

## Hydrazine Synthesis in A Silent Electrical Discharge.

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### INTRODUCTION.

The synthesis of hydrazine from ammonia using the silent electric discharge was first demonstrated by Besson in 1911 (1). Subsequent investigation showed that both the electrical energy yield and percentage conversion obtained were very low (2,3) and interest in the process waned. Further work was introduced in the early 1950's enabling substantial improvements in yields to be obtained in certain circumstances and a better understanding of the kinetic mechanisms in the discharge to emerge. Devins and Burton (4) showed that significant hydrazine formation only took place in the positive column of a D.C. discharge. Moreover, they found that yields could be substantially increased if the atomic hydrogen concentration in the discharge could be reduced by recombination. These general observations were later confirmed by Rath sack (5). As a result mechanisms were proposed for hydrazine synthesis based on the underlying premise that the hydrazine was first formed in the discharge and then degraded by back reactions. Ouchi (6) showed that yields could be increased by reducing the residence time of the hydrazine in the discharge in agreement with the general premise of hydrazine degradation in the discharge. Subsequent work has not been at variance with this finding (7,8).

Recently, I.C.I. of the U.K. have reported (9) that removal of product hydrazine in a liquid absorbent gives a substantial increase in yield and an improvement in percentage conversion. This is, of course, a modification of the general premise of hydrazine degradation in the discharge proposed by Devins and Burton (4) and Ouchi (6). Furthermore, following on the pioneering work of Ouchi (6), and others (10), I.C.I. apparently were able to achieve even better yields by suitable modification of the waveform characteristics of the discharge. In order to confirm their claim and to help clarify the mechanisms taking place in the discharge, work was commenced on this system at the University of Newcastle-upon-Tyne in 1965. This is a preliminary statement of the results obtained to date.

### EXPERIMENTAL.

The main aim of this work was to attempt to increase hydrazine yields by reducing the residence time of the product in the discharge. A concentric barrier discharge reactor was employed with and without the use of a liquid absorbent. Reactant flow rate was increased up to the

maximum pumping capacity of the apparatus after which the discharge voltage was reduced by changing the electrode area in order to give a further reduction in product residence time. Finally a D.C. parallel electrode reactor was used in which the discharge waveform characteristics were altered so that only a short activating pulse was supplied to the reactant in the electrode gap as it passed through the reactor.

The apparatus consisted essentially of a discharge reactor set between measuring and analysing sections in a flowing gas train. Commercially pure ammonia was fed into the measuring section of the apparatus via a reduction valve and a regulating needle valve. The flow rate was measured on a rotameter which had been previously calibrated under operating conditions by using a soap film manometer. Gas temperatures and pressures also were measured before the discharge reactor. The hydrazine formed in the discharge was absorbed in ethylene glycol either in situ or in a separate absorption train. Hydrazine was determined using the spectrophotometric method of Watt and Crisp (11). Vacuum control was achieved by a cartesian manostat located before the vacuum pump.

The A.C. radio frequency power (1.2 meg c/s) to the A- and B-type reactors was supplied by a modified C-12 Radyne generator of 1KW rated output. Measurement of the power dissipated in the discharge was achieved by firstly determining the power factor directly on a suitable oscilloscope. This value in conjunction with the direct readings of an R.M.S. voltmeter (Airmec 314) and a radio frequency ammeter (Cambridge Unipivot) enabled a reasonably accurate determination of the power in the discharge to be achieved. The D.C. power for the C-type reactor was provided by a specially engineered SKW generator. Measurement of the actual discharge power was made using a combination of an oscilloscope trace and the appropriate meter readings.

The various types of discharge reactors used in this work are illustrated schematically in Fig.1. Other essential geometric details of these reactors and their operating data are given in Table 1. The A-type series of reactors consisted of a precision silica tube (which acted as the capacitive barrier) with the high tension electrode attached around the outside. The inner electrode was a spinning cylinder so constructed that absorbent liquid could be sprayed onto the inside of the tube to flow down through the annular discharge gap. Co-current gas and liquid flow was employed.

