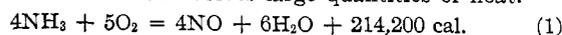


The Gauze Catalyst in Ammonia Oxidation¹

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ONE of the most common forms of catalyst employed in the ammonia oxidation reaction is that obtained by the use of several layers of platinum gauze. The fundamental reaction evolves large quantities of heat.



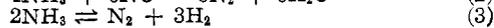
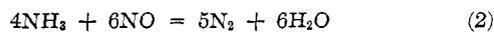
A high gas and catalyst temperature is an essential feature for efficient operation and Taylor² has shown that electric heating, preheating, and the utilization of high partial pressures of oxygen produce equally satisfactory results. The influence of temperature change in a single flat gauze catalyst has been noted by Curtis³ and the effect on a multi-layer flat gauze has been studied by one of the authors.⁴

Curtis³ pointed out that it was possible to secure 95 per cent oxidation efficiency with a 0.076-mm. (0.003-inch) diameter platinum wire gauze of 80 mesh only if the rate of gas flow was 0.305 liter per minute per square centimeter (10 cubic feet per square foot). However, with a rate of 1.815 liters per square centimeter per minute (60 cubic feet per square foot) he secured only 68 per cent conversion. Such a gauze has space openings equivalent to 67.8 per cent of the total exposed gauze surface, and it is remarkable that sufficient gas contact is secured on the 32.2 per cent of catalyst area as to obtain 95 per cent conversions under any set of space velocity relationships. It was a logical step to utilize at least two superimposed layