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PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
THE JAMES FORRESTAL RESEARCH CENTER

31 December 1952

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Chief of Naval Research,
Office of Naval Research,
Department of the Navy,
Washington 25, D. C.
Code 429

Dear Sir:

Subject: Quarterly Report for the Period,
October 1 to January 1, 1953.

During the last three months we have continued to study the changes in power yield and degree of conversion of ammonia to hydrazine in the presence of water flowing through the reactor as a liquid. To obtain fully comparable data a number of measurements were first carried out at different pressures and flow rates using anhydrous ammonia and then the same reactor was employed for the study of the effect of introducing water in the discharge. A summary of the data for anhydrous ammonia obtained at pressures of 30, 40 and 50 mm Hg using gas flows of 3 to 8 cubic feet per minute is given in Table I.

Table I. Yield of hydrazine in grams per KWH & degree of conversion in percent of ammonia input at various pressures & flows. Reactor data: length of fluted section 30"; distance between electrodes 35"; main inner diameter of fluted section 36.5 mm; pitch of flutes 126 mm; lead 63 mm; depth 12.5 mm; inner volume of fluted section about 475 cc, between electrodes about 600 cc.

Flow	Pressure 30 mm		Pressure 40 mm		Pressure 50 mm	
CFM	Yield	Conv. %	Yield	Conv. %	Yield	Conv. %
3	5.62	0.200	4.57	0.194	3.70	0.174
4	6.27	0.200	5.10	0.182	4.13	0.179
5	6.60	0.199	5.36	0.188	4.35	0.179
6	6.74	0.207	5.46	0.188	4.45	0.178
7	6.87	0.202	5.55	0.203	4.52	0.187
8	6.97*	-	5.63	0.203	4.59	0.179

*Extrapolated value

The most interesting point about the data given in Table I is the constancy of the degree of conversion of the ammonia which appears to be independent of the flow rate. As shown in earlier kinetic studies of the reactions taking place in the electric discharge, after a contact time of only a few milliseconds between the streaming gas and the plasma, the yield levels off to a prectically constant value. In the case of the reactor employed the length of the contact time at a pressure of 30 mm and a flow of 3 CFM is approximately 16 milliseconds while our kinetic data show that a contact time of only 6 milliseconds would have been ample to give maximum yield. Since an approximately threefold increase in flow raises the power yield by only 25 per cent, and the power required to sustain the discharge increases rapidly with its length, we must conclude that considerably higher hydrazine yields would have been obtained with a shorter reactor while simultaneously allowing the use of still higher ammonia flow rates. As a matter of fact data obtained earlier (Annual Report, 1950, Table IX, Part 3) using another reactor with a similar helically fluted tube with a length of only 18 inches and having an inner volume of about 180 cc, showed at contact times of 9 milliseconds yields of up to 12 grams of hydrazine per KWH with a conversion of 0.28 per cent. In view of these facts we have built and set up a new reactor with a 2 inch straight bore and having a distance of 21 inches between the electrodes. To make it possible to change the cross section area of the gas stream, the reactor has provisions made for inserting water cooled center tubes of different diameters. These tubes may be either straight or helically fluted. The ammonia is introduced through a conical cavity to give the gas stream a high rotational velocity.

To return to our original subject let us now take a look at some of the data obtained with water flowing through the reactor. Yield and conversion data

at various pressures for an ammonia flow of 3 CFM and at a pressure of 40 mm with ammonia flows varying over the range 3 to 8 CFM using in all cases water flows of 100-200 cc per minute are summarized in Table II.

Table II. Yield of hydrazine in grams per KWH & degree of conversion in percent of ammonia input: A) at constant ammonia flow of 3 CFM at various pressures and B) at constant pressure of 40 mm at various ammonia flows. All reactor data same as those given in Table I. Water flow 100-200 cc per minute.

