# Temperature Control in Ammonia Oxidation<sup>1</sup>

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THE influence of temperature upon the catalytic oxidation of ammonia has been recognized in a qualitative way by all investigators in this field.

Taylor<sup>2</sup> found that with a so-called normal flow rate and 11.55 per cent ammonia by volume an oxidation efficiency of 85.8 per cent resulted with no electrical heat and a gauze temperature, in his particular apparatus, of 745° C., whereas with electrical heat on the gauze and a temperature of 824° C. 11.45 per cent ammonia gave a 90.0 per cent conversion with the given fixed rate of gas flow.

He also preheated the ammonia-air mixture of 11.55 per cent ammonia content to a temperature of 280° C., and with no other heat application secured a gauze temperature of 805° C. and a conversion of 88.3 per cent under the fixed conditions of gas flow. His conclusions were that any suitable method of maintaining gauze temperature would result in satisfactory conversion efficiencies. The effect of temperature change in a single flat

gauze catalyst has also been noted by Curtis.<sup>3</sup> At normal flow rates and a single gauze, using 11.3 per cent ammonia by volume, an oxidation efficiency of 87.1 per cent resulted with no electrical heat and a gauze temperature of 687° C., while an efficiency of 90 per cent resulted with electrical heat on the gauze and a temperature of 765° C. Probably Curtis did not use the same black body temperature correction as used by Taylor.

Electrical heat as applied to a platinum gauze catalyst serves merely to give the desired catalyst temperature control. As the ammonia oxidation reaction is strongly exothermic, it was long ago recognized that on high-grade ammonia a proper design of catalyst and catalyst chamber, whereby this heat energy could be utilized, was more economical than electrical heat.

A study of the literature seems at first to reveal conflicting ideas as to the effect of heat on an ammonia-air mixture. Ramsay and Young,<sup>4</sup> Perman and Atkinson,<sup>5</sup> and White and Melville<sup>6</sup> have all shown that under certain conditions ammonia can be easily decomposed at moderate temperatures. A patent issued to Landis<sup>7</sup> points out the great advantage in commercial ammonia oxidation through precooling the intake ammonia-air mixture and thereby preventing pre-ignition of the ammonia to hitrogen. Kaiser<sup>8</sup> pointed out that air should be heated separately and added to the ammonia just at the entrance of the gauze. As a matter of fact, this patent states that by preheating an ammonia-air mixture in a quartz tube to 320° C. he obtained an oxidation yield of only 66.8 per cent, but when heating the air separately he secured an oxidation efficiency of 99.8 per cent. In contrast to these

• J. Am. Chem. Soc., 27, 373 (1905).

statements we find that Ostwald's<sup>9</sup> initial patent has as a part of its fourth claim "conducting the reaction products in heat interchanging relation to the gas mixture flowing to the catalytic agent and thereby transferring more heat from the reaction products to the gas mixture." Taylor<sup>2</sup> passed a 10 per cent mixture of ammonia and air through a combustion tube filled with bits of fire brick and heated to 700° C., and found but traces of decomposition. Curtis found that with a space velocity of 600 the ammonia gas in contact with metal

The operation of an ammonia oxidation process from a consideration of gauze temperature is misleading. A high ammonia content (above 11 per cent by volume) favors a high gauze temperature, yet gives a low conversion. A recording pyrometer located near the catalyst intake and calibrated for a given equipment is most advantageous. Preheating the gas to between 460° and 500° C. favors greater capacities for a given oxidation efficiency.

walls at 700° C. showed 99.7 per cent decomposition. Of course, the decomposition depends upon the nature of the walls. One of the authors<sup>10</sup> found that serious pre-decomposition results when using a steel tube heat interchanger on the commercial ammonia oxidation apparatus; yet when using a silica lining under suitable conditions this decomposition may be prevented. The serious limitation to the use of silica lies in its poor heat transfer qualities. However,

a separate heat interchange for the air and then admixture of ammonia just prior to entrance at the gauze make the commercial application quite inviting provided preheating has real merits. There is good evidence that ammonia is decomposed at elevated temperatures when in contact with many surfaces other than silica.

Preheating an ammonia-air mixture prior to a catalyst should give a far more stable catalyst condition than securing a catalyst temperature by means of electrical heat on the gauze, because the volume changes on the intake gas are less abrupt in the case of preheating. At fairly high gas flow rates it would be impossible to heat the whole gas mixture up to the ideal temperature by electrical heat on the gauze, since the time of contact with the catalyst is exceedingly short even at low rates of flow. Since the speed of the reaction depends greatly upon the temperature in the gas phase, it would seem that the higher the intake gas temperature could be maintained the greater would be the capacity of a unit weight of catalyst. The design of the Parsons-Jones<sup>11</sup> ammonia oxidation apparatus was an early step in efforts to secure a good gas temperature gradient.

The use of a multi-layer gauze, whereby increased volumes of the ammonia-air mixture are used per given catalyst body, was another step in an effort better to utilize the heat of reaction; yet this method of securing increased catalyst temperature is only partly successful. There is still much difference of opinion as to the most economical number of platinum gauze layers to employ. The writers were led to consider that a two-layer platinum catalyst, with a possible backing of a more rigid nonplatinum gauze as a support when the two layers become fragile by long use, represents a most economical equipment. Curtis<sup>3</sup> showed that when the ammonia-air mixture was increased from 0.45 liter per minute per sq. cm. (15 cubic feet per square foot) of single

U. S. Patent 858,904 (1907).

11 Ibid., 11, 541 (1919).

<sup>&</sup>lt;sup>1</sup> Received September 24, 1924.

<sup>&</sup>lt;sup>2</sup> THIS JOURNAL, 11, 1121 (1919).

<sup>&</sup>lt;sup>8</sup> Chem. Met. Eng., 27, 699 (1922). 4 J. Chem. Soc. (London), 45, 88 (1884).

<sup>5</sup> Ibid., 74, 110 (1904).

<sup>7</sup> U. S. Patent 1,193,796 (1916).

<sup>&</sup>lt;sup>8</sup> U. S. Patent 987,375 (1911).

<sup>&</sup>lt;sup>10</sup> This Journal, **12**, 119 (1920).

gauze surface to 1.21 liters per sq. cm. (40 cubic feet per square foot) per minute the average oxidation efficiency was only decreased from 93.1 to 81.7 per cent. A single gauze layer of 80-mesh and 0.076-mm. (0.003-inch) diameter wire has gas space openings equivalent to 0.678 sq. cm. per sq. cm. of total area. By using a second gauze layer



these free spaces can be materially decreased, and by such a construction the rate of gas flow per unit weight of platinum catalyst should be increased over that for a single gauze layer. From the above it is seen that a threefold increase in gas flow only makes it necessary for the second gauze to do about 13 per cent of the total work if a 93 per cent efficiency could be secured at the increased rate. It would seem as if more than the second gauze layer would not be economical as far as the platinum investment was concerned.

In general, the speed of a chemical reaction is increased with increase in temperature. The two vital reactions involved in ammonia oxidation are:

$$\begin{array}{l} 4 \ \mathrm{NH}_{8} + 5\mathrm{O}_{2} \rightarrow 4 \ \mathrm{NO} + 6 \ \mathrm{H}_{2}\mathrm{O} + 214, \ 200 \ \mathrm{cal.} \\ 4 \ \mathrm{NH}_{8} + 3\mathrm{O}_{2} \rightarrow 2 \ \mathrm{N}_{2} + 6 \ \mathrm{H}_{2}\mathrm{O} + 300, \ 600 \ \mathrm{cal.} \end{array} \tag{1}$$

An increase in temperature probably affects the speed of one of these reactions differently than the other. No data were available as to the temperature factor for multilayer platinum gauze catalysts, and since considerable data have been gathered in the writers' laboratories during the past three years by four different individuals, it seemed wise to have them recorded.

The real problem confronting industry is not so much how the gauze temperature alone affects the yield, but rather as to how one can preheat every molecule of the ingoing gas mixture to a known temperature and be sure that all the gas approaches the catalyst temperature just as it passes through the wire meshes. In other words, owing to the tremendously short times of catalyst contact, and as in 1 sq. cm. of average gauze layer there is 0.678 sq. cm. of gas opening, a part of the gas actually passes through to the exit zone before it becomes heated anywhere near to the catalyst temperature. There are, then, a number of molecules of ammonia that do not burn to nitric oxide at the catalyst, but later burn to nitrogen in the hot gases just beyond the catalyst, in accord with Equation 2. When this last reaction occurs in the very spaces of the catalyst, a resultant high gauze temperature might give erroneous conclusions as to the operation.