The B-type series of reactors were of similar construction except that a central wire electrode was used and the absorbent liquid was fed into the incoming gas as a spray. Dispersion of the liquid was achieved ultrasonically using a vibratory generator. The spray was fed into the gas stream through an annular orifice placed at a sufficient distance

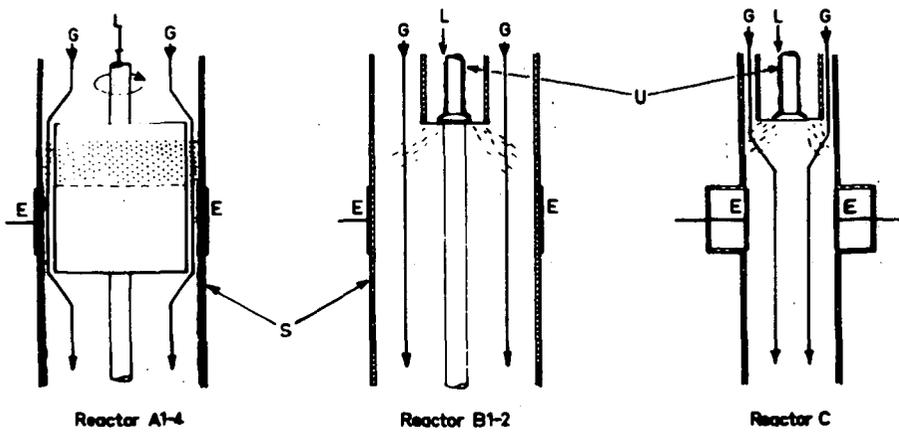


Fig.1 Schematic diagram of reactors used for hydrazine synthesis  
 E = Electrodes      L = Liquid Inlet      G = Gas Flow  
 S = Silica Barrier      U = Ultrasonic Vibrator

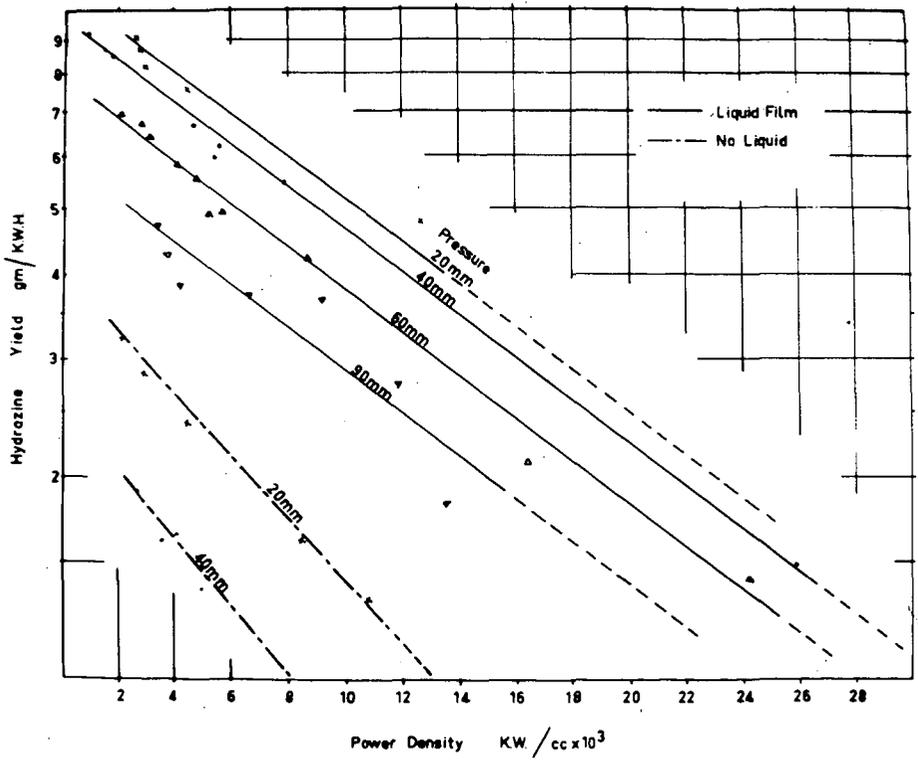


Fig. 2 Hydrazine yield for the co-axial reactor A1 with & without Liquid film

downstream from the discharge to ensure proper dispersal of spray in the electrode gap. The C-type reactor employed a pair of rectangular electrodes so set in the gas flow as to avoid reactant by-passing. The use of D.C. power necessitated stabilization of the discharge by means of a resistive load in the electrical circuit. Provision was made to admit liquid spray into the inlet gas stream using the same aerosol generator used in the type-B reactors.

Table 1.  
Reactor units employed.

Type	Reactor Code	Flow Area cm <sup>2</sup>	Discharge Width cm	Discharge Volume cm <sup>3</sup>	Dillectic Barrier Thickness cm
Tubular	A1	2.203	1.270	2.798	0.15875
Centrifugal	A2	"	0.254	0.560	"
Film Reactor	A3	"	0.127	0.280	"
	A4	"	0.040	0.089	"
Tubular	B1	1.089	1.270	1.383	"
Spray Reactor	B2	"	0.254	0.277	"
Pulsed Reactor	C1	1.411	0.635	0.896	0

#### RESULTS.

Hydrazine yields for the various reactor geometries and the operating variables employed are given in Figs. 2 to 6. From the data presented in Fig 2 to 4, it is evident that the yield varies inversely as an exponential function of the power density at pressures under 100mm of mercury. The effect of pressure also follows a negative exponential variation therefore a general equation of the form

$$Y = a \exp(-bP - c\pi)$$

adequately describes the results. Of course this correlation of the results does not in any sense give a complete description of the underlying physical chemistry involved in the synthesis. Ideally, it would have been preferable to develop separate rate equations in terms of the partial pressures of the various components in the overall hydrazine synthesis. This would have necessitated a complete product analysis and since, in the present case, these data are lacking the phenomenological approach had to be used. The constants in the equation for the various reactors and operating conditions used were evaluated using the method of least squares (12). These are tabulated in Table 2. It should be noted in this Table that certain pressure exponential values were bracketed. Here the relevant data were lacking for calculation and, therefore, the dependence of energy yield upon pressure for reactors A2 to A4 and B2 were assumed to be the same as those found experimentally for Reactors A1 and B1.

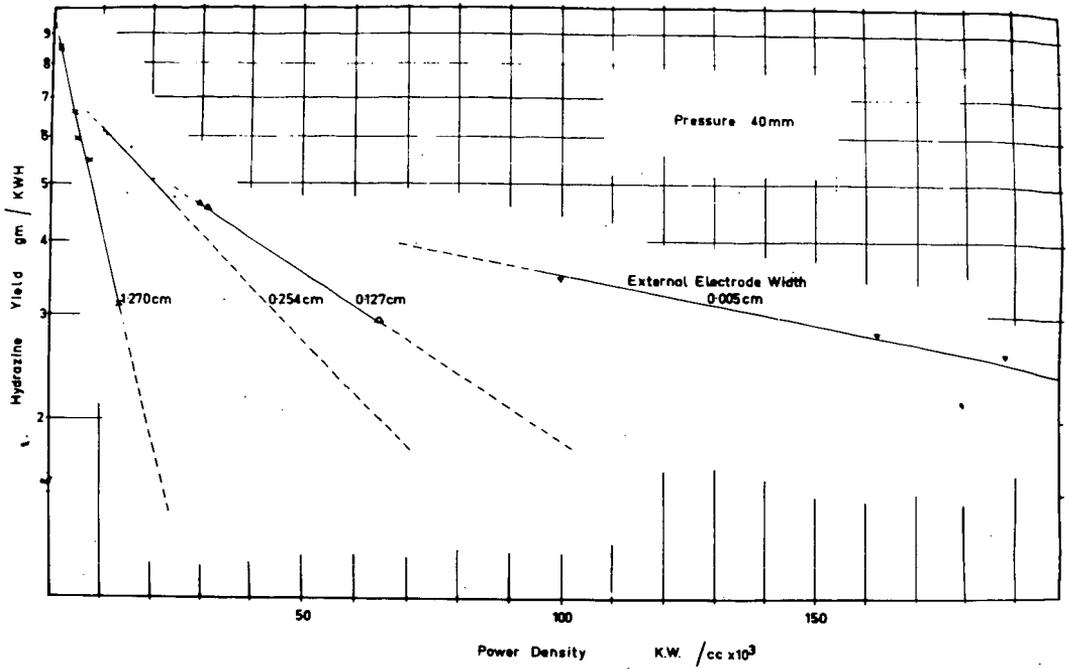


Fig. 3 Hydrazine yield for the liquid film co-axial reactors A1-4

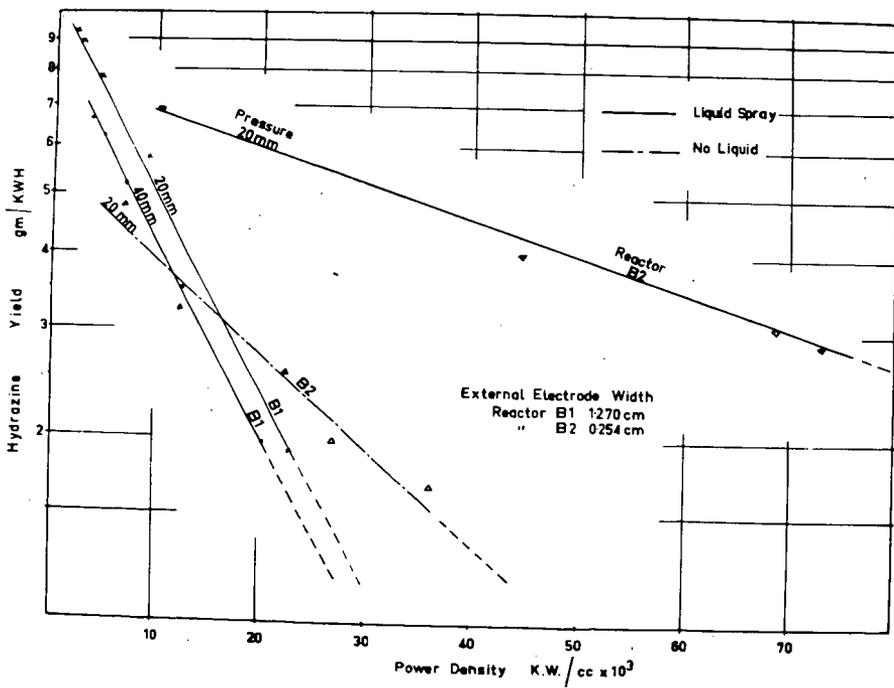


Fig. 4 Hydrazine yield for the co-axial reactors B1-2 with & without Liquid spray

Table 2.  
Derived constants for the equation  $Y = a \exp(-bF - cT)$

Reactor	a gm/KWH	b mmHg <sup>-1</sup>	c cc/Kwatt	liquid absorbent
A1	13.14	0.0087	73.81	film
A1	6.35	0.0236	118.74	none
A2	10.70	(0.0087)	19.43	film
A3	9.56	"	12.93	"
A4	7.28	"	3.73	"
B1	12.99	0.0098	73.58	spray
B2	9.26	(0.0098)	13.69	"
B2	8.88	(0.0236)	35.15	none

This is a reasonable procedure within any one particular series of reactors such as A1 to 4, but it is only approximate with differing reactor series (e.g. Reactor series A and B) due to dissimilarities in discharge geometries.

#### DISCUSSION.

The most notable overall feature of the results is the progressive increase in hydrazine yield obtained by the use of a liquid absorbent and by pulsing the discharge. The highest average yield was obtained with the pulsing technique with or without liquid absorbent and was approximately 15 gms  $N_2H_4$ /KWH. Isolated values as high as 20 gms/KWH were obtained but further experimental work is required before these values can be made reproducible. It is noteworthy that a yield of 15 gms/KWH is beginning to look commercially attractive although it must be remembered that the final product cost will depend to a great extent on the cost of the product purification process downstream of the reactor.

There are several interesting features shown by this work which bear discussion. From the results set out in Fig. 2 to 4 it is evident that the hydrazine yield decreases with increasing discharge power intensity despite a corresponding increase in the decomposition of ammonia. The only reasonable explanation for this which has been advanced is that hydrazine is formed in the discharge by a complex reaction mechanism and is subsequently decomposed by electron bombardment or other collision phenomena (4,6).

The use of a liquid absorbent results in a decrease in the slope of the energy yield-power density plot. This is well illustrated in both Fig. 2 and Fig. 4 by comparing the slope of the plots with and without the use of liquid absorbent. This indicates that hydrazine is being removed from the discharge by the liquid absorbent instead of being degraded. If the hydrazine were completely removed so that degradation did not occur the slope of this plot would be either independent of discharge power or possibly positive. The very

fact that the slope is still negative with the use of liquid absorbent may indicate that a significant amount of hydrazine is still being degraded in the discharge in this case. Therefore, the use of a more efficient absorption process would reasonably be expected to recover more of the hydrazine being degraded and thus increase yields still further. Moreover, the observed decreasing effect of pressure on the yield with the use of liquid absorbent (shown in Fig.2) adds weight to this suggestion.

