Used: 14.6 % Reforming to CO_2: 27.7 % to CO: 1.17

Moles NH_3 Formed/hr: .065

Moles Dimethylamine Formed/hr: .007

g atom Carbon Deposition/hr: ______

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 2.0

Moles H_2 per 100 g total input: 0.61

Hydrogen efficiency = 15.1

UDMH STEAM REFORMING DATA SHEET

Catalyst G47 — Temperature, °C 300

Pressure, psig 50 — Gas Volume Rate, l/hr 1.135

Moles Gas Produced/Hr 0.046 — % UDMH Used 75.1

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.02	14.06	20.08
Feed Composition, mole/hr	0.100	0.781	0.881

Total Output Composition, mole-%: UDMH 2.5 H_2O 82.0

N_2H_4 - NH_3 4.9 Dimethylamine 5.7 H_2 0.1

N_2 2.6 CH_4 2.1 CO 0 CO_2 0

Ethane 0 Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	3.5	54.0	42.5	-	-	-
1-1/2 hour:	2.9	53.7	43.4	-	-	-

% H_2O Used: 0 — % Reforming to CO_2: 0 — % to CO: 0

Moles NH_3 Formed/hr: .047 }
Moles Dimethylamine Formed/hr: .054 } calculated to complete mass balance
g atom Carbon Deposition/hr: .022 }

Moles H_2 per 100 g UDMH input: 0.03

Moles H_2 per 100 g total input: 0.01

Hydrogen efficiency = 0.2

UDMH STEAM REFORMING DATA SHEET

Catalyst G-47 Iron Oxide

Temperature, °C 400

Pressure, psig 50

Gas Volume Rate, l/hr 3.10

Moles Gas Produced/Hr 0.126

% UDMH Used 87.6

	UDMH	H_2O	Total
Feed Composition, mole-%	71.4	88.6	100
Feed Composition, g/hr	5.96	13.90	19.86
Feed Composition, mole/hr	0.099	0.772	0.871

Total Output Composition, mole-%: UDMH 1.2 H_2O 76.1

N_2H_4 - NH_3 6.1 Dimethylamine 3.8 H_2 1.5

N_2 3.8 CH_4 6.3 CO 0.2 CO_2 0.8

Ethane 0.1 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	13.4	31.4	47.5	2.1	4.6	1.0
1-1/2 hour:	11.9	29.8	48.9	1.9	6.5	1.0

% H_2O Used: 2.5 % Reforming to CO_2: 4.1 % to CO: 1.2

Moles NH_3 Formed/hr: 0.060

Moles Dimethylamine Formed/hr: 0.038

g atom Carbon Deposition/hr: 0.022

} calculated to complete mass balance

Moles H_2 per 100 g UDMH input: 0.25

Moles H_2 per 100 g total input: 0.08

Hydrogen efficiency = 1.9

UDMH STEAM REFORMING DATA SHEET

Catalyst G-47 Iron Oxide   Temperature, °C 500

Pressure, psig 50   Gas Volume Rate, l/hr 8.37

Moles Gas Produced/Hr 0.340   % UDMH Used 99.5

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	6.05	14.13	20.18
Feed Composition, mole/hr	0.101	0.785	0.886

Total Output Composition, mole-%: UDMH 0 H_2O 62.8

N_2H_4 - NH_3 4.4   Dimethylamine 1.7 H_2 9.5

N_2 6.1 CH_4 10.5   CO 0.5 CO_2 4.0

Ethane 0.4   Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	32.9	19.0	33.9	1.4	11.7	1.2
1-1/2 hour:	30.9	19.6	34.0	1.4	12.9	1.2

% H_2O Used: 11.7   % Reforming to CO_2: 21.8   % to CO: 2.5

Moles NH_3 Formed/hr: 0.049

Moles Dimethylamine Formed/hr: 0.019

g atom Carbon Deposition/hr: ______

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 1.74

Moles H_2 per 100 g total input: 0.52

Hydrogen efficiency = 13.0%

UDMH STEAM REFORMING DATA SHEET

Catalyst G-47   Temperature, °C 300

Pressure, psig 150   Gas Volume Rate, l/hr 0.26

Moles Gas Produced/Hr 0.011   % UDMH Used 0.5%

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.91	13.79	19.70
Feed Composition, mole/hr	0.0985	0.766	0.865

Total Output Composition, mole-%: UDMH ____ H_2O ____

N_2H_4 ____ NH_3 ____ Dimethylamine ____ H_2 ____

N_2 ____ CH_4 ____ CO ____ CO_2 ____

Ethane ____ Other ____

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
1-1/2 hour:						