### Experimental

The writers have accumulated considerable data for a double gauge of the close contact type at varying degrees of preheat temperature, the temperatures referring to that of the gas phase just prior to entry into the platinum catalyst. They empirically chose  $85^{\circ}$ ,  $275^{\circ}$ ,  $470^{\circ}$ , and  $635^{\circ}$  C. in order to secure comparisons of the temperature effect over a fairly wide range. As shown by Taylor,<sup>2</sup> the theoretical temperature rise at 100 per cent conversion for a 10 per cent by volume ammonia-gas mixture is  $723^{\circ}$  C.; hence, allowing for a certain conduction and radiation loss in the apparatus, it seemed that the foregoing preheat temperatures should give a fair range as applied to possible working conditions.

The ammonia used in the several hundred efficiency tests was in the form of synthetic liquid ammonia.<sup>12</sup> This was vaporized in a small tank. The air was delivered through sulfuric acid scrubbers in order to use the same dry air basis on all runs. Care was taken to run the ammonia-air mixture through sodium hydroxide and charcoal scrubbers and thence to a large tank where possible line surges could be eliminated. The same two-layer horizontal platinum gauze catalyst was employed in all the tests. This gauze was of 0.076-mm. (0.003-inch) diameter wire and 80 mesh. The converter was constructed of a silica-lined iron pipe, and the entrance chamber was wound with resistance wire. The whole was properly insulated on the outside in order to secure good control of the preheat temperatures.

A protected iron-constantan thermocouple was used to measure the gas temperature just prior to the entrance at the catalyst. The temperature was taken at a central point and about 13 mm. (0.5 inch) in front of the catalyst. The actual readings were corrected for errors due to radiation from the heated gauze upon the hot junction.<sup>13</sup> An optical pyrometer



was employed for the measurement of the gauze temperatures and the true temperature corrections were made to the observed readings as recommended by the Bureau of Standards when employing a heated platinum gauze,<sup>14</sup> as follows:

<sup>12</sup> Supplied by the Atmospheric Nitrogen Corporation of Syracuse, N. Y. <sup>13</sup> Walker, Lewis, and McAdams, "Principles of Chemical Engineering," p. 165.

14 Liddell, "Chemical Engineering," Vol. I, p. 456.

Observed temperature ° C.	True temperature ° C.	Observed temperature °C.	True temperature C.
600	675	850	975
650	730	900	1035
700	790	950	1095
750	850	1000	1160
800	910		

Care was taken to maintain the exit chamber at a temperature above the condensation point of the gas mixture. It became necessary to keep the exit sample line heated during the taking of all samples.

All intake and exit samples for a given test were taken simultaneously, in special 500-cc. evacuated gas sample bottles, and a gas sample averaging 0.5 gram was always secured. The method used for the estimation of the intake and exit combined nitrogen is exceedingly important, since very small errors greatly affect the numerical value of the resultant efficiency determination.

One-twentieth normal acid and alkali probably give a minimum error in the titrations. Methyl red was used as an indicator on the intake sample, and phenolphthalein was used as the exit sample indicator. Oxygen was added to the exit samples of all tests where the ammonia content was in excess of 9 per cent by volume, and ample time was permitted for the oxidation of all nitric oxide in the gas phase prior to addition of alkali. Thus, the method of Gaillard<sup>15</sup> was modified in several respects. Since the intake contains ammonia salts and as the exit contains some nitrite, a different indicator must be used on each. The choice of correction factors for the two indicators used is very important.

The flow of the air and the ammonia was regulated by the use of glass flowmeters which had been calibrated against a standard wet flowmeter.

#### Results

A long tabulation of the data of the several hundred efficiency determinations will not point out conclusions of greater value than will summarized data of a number of similar tests. Condensation within the exit sample line, failures to oxidize all the nitric oxide in the sample flasks, peroxide action on various indicators, the choice of indicators that were affected by the nitrite in the exit sample flask, the use of too concentrated acid and alkali, and several other factors caused analytical errors in many determinations during the early portion of the work. Since this account has to do with the temperature factor, the various effects in the different analytical procedures will not be discussed in detail. Only the data that were secured under the latest improved analytical procedure are summarized. Some of the previously published efficiency data are undoubtedly incorrect owing to analytical errors.