As the pressure was decreased below 100mm of mercury the yield of hydrazine increased steadily while the slope of the yield-power density curve remained constant for similar reactor operating conditions such as the use of a liquid absorbent. A reasonable explanation for this behaviour is that at the lower pressures the electrons passing into the discharge are less likely to suffer collisions in the immediate vicinity of the electrode so that the average energy of the electrons will be high just prior to the required activating collisions. Therefore, activating collisions are more likely to occur and yields to increase correspondingly. Degradation of product by electrons is, by the same argument, more likely under these conditions but other product degrading discharge collisional phenomena e.g. the reaction with hydrogen atoms, are reduced because of the greater mean free path at the lower operating pressure. The overall result is that hydrazine yields increase. Secondary effects become increasingly important at higher pressures and it is likely that other variations in the effect of pressure on yield may well occur. One such variation is reported to occur at about 5mm pressure where the energy yield passes through a maximum (8).

Product yields were increased by removing hydrazine in a liquid absorbent and it was considered that a more efficient absorption technique should lead to even greater yields. In order to obtain a more intimate gas liquid dispersion a spray reactor was used of the general design shown for Reactors B1 and 2 in Fig.1. The results (Fig.4) show that yields were slightly below that of the film reactor. In practice there were difficulties caused by dissimilarities in the construction of Reactors A and B which led to radically different discharge conditions being obtained. The film reactor (A1) had a more uniform discharge density because it was of an annular construction where the annulus width was small compared to the reactor diameter. The spray reactor, on the other hand, employed a central wire electrode and consequently there was a non-uniform field in the discharge gap with a higher local discharge density in the vicinity of the wire electrode. Because the yield is known to depend on an inverse function of the power density, it is only reasonable to expect that the reactor design B1 would give somewhat lower yield than the Reactor design A1 under similar operating conditions. This means that the more intimate gas-liquid contact in the spray reactor had no measurable effect on the product yield.

On the other hand, if hydrazine is formed and degraded uniformly in the activating section of the discharge this result is difficult to explain. It is suggested from this that, under these conditions, the absorption process is no longer the controlling factor since an increase in the overall potential absorption rate, through an increase in the interfacial area, produces no corresponding rise in hydrazine yields. It may be that liquid surface activation phenomena are taking place and the increased hydrazine yield which is observed with the use of an absorbent liquid is caused by hydrazine formed by other mechanisms in which the liquid surface plays an important role. If this were the case the liquid film, which presents a complete barrier to the discharge, would naturally give maximal yield and the spray reactor would only tend to this value in the limit.

It was found experimentally that a decrease in the residence time of the reactant in the discharge is accompanied by an increase in energy yield of hydrazine and a corresponding fall in percentage conversion. The results are detailed in Fig. 5 and appear to be in general agreement with those of Ouchi (6). When a liquid absorbent is used the change of yield and percent conversion is steady but without the use of an absorbent the effect becomes very marked at low residence times. Ouchi (6) has concluded from his results that some of the hydrazine formed in the discharge is preserved from degradation by rapid physical removal out of the discharge. This would adequately explain, in general terms, the increase in energy yield with reduced residence time. The degree of activation of species in the discharge must fall as the reactant throughput is increased. This would result in a decrease in percent conversion as residence time was reduced. Furthermore, as the concentration of hydrazine governs the rate of the degrading reaction the smaller percent conversion achieved at high flow rates will result in a higher overall energy yield being achieved. With the use of a liquid absorbent some effect on the yield may well arise because of changes in the absorption rates due to increased turbulence and a decrease in the gas liquid contact time.

Another point which must be borne in mind is that physical removal of the product or even, for that matter, the use of the pulsed discharge technique cannot give better conversions than that dictated by the equilibrium concentration of hydrazine for the basic reactions taking place in the discharge. The use of the liquid absorbent, on the other hand, permits higher conversion to be achieved because of the inability of the discharge reaction to reach equilibrium as hydrazine is being continuously removed after it is formed in the discharge.

The negative slope of the energy yield-residence time plot (Fig. 5), when liquid absorbent was used, implies that it is possible to increase yields still further by some other suitable modification of technique.