% H_2O Used: ____ % Reforming to CO_2: ____ % to CO: ____

Moles NH_3 Formed/hr: ____

Moles Dimethylamine Formed/hr: ____ } calculated to complete mass balance

g atom Carbon Deposition/hr: ____

Moles H_2 per 100 g UDMH input: ____

Moles H_2 per 100 g total input: ____

Hydrogen efficiency =

Not enough gas produced to analyze

UDMH STEAM REFORMING DATA SHEET

Catalyst G-47 Iron oxide — Temperature, °C 400

Pressure, psig 150 — Gas Volume Rate, l/hr 3.30

Moles Gas Produced/Hr 0.134 — % UDMH Used 77.7

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.63	13.12	18.75
Feed Composition, mole/hr	0.094	0.729	0.823

Total Output Composition, mole-%: UDMH 2.2 H_2O 77.0

N_2H_4 - NH_3 3.5 Dimethylamine 2.7 H_2 0.9

N_2 4.7 CH_4 8.1 CO 0.2 CO_2 0.4

Ethane 0.2 Other ____

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	6.6	31.3	55.9	1.5	3.4	1.3
1-1/2 hour:	6.5	32.8	56.2	1.3	2.9	1.2

% H_2O Used: 1.4 % Reforming to CO_2: 2.1 % to CO: 1.1

Moles NH_3 Formed/hr: 0.032 }
Moles Dimethylamine Formed/hr: 0.026 } calculated to complete mass balance
g atom Carbon Deposition/hr: 0.006 }

Moles H_2 per 100 g UDMH input: 0.15

Moles H_2 per 100 g total input: 0.05

Hydrogen efficiency = 1.1%

UDMH STEAM REFORMING DATA SHEET

Catalyst G-47 | Temperature, °C 500

Pressure, psig 150 | Gas Volume Rate, l/hr 7.71

Moles Gas Produced/Hr 0.313 | % UDMH Used 98.9

	UDMH	H_2O	Total
Feed Composition, mole-%	11.4	88.6	100
Feed Composition, g/hr	5.91	13.79	19.70
Feed Composition, mole/hr	0.0985	0.766	0.865

Total Output Composition, mole-%: UDMH 0.1 H_2O 64.6

N_2H_4 - NH_3 5.5 Dimethylamine 0.7 H_2 8.0

N_2 5.9 CH_4 11.6 CO 0.4 CO_2 3.0

Ethane 0.2 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	27.3	20.3	39.0	0.9	11.6	0.9
1-1/2 hour:	27.4	20.4	39.8	1.2	10.4	0.8

% H_2O Used: 9.0 % Reforming to CO_2: 16.5 % to CO: 1.9

Moles NH_3 Formed/hr: 0.059

Moles Dimethylamine Formed/hr: 0.008

g atom Carbon Deposition/hr: 0.013

(calculated to complete mass balance)

Moles H_2 per 100 g UDMH input: 1.46

Moles H_2 per 100 g total input: 0.44

Hydrogen efficiency = 10.9

APPENDIX IIB

AEROZINE STEAM REFORMING DATA

AEROZINE STEAM REFORMING DATA SHEET

Catalyst G-56B | Temperature, °C 300

Pressure, psig 25 | Gas Volume Rate, l/hr 2.677

Moles Gas Produced/Hr 0.109 | % UDMH Used 94.9

% N_2H_4 Used 100

	UDMH	H_2O	N_2H_4	Total
Feed Composition, mole-%	9.4	73.0	17.6	100
Feed Composition, g/hr	4.75	11.06	4.75	20.56
Feed Composition, mole/hr	0.0792	0.6144	0.1484	0.8420

Total Output Composition, mole-%: UDMH 0.4 H_2O 57.8

N_2H_4 0 NH_3 26.5 Dimethylamine 4.7 H_2 2.9

N_2 6.1 CH_4 0.4 CO 0.6 CO_2 0.6

Ethane Trace Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	30.7	52.4	3.8	5.6	7.4	0.1
1-1/2 hour:	23.5	63.1	4.1	5.3	4.0	0.1
one	27.1	57.8	3.9	5.5	5.7	0.1

% H_2O Used: 3.0 % Reforming to CO_2: 3.9 % to CO: 3.8

Moles NH_3 Formed/hr: 0.2731

Moles Dimethylamine Formed/hr: 0.0480

g atom Carbon Deposition/hr: 0.0376

(calculated to complete mass balance)