Data for A			Data for B		
Pressure mm Hg	Yield gr/KWH	Conv. %	Flow CFM	Yield gr/KWH	Conv. %
30	4.50	0.30	3	4.09	0.28
40	4.09	0.28	4	3.97	0.27
50	2.83	0.24	5	3.70	0.23
60	2.00	0.19	6	4.40	0.25
70	1.71	0.16	7	3.54	0.19
			8*	4.13	0.23

The data in Table II show again that the degree of conversion seems to be approximately independent of the ammonia flow rate and considerably higher than the corresponding values obtained at a pressure of 40 mm in the absence of water or, in other words, the amount of hydrazine collected per unit time is increased by the presence of water. However, if we compare the conversion data obtained at constant flow and different pressures we find that while a large increase is noted at the lowest pressures the picture changes entirely with increasing pressure and at higher pressures the conversion tends to become smaller in the presence than in the absence of water in the discharge. Finally the data show that in all cases the power yield is lower in the presence of water than when anhydrous ammonia was employed.

*Measurement at a pressure of 42 mm Hg.

A semi-quantitative explanation of these results is easily obtained. Ammonia dissolves readily in water as a weak base which has a dissociation constant with a value of $1.8 \cdot 10^{-5}$ at a temperature of 25°C. At a total pressure of 30 mm Hg the equilibrium concentration in water is about 2 molal. Using the known values for the equivalent conductivities of the ammonium and hydroxide ions and assuming that the inside surface of the reactor is uniformly covered with a layer of ammonia solution only 0.1 mm thick or that the solution forms a more or less narrow stream of the same cross section area as the thin film, we find that under the operating conditions for the electric discharge the water loss in the ammonia solution would have an order of magnitude of 1500 watts. This huge power loss readily explains the lowering of the yield in the presence of water but it does not explain the highly increased degree of conversion at lower pressures. With increasing pressures the equilibrium concentration of ammonia in the liquid phase also increases very rapidly and thus simultaneously increasing the conductivity and the power losses in this phase.

The higher degree of conversion in the presence of water found at lower pressures may be explained very simply using the results of our earlier kinetic studies. Due to the high rate of decomposition of hydrazine in an electric discharge, which was shown to be about five hundred times larger than its rate of formation, the total yield collected is only a fraction of the amount formed. If any part of the hydrazine formed thus could be removed from exposure to the destructive forces of the electric plasma the degree of conversion would appear to increase just as the power yield would be improved if losses occurring in a liquid phase of aqueous ammonia could be eliminated. This solution reacts with

hydrazine under formation of hydrazonium hydrate which latter is retained in the liquid phase and in this manner shielded from the discharge giving an increased amount of hydrazine collected per unit of time.

Power losses due to the presence of an aqueous ammonia liquid phase in the electric discharge would obviously be decreased by 1) extending the length, and thus increasing the resistence, of the liquid film, 2) making the film discontinuous by breaking it up in a number of short sections separated by layers of the gas phase and 3) eliminating the formation of a liquid film on the walls of the reactor. The first alternative represents large mechanical difficulties in reactor design and would have dubious value due to the necessarily limited contact with the gas phase defeating the purpose intended. The second alternative should provide somewhat better contact with the gas phase, does not represent any particular reactor design difficulties and may be worth a trial.

To eliminate the formation of a continuous liquid film on the reactor walls it is obviously necessary first to introduce the liquid in the form of very small droplets and then to prevent them from joining each other on the reactor walls before leaving the discharge space. The liquid introduced must contain sufficient ammonia dissolved that the droplets to be formed tend to give off rather than absorb more of the solute, since strong absorption inevitably increases their size and causes them to join each other. In the design of the new reactor with 2 inch bore mentioned above provision has been made for the use of conventional type high pressure spray nozzles to produce a fog-like dispersion of aqueous ammonia droplets. Since the high rotational velocity of the ammonia gas stream as it emerges from the conical cavity into the reactor would tend to throw the droplets against the

walls, provision has also been made to make it possible to introduce the ammonia spray at different levels and to moderate the angular velocity of the gas stream.

To summarize the above a preliminary study has been completed of the effect of introducing water as a liquid phase on the formation of hydrazine from ammonia in an electric discharge. If proper allowances are made for power losses in the liquid phase, not only the degree of conversion of ammonia to hydrazine but also the yield per KWH would be higher than the corresponding values obtained for an anhydrous system. A short discussion is given of the design of a new reactor allowing measurements for ammonia flows up to 12 CFM at a pressure of 30 mm Hg.

Very truly yours,

G. C. Akerlof

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