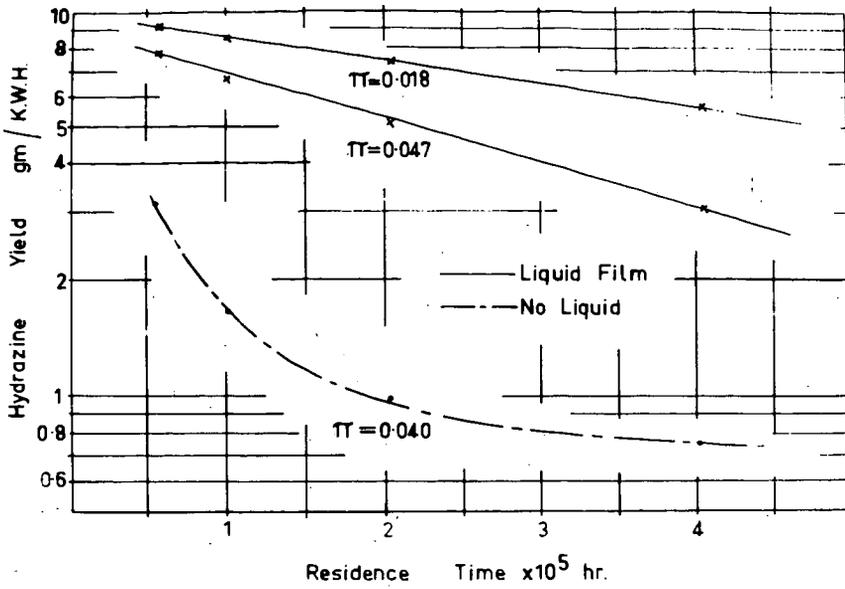


Fig.5 Variation of hydrazine yield with flow rate for reactor A1

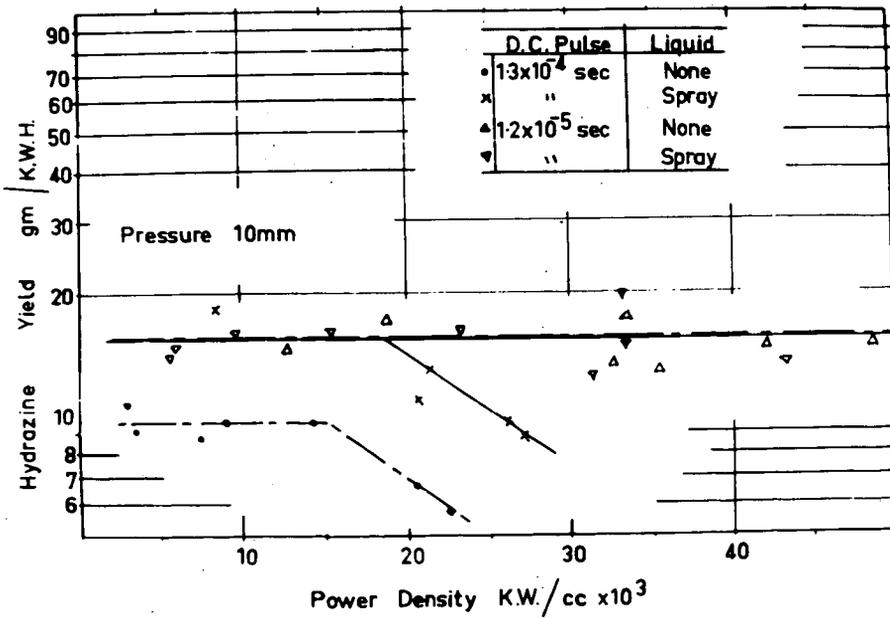


Fig.6 Hydrazine yield for pulsed D.C. reactor C1

The results, for the case when liquid absorbent was not used, show a very marked increase in yield with reduction of residence time. This abnormal behaviour suggests that the process resulting in increased hydrazine yields is not just the physical removal of product alone but a change may also be occurring in the basic reaction mechanisms.

In an endeavour to reduce the residence time below the level dictated by the capacity of the vacuum system the electrode area was steadily reduced (Reactors A1 to 4). The results obtained (Fig. 3) show that the yield fell and the discharge itself altered radically due to the increased influence of electrode edge effects.

Discharge pulsing gave a substantial increase in yields over the other methods employed. As the duration of the discharge pulse was shortened the yield was found to rise and become independent of power density. Furthermore, the yield was not affected by the use of a liquid absorbent. Up to this point the usual variations with these two variables were observed. Indications are that hydrazine yields can be increased well beyond 15 gms/KWH by suitable modification of the pulsed discharge technique.

It is clear from these results that the yield of hydrazine from ammonia using the silent discharge can be increased if the residence time of the product in the discharge is reduced by the use of liquid absorbent, physical flow rate of reactant or discharge pulsing. Several aspects of the results seem to imply that the underlying mechanism involved is not entirely that of physical removal of product but other factors, such as changes in the basic reaction mechanisms, are also involved.

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