Moles H_2 per 100 g aerozine input: 0.31

Moles H_2 per 100 g total input: 0.14

Hydrogen efficiency = 3.2

AEROZINE STEAM REFORMING DATA SHEET

Catalyst G-56B | Temperature, °C 400

Pressure, psig 25 | Gas Volume Rate, l/hr 7.221

Moles Gas Produced/Hr 0.294 | % UDMH Used 99.7

% N_2H_4 Used 100

	UDMH	H_2O	N_2H_4	Total
Feed Composition, mole-%	9.4	73.0	17.6	100
Feed Composition, g/hr	4.75	11.06	4.75	20.56
Feed Composition, mole/hr	0.0792	0.6144	0.1484	0.8420

Total Output Composition, mole-%: UDMH 0 H_2O 45.2

N_2H_4 0 NH_3 28.1 Dimethylamine 0.7 H_2 11.7

N_2 5.7 CH_4 3.8 CO 0 CO_2 4.8

Ethane 0 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	44.6	22.0	13.8	none	19.6	none
1-1/2 hour:	45.3	22.0	15.4	none	17.4	none
one	45.0	22.0	14.6	none	18.5	none

% H_2O Used: 16.9 % Reforming to CO_2: 34.3 % to CO: 0

Moles NH_3 Formed/hr: 0.3178
Moles Dimethylamine Formed/hr: .0075
g atom Carbon Deposition/hr: 0.0456
} calculated to complete mass balance

Moles H_2 per 100 g aerozine input: 1.39

Moles H_2 per 100 g total input: 0.64

Hydrogen efficiency = 14.2

AEROZINE STEAM REFORMING DATA SHEET

Catalyst G-56B — Temperature, °C 300

Pressure, psig 50 — Gas Volume Rate, l/hr 1.832

Moles Gas Produced/Hr 0.074 — % UDMH Used 64.1

% N_2H_4 Used 97.3

	UDMH	H_2O	N_2H_4	Total
Feed Composition, mole-%	9.4	73.0	17.6	100
Feed Composition, g/hr	4.69	10.92	4.69	20.30
Feed Composition, mole/hr	0.0781	0.607	0.1464	0.831

Total Output Composition, mole-%: UDMH 2.7 H_2O 58.8

N_2H_4 0.4 NH_3 30.9 Dimethylamine 0 H_2 0.3

N_2 6.1 CH_4 0.8 CO 0 CO_2 0

Ethane 0 Other ______

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	5.3	84.7	10.0	none	none	none
1-1/2 hour:	4.0	84.8	10.9	0.3	none	none

% H_2O Used: 0.1 % Reforming to CO_2: 0 % to CO: 0.1

Moles NH_3 Formed/hr: 0.319

Moles Dimethylamine Formed/hr: 0

g atom Carbon Deposition/hr: 0.089

} calculated to complete mass balance

Moles H_2 per 100 g aerozine input: 0.032

Moles H_2 per 100 g total input: 0.015

Hydrogen efficiency = 0.3%

AEROZINE STEAM REFORMING DATA SHEET

Catalyst G56B Temperature, °C 400

Pressure, psig 50 Gas Volume Rate, l/hr 6.855

Moles Gas Produced/Hr 0.279 % UDMH Used 98.3

% N_2H_4 Used 100

	UDMH	H_2O	N_2H_4	Total
Feed Composition, mole-%	9.4	73.0	17.6	100
Feed Composition, g/hr	4.60	10.72	4.60	19.92
Feed Composition, mole/hr	0.0767	0.5955	0.1438	0.8160

Total Output Composition, mole-%: UDMH 0.1 H_2O 43.5

N_2H_4 0 NH_3 30.4 Dimethylamine 0.5 H_2 12.5

N_2 4.7 CH_4 2.6 CO 0.4 CO_2 5.3

Ethane Trace Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	49.6	23.6	8.8	1.6	16.5	none
1-1/2 hour:	49.0	18.2	10.2	1.6	20.9	0.1

% H_2O Used: 20.3 % Reforming to CO_2: 38.0 % to CO: 2.9

Moles NH_3 Formed/hr: 0.3318

Moles Dimethylamine Formed/hr: 0.0050

g atom Carbon Deposition/hr: 0.0490

} calculated to complete mass balance

Moles H_2 per 100 g aerozine input: 1.49

Moles H_2 per 100 g total input: 0.69

Hydrogen efficiency =15.2

AEROZINE STEAM REFORMING DATA SHEET

Catalyst G-56B

Temperature, °C 500

Pressure, psig 50

Gas Volume Rate, l/hr 12.02

Moles Gas Produced/Hr 0.489

% UDMH Used 100

% N_2H_4 Used 100

	UDMH	H_2O	N_2H_4	Total
Feed Composition, mole-%	9.4	73.0	17.6	100
Feed Composition, g/hr	4.60	10.72	4.60	19.92
Feed Composition, mole/hr	0.0767	0.5955	0.1438	0.8160