In the accompanying table the flow rates are for the twolayer horizontal gauze, but based on a given rate of flow per square centimeter of single layer. Thus, 0.609 liter per sq. cm. of single gauze actually means 1.218 liters per sq. cm. of gauze entrance area consisting of a double layer. The ammonia content of the summarized table is given for a general average; a 9.5 per cent might mean 9.3 per cent in one case of the several in any average set, and in another 9.7 per cent. It is doubtful whether many efficiency determinations are closer than between 1 to 2 per cent. The preheat gas temperature as given should be within  $\pm 10^{\circ}$  C. The gauze temperatures depend in part upon the Bureau of Standards corrections.

It should be noted that the efficiency data for one set of conditions in the table may represent the average of as many as ten separate efficiency runs. However, in all cases for a given set but slight variations from the average were found. Although there are only a limited number of points to be obtained over the fairly wide ammonia concentration range, it is possible to show these data in the form of curves. Figures 1 and 2 clearly indicate the necessity of securing a fair control of the ingoing gas temperature in this process.

Temperature Control in Ammonia Oxidation Preheat tem-Corrected Average volume gauze Average per cent effiperature in gas phase C. temperature C. per cent of NH. ciency 0.609 liter per sq. cm. (20 cu. fl. per sq. fl.) of total platinum gauze<sup>a</sup> 7.5 Low Low 85  $\begin{array}{c} 75.4\\ 77.7\\ 73.9\\ 82.2\\ 87.0\\ 79.9\\ 89.3\\ 91.3\\ 86.6\\ 89.3 \end{array}$ 85 85 275 275 275 275 470 13 825 5 7 735 13 7 9 925820 470 470 635 575 860 13 7.5 9.5 13.7 937 86.1 83.7 635 635 975 1095 1.218 liters per sq. cm. (40 cu. ft. per sq. ft.) of total platinum gauze 85 7 2 Low 725  $\begin{array}{c} 79.9\\ 81.0\\ 76.9\\ 85.5\\ 89.0\\ 78.0\\ 91.0\\ 91.3\\ 82.2\\ 89.9\\ 87.4 \end{array}$ 85 85 275 275 10 13 7 37 725 940 2 73010 37 865 275 470 13 2 7.210.3 13.7 7.2 10.3 13.7 845 1035 470470 1119 635 635 1025 635 1170 83.4 1.827 liters per sq. cm. (60 cu. fi. per sq. fi.) of total platinum gause 10.710.710.710.710.7 $\begin{array}{r} 85 \\ 275 \\ 470 \\ 635 \end{array}$  $\frac{840}{925}$  $79.6 \\ 89.0$  $1050 \\ 1175$ 90.5 88.3 3.045 liters per sq. cm. (100 cu. ft. per sq. ft.) of total platinum gauze<sup>a</sup>  $\frac{85}{275}$  $10.7 \\ 10.7 \\ 10.7 \\ 10.7$  $\frac{869}{975}$  $\frac{76.2}{85.0}$ 470 1119 88.3 <sup>a</sup> Rate of gas flow.

#### Conclusions

1—An entrance gas temperature much below  $470^{\circ}$  C. on the ammonia-air mixture at a point approximately 1.3 cm. (0.5 inch) in front of the double gauze catalyst results in greatly decreased conversions.

2—The operation of an ammonia oxidation process from a consideration of gauze temperature alone is misleading. All things being equal, the burning of the ammonia to nitrogen will give a higher temperature than when ammonia is oxidized to nitric oxide. Thus, both the desirable and undesirable reactions are strongly exothermic. Slight variations in ammonia content affect the gauze temperature greatly, yet the preheat temperature may be fairly easily and accurately controlled. The rate of gas flow also alters the heat conductivity of the equipment. The use of a recording pyrometer equipment located at the catalyst intake and a calibration of a given apparatus when installed should be a distinct advantage in the operation of any ammonia oxidation equipment.

3—A gas intake temperature greatly in excess of  $600^{\circ}$  C. at approximately 1.3 cm. (0.5 inch) in front of the gauze leads to reduced oxidation efficiencies.

4—Ammonia concentrations much in excess of 11 per cent by volume do not permit sufficient oxygen concentration in the accompanying air to give good oxidation speeds and high yields under given conditions of preheat.

5—It is possible to secure distinctly average oxidation conversions by control of the intake gas temperature and using even more than 1.827 liters of intake gas per minute per sq. cm. (60 cubic feet per square foot) of actual gauze employed in the two layers. With these high flow rates all the molecules of the cool intake gas do not remain in contact with the catalyst sufficiently long to become heated to the temperature of the catalyst; hence the preheating makes possible far greater capacities without greatly decreased conversions.