Total Output Composition, mole-%: UDMH 0 H_2O 42.4

N_2H_4 0 NH_3 15.7 Dimethylamine 0 H_2 17.6

N_2 11.0 CH_4 8.9 CO 0.1 CO_2 4.3

Ethane 0 Other 0

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:	40.8	25.0	20.3	none	13.9	none
1-1/2 hour:	43.2	27.6	22.3	0.3	6.6	none
One	42.0	26.3	21.3	0.2	10.2	none

% H_2O Used: 16.9 % Reforming to CO_2: 32.5 % to CO: 0.7

Moles NH_3 Formed/hr: 0.184

Moles Dimethylamine Formed/hr: 0

g atom Carbon Deposition/hr: 0

} calculated to complete mass balance

Moles H_2 per 100 g aerozine input: 2.23

Moles H_2 per 100 g total input: 1.03

Hydrogen efficiency = 22.8%

AEROZINE STEAM REFORMING DATA SHEET

Catalyst Girdler T-1144 Temperature, °C 400

Pressure, psig 50 Gas Volume Rate, 1/hr 6.923

Moles Gas Produced/Hr 0.2814 % UDMH Used 94.6

% N_2H_4 Used 100

	UDMH	H_2O	N_2H_4	Total
Feed Composition, mole-%	9.4	73.0	17.6	100
Feed Composition, g/hr	4.576	10.658	4.576	19.81
Feed Composition, mole/hr	0.0763	0.5921	0.1430	0.8114

Total Output Composition, mole-%: UDMH 0.4 H_2O 45.6

N_2H_4 0 NH_3 25.4 Dimethylamine 2.4 H_2 13.7

N_2 6.0 CH_4 1.4 CO 0.6 CO_2 4.3

Ethane 0 Other

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
avg - 2 hr:	52.4	23.1	5.5	2.4	16.6	0

% H_2O Used: 16.9 % Reforming to CO_2: 30.6 % to CO: 4.4

Moles NH_3 Formed/hr: 0.2740
Moles Dimethylamine Formed/hr: 0.0264
g atom Carbon Deposition/hr: 0.0227

} calculated to complete mass balance

Moles H_2 per 100 g aerozine input: 1.61

Moles H_2 per 100 g total input: 0.74

Hydrogen efficiency = 16.2%

AEROZINE STEAM REFORMING DATA SHEET

Catalyst Girdler T-1144 Temperature, °C 500

Pressure, psig 50 Gas Volume Rate, l/hr 13.175

Moles Gas Produced/Hr 0.5356 % UDMH Used 98.8

% N_2H_4 Used 100

	UDMH	H_2O	N_2H_4	Total
Feed Composition, mole-%	9.4	73.0	17.6	100
Feed Composition, g/hr	4.576	10.658	4.576	19.81
Feed Composition, mole/hr	0.0763	0.5921	0.1430	0.8114

Total Output Composition, mole-%: UDMH 0.1 H_2O 45.9

N_2H_4 0 NH_3 8.1 Dimethylamine 1.0 H_2 20.9

N_2 13.7 CH_4 8.5 CO 0.2 CO_2 1.7

Ethane 0 Other 0

Output Gas Composition:
(not including UDMH, H_2O, N_2H_4, NH_3 or Amines)

	H_2	N_2	CH_4	CO	CO_2	Ethane
45 minutes:						
avg - 2 hr:	46.1	30.6	19.0	0.4	3.9	0

% H_2O Used: 7.4 % Reforming to CO_2: 13.4 % to CO: 1.4

Moles NH_3 Formed/hr: 0.0968 }
Moles Dimethylamine Formed/hr: 0.0121 } calculated to complete mass balance
g atom Carbon Deposition/hr: 0.0017 }

Moles H_2 per 100 g aerozine input: 2.70

Moles H_2 per 100 g total input: 1.25

Hydrogen efficiency = 27.1%

APPENDIX III

N_2O_4 CATALYST DATA

APPENDIX III

CATALYST DATA

Type Number: G-43 Manufacturer: Girdler

Classification: Reduction of Nitrogen Oxides

Temperature Range: Not specified

Active Material: Platinum Promoted

Substrate or Support:

Size: 1/4"x 1/4" Shape: Tablets

Additional Information: Highly active, physically rugged. Presently in commercial use in petrochemical industry.

Type Number: T-1144 Manufacturer: Girdler

Classification: Experimental

Temperature Range:

Active Material: Nickel Oxide 50% Nickel

Substrate or Support: Refractory Oxide

Size: 3/16"x 1/8" Shape: Tablets

Additional Information:

Type Number: T-310 Manufacturer: Girdler

Classification: Experimental

Temperature Range: Not specified

Active Material: Nickel Oxide 10-12% nickel

Substrate or Support: Activated Alumina

Size: 3/16" x 1/8" Shape: Tablets

Additional Information:

Type Number: T-366 Manufacturer: Girdler

Classification: Experimental

Temperature Range: Not Specified

Active Material: Copper 50%

Substrate or Support: Kieselguhr

Size: Powder Shape:

Additional Information: Stabilized to be non-Pyrophoric.

Type Number: T-317 Manufacturer: Girdler

Classification: Experimental

Temperature Range: Not Specified

Active Material: Copper Oxide 10-12%

Substrate or Support: Activated Alumina

Size: 3/16" x 1/8" Shape: Tablets

Additional Information:

Type Number: T-315 Manufacturer: Girdler

Classification: Experimental

Temperature Range: Not Specified

Active Material: Copper Oxide (3 to 4%)

Substrate or Support: Activated Alumina

Size: 3/16" x 1/8" Shape: Tablets

Additional Information: Active material concentrated in thin outer layer.

Type Number: T-313 Manufacturer: Girdler

Classification: Experimental

Temperature Range: Not Specified

Active Material: Nickel 3-4%, Copper 0.2%

Substrate or Support: Activated Alumina

Size: 3/16" x 1/8" Shape: Tablets

Additional Information: Active materials concentrated in thin outer layer.

Type Number: G-31 Manufacturer: Girdler

Classification: Steam Reforming

Temperature Range: 950°-1150°C

Active Material: Nickel

Substrate or Support: Alumina

Size: 5/8" to 1-1/2 Shape: Lump

Additional Information: High activity may have to be crushed for trials.

Type Number: ICI-35-4 Manufacturer: Girdler

Classification: Ammonia Synthesis

Temperature Range: Not Specified

Active Material: Triple Promoted Iron Oxide

Substrate or Support:

Size: 2-8 mm Shape: Granules

Additional Information: Long life - High or low temperature operation - Poisoned by sulfur or oxygen compounds.

Type Number: G-56 Manufacturer: Girdler

Classification: Ammonia Dissociation and Steam Reforming

Temperature Range: Not Specified

Active Material: Nickel

Substrate or Support:

Size: 5/8 x 3/8 Shape: Raschig Rings

Additional Information:

Type Number: Manufacturer: Engelhard Industries

Classification: Ammonia Dissociation Type

Temperature Range: N/S

Active Material: Platinum 90%, Rhodium 10%

Substrate or Support: Wire

Size: Shape: 80 mesh gauze

Additional Information:

Type Number: H-BPS-55 Manufacturer: Norton Company

Classification: Acid

Temperature Range: 100-650°C

Active Material: Synthetic Zeolites

Substrate or Support:

Size: 1/16 Shape: Pellets

Additional Information:

Type Number: G-49A Manufacturer: Girdler

Classification: Hydrogenation

Temperature Range: N/S

Active Material: Reduced Nickel

Substrate or Support: Kieselguhr

Size: 3/16 x 1/8 Shape: Tablets

Additional Information:

Type Number: Manufacturer:

Classification:

Temperature Range:

Active Material:

Substrate or Support:

Size: Shape:

Additional Information:

Type Number: 73578-B Manufacturer: MRC

Classification: Proprietary

Temperature Range:

Active Material: Same as 77604-1

Substrate or Support: On special substrate

Size: Powder Shape:

Additional Information:

Type Number: T-325 Manufacturer: Girdler

Classification: Experimental

Temperature Range:

Active Material:

Substrate or Support: No support

Size: 1/8 Shape: Tablets

Additional Information:

Like G-49B only in tablet form.

Type Number: - Manufacturer: MRC

Classification:

Temperature Range:

Active Material: Titanium

Substrate or Support:

Size: Powder Shape:

Additional Information:

Heat treated in air for 2 minutes at 700°C.

Type Number: 73578-A Manufacturer: MRC

Classification: Proprietary

Temperature Range:

Active Material: Same as 77604-1

Substrate or Support: Shawinigan black

Size: powder Shape:

Additional Information:

Type Number: 77604-2 Manufacturer: MRC

Classification: Proprietary

Temperature Range:

Active Material:

Substrate or Support:

Size: Powder Shape:

Additional Information:

Type Number: - Manufacturer: MRC

Classification:

Temperature Range:

Active Material: Thorium

Substrate or Support:

Size: Powder Shape:

Additional Information:

Heat treated in argon for 2 hours at 700°C.

Type Number: 77604-5 Manufacturer: MRC

Classification: Proprietary

Temperature Range:

Active Material:

Substrate or Support:

Size: Powder Shape:

Additional Information:

Type Number: 77604-1 Manufacturer: MRC

Classification: Proprietary

Temperature Range:

Active Material:

Substrate or Support:

Size: Powder Shape:

Additional Information:

Type Number: Manufacturer: Engelhard

Classification:

Temperature Range:

Active Material: Rhodium metal

Substrate or Support: none

Size: Powder Shape:

Additional Information:

Type Number: 77604-4 Manufacturer: MRC

Classification: Proprietary

Temperature Range:

Active Material:

Substrate or Support:

Size: Powder Shape:

Additional Information:

Type Number: Ni-4305E **Manufacturer:** Harshaw

Classification: Acidic Hydrogenation and Desulfurization

Temperature Range:

Active Material: Nickel-Tungsten

Substrate or Support: Alumina

Size: 1/8" **Shape:**

Additional Information:

Type Number: Ag-0101E **Manufacturer:** Harshaw

Classification: Oxidation of methanol

Temperature Range: N/S

Active Material: 3.5%-4.0% Silver

Substrate or Support: Alumina

Size: 1/8" **Shape:**

Additional Information:

Type Number: Cu-0402T **Manufacturer:** Harshaw

Classification: Hydrogenation

Temperature Range: N/S

Active Material: Copper Chromite

Substrate or Support: Alumina

Size: 1/8" **Shape:** Tablets

Additional Information:

Type Number: Cu-2501G **Manufacturer:** Harshaw

Classification: Dehydrogenation

Temperature Range: N/S

Active Material: Copper Carbonate

Substrate or Support: Silica

Size: 1/8" **Shape:**

Additional Information:

Type Number: Cu-0307T **Manufacturer:** Harshaw

Classification: Oxygen or Hydrogen Removal

Temperature Range: N/S

Active Material: CuO 99%

Substrate or Support: None

Size: 1/8" **Shape:** Tablets

Additional Information:

Type Number: Cu-0905T **Manufacturer:** Harshaw

Classification: Chlorination

Temperature Range: N/S

Active Material: $CuCl_3$

Substrate or Support: Alumina

Size: 1/8" **Shape:** Pellets

Additional Information:

Type Number: MRC-Ag **Manufacturer:** Monsanto

Classification: Proprietary

Temperature Range: 300°-400°C

Active Material: 0.2-0.4% Silver

Substrate or Support: Alumina

Size: 1/8" **Shape:** Chips

Additional Information: Borohydride Reduced

Type Number: MRC-Ag-HG **Manufacturer:** Monsanto

Classification: Proprietary

Temperature Range: 300°-400°C

Active Material: Silver and Mercury 0.2-0.4%

Substrate or Support: Alumina

Size: 1/8" **Shape:** Chips

Additional Information: Borohydride Reduced

Type Number: T-309 **Manufacturer:** Girdler

Classification: Experimental

Temperature Range: N/S

Active Material: Platinum Oxide

Substrate or Support: Alumina

Size: 3/16 x 1/8 **Shape:** Tablets

Additional Information: Platinum Oxide Concentrated in thin outer layers

Type Number: T-366 **Manufacturer:** Girdler

Classification: Experimental

Temperature Range: N/S

Active Material: Copper 55%

Substrate or Support: Kieselghur

Size: Powder **Shape:**

Additional Information: Stabilized

Type Number: G-49A **Manufacturer:** Girdler

Classification: Hydrogenation

Temperature Range: N/S

Active Material: Reduced Nickel

Substrate or Support: Kieselguhr

Size: 3/16 x 1/8 **Shape:** Tablets

Additional Information:

Type Number: G-43 **Manufacturer:** Girdler

Classification: Reduction of Nitrogen Oxides

Temperature Range: N/S

Active Material: Platinum Promoted

Substrate or Support:

Size: 1/4 x 1/4 **Shape:** Tablets

Additional Information: Highly Active

Type Number: G-47 **Manufacturer:** Girdler

Classification: Ammonia Dissociation

Temperature Range: 850-980°C

Active Material: Iron Oxide

Substrate or Support:

Size: 1/4" **Shape:** Spheres

Additional Information: High Space Velocities

Type Number: **Manufacturer:** Engelhard

Classification:

Temperature Range: N/S

Active Material: 0.5% Palladium

Substrate or Support: Activated Alumina

Size: 1/8 x 1/16 **Shape:** Cylinders

Additional Information:

Type Number: **Manufacturer:** Fisher Scientific

Classification:

Temperature Range: N/S

Active Material: CaO

Substrate or Support:

Size: 1/4" **Shape:** lump

Additional Information:

Type Number: **Manufacturer:** Engelhard

Classification:

Temperature Range: N/S

Active Material: 0.5% Rhodium

Substrate or Support: Alumina

Size: 1/8" **Shape:** Pellets

Additional Information:

Type Number: MRC-Pt-Hg   Manufacturer: Monsanto

Classification: Proprietary

Temperature Range: 200 - 800°C

Active Material: 0.2 - 0.4% Pt-Hg

Substrate or Support: Alumina

Size: 1/8 in.   Shape: Chips

Additional Information: Borohydride Reduced

Type Number: Ag-0101E   Manufacturer: Harshaw

Classification: Methanol Oxidation

Temperature Range: 200 - 800°C

Active Material: Silver

Substrate or Support: Alumina

Size: 1/8 in.   Shape: Extruded pellets

Additional Information:

Type Number: Cu0402T Manufacturer: Harshaw

Classification: Hydrogenation

Temperature Range: 200 - 800°C

Active Material: Copper Chromite CuO-35%, Cr_2O_3-38%, BaO-10%

Substrate or Support:

Size: 1/8 in. Shape: Tablets

Additional Information: BaO stabilized

Type Number: Ni-4305E Manufacturer: Harshaw

Classification: Hydrogenation

Temperature Range: 200 - 800°C

Active Material: Nickel Tungsten Sulfides 4.5%N. 9.5%W

Substrate or Support: Alumina

Size: 1/8 in. Shape: Extruded pellets

Additional Information:

Type Number: II-077 **Manufacturer:** Engelhard

Classification:

Temperature Range: 200 - 800°C

Active Material: 0.5% Pt

Substrate or Support: Alumina

Size: 1/8 in. **Shape:** Extruded pellets

Additional Information:

Type Number: Cu2501G **Manufacturer:** Harshaw

Classification: Dehydrogenation

Temperature Range: 200-800°C

Active Material: Copper Carbonate 6%

Substrate or Support: Silica

Size: 4-10 mesh **Shape:** chip

Additional Information:

Type Number: Cu-0803 Manufacturer: Harshaw

Classification: Oxygen Removal

Temperature Range: 200 - 800°C

Active Material: Copper Oxide

Substrate or Support: Alumina

Size: 1/8 Shape: Tablets

Additional Information:

Type Number: Manufacturer:

Classification:

Temperature Range:

Active Material:

Substrate or Support:

Size: Shape:

Additional Information:

APPENDIX IV

ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF NITRITE-NITRATE

This method of quantitative determination of Nitrite-Nitrate in acid solution makes use of the distinct absorption bands in the UV region for these materials.

Absorbance maxima are at 357 mμ for nitrite and at 301 mμ for nitrate. Nitrate does not absorb at 357 mμ; therefore, no correction for absorption is necessary. However, nitrite does absorb at 301 mμ, and correction is necessary for nitrate analysis.

A Cary Recording Spectrophotometer, Model 14M with matched 1.00-cm quartz cells was used. The solvent used was 2.5M H_3PO_4 diluted from 85% J. T. Baker Reagent-grade phosphoric acid.

Absorption data for NO_2- and NO_3-ions were obtained. Beer's law was followed and was used to obtain the following equations:

1) $A_{357} = 46.9[NO_2^-]$

2) $A_{301} = 3.80[NO_2^-] + 7.76[NO_3^-]$

Since cell length is 1.00 cm, no correction is necessary and absorption constants are molar absorptivities.

Utilizing the following formula for solution of N_2O_4, the quantity of N_2O_4 is easily calculated:

$$N_2O_4 + H_2O \longrightarrow HNO_2 + HNO_3$$

In the presence of air, some or all of the nitrous acid will oxidize to nitric acid

$$2HNO_2 + O_2 \longrightarrow 2HNO_3$$

Therefore, the nitrite-nitrate concentrations will not be equimolar but may be easily corrected as follows to determine N_2O_4 concentration:

$$[N_2O_4] = \frac{[NO_2^-] + [NO_3^-]}{2}$$

APPENDIX V

CALCULATIONS OF VOLUME N_2/A.H. FACTOR FOR AEROZINE-50 ELECTROOXIDATION

The test conditions used (described in section IV, B, 3) correspond to excess fuel conditions: any component of the fuel may be used in any proportion with the unreacted components discarded. There are four reactions which can take place:

H-1 N_2H_4 oxidizes by a 4 electron process to yield 1 mole of N_2 per mole of N_2H_4 reacted

U-1 UDMH oxidizes by a 6 electron process to yield 1 mole of N_2 per mole of UDMH reacted

U-2 UDMH oxidizes by a 2 electron process yielding no N_2

U-3 UDMH oxidizes by a 4 electron process yielding no N_2

The justification for the UDMH reactions is found in ref. 4. No apriori assumptions can be made, any or all of these reactions can take place, any or all may contribute to the Ampere-Hour capacity of the cell. Calculation of capacity and volume factors leads to the following:

Species reacting	Reaction Code	A.H/gm Reacting	$ft^3 N_2$/gm reacting
N_2H_4	H-1	3.35	24.7×10^{-3}
UDMH	U-1	2.68	13.1×10^{-3}
UDMH	U-2	0.89	0
UDMH	U-3	1.78	0

Let: w = g UDMH reacting by reaction U-1
u = g UDMH reacting by reaction U-2
y = g UDMH reacting by reaction U-3
z = g N_2H_4 reacting by reaction H-1
v = number of 1/1000 ft^3 of N_2 produced per A.H. The Ampere-hours produced by any or all of the possible anodic processes is given by:

$$A.H. = 2.68\,w + 3.35\,z + 0.89\,u + 1.78\,y$$

The volume of N_2 produced at the same time is:

$$ft^3\,N_2 = 13.1 \times 10^{-3}\,w + 24.7 \times 10^{-3}\,z$$

There are three possible conditions to be analyzed:

1. N_2H_4 the only reactive component
2. Both UDMH and N_2H_4 active
3. UDMH the only reactive component

Case 1 N_2H_4 the only reactive component.

In this case w=u=y=0 and A.H. = 3.35 z and $ft^3\ N_2 = 24.7 \times 10^{-3}\ z$ for 1 A.H.:

$$z = 1/3.35 = 0.30\ g$$

Substituting this value into the volume equation:

$$ft^3\ N_2 = 24.7 \times 10^{-3}\ (0.30) = 7.4 \times 10^{-3} \quad ; \quad V = 7.4$$

Now the objective of the remaining analyses is to show that this value of V = 7.4 cannot be obtained with any conditions.

Case 2 Both N_2H_4 and UDMH active

For V to equal 7.4, the volume of N_2 produced in 1 A.H. must equal $7.4 \times 10^{-3}\ ft^3$

Thus for 1 A.H.

$$7.4 \times 10^{-3} = 13.1 \times 10^{-3}\ w + 24.7 \times 10^{-3}\ z$$

rearranging and combining terms:

$$z = 0.30 - 0.53\ w$$

substituting this expression into the A.H. equation:

$$A.H. = 2.68\ w + 3.35\ (0.30 - 0.53\ w) + 0.89\ u + 1.78\ y$$

rearranging and combining terms:

$$A.H. = 1.0 + 0.90\ w + 0.89\ u + 1.78\ y$$

Now the assumption behind this equation was that 1 A.H. produced $7.4 \times 10^{-3}\ ft^3$ of N_2. The only case in which this is satisfied is for w=u=y=0, i.e., the UDMH does not participate in the reaction in any manner at all. Thus if N_2H_4 is active at all, the maximum V is 7.4 and this occurs when N_2H_4 is the only active species. The participation of UDMH in the reaction in any mode will decrease V.

Case 3 UDMH the only reactive component

In this case N_2H_4 does not participate in the reaction at all and the two general equations are:

$$A.H. = 2.68\ w + 0.89\ u + 1.78\ y$$

$$ft^3\ N_2 = 13.1 \times 10^{-3}\ w$$

Again for V to equal 7.4, the volume of N_2 produced in 1 A.H. must equal 7.4×10^{-3} ft^3. Thus for 1 A.H.:

$$7.4 \times 10^{-3} = 13.1 \times 10^{-3}\ w$$

$$w = 0.565\ g$$

substituting into the ampere-hour expression:

$$A.H. = 2.68\ (0.565) + 0.89\ u + 1.78\ y$$

$$\text{or } A.H. = 1.51 + 0.89\ u + 1.78\ y$$

The assumption again was that 1 amp-hour produced 7.4×10^{-3} ft^3 of gas. However, this cannot occur for any actual values of u and y. The maximum V which can occur if N_2H_4 is inactive is at u=y=0 where V = 4.9.

These analyses have indicated that V values below 7.4 indicate participation of UDMH in the electrode reaction, while V = 7.4 (within experimental error) indicates N_2H_4 is the only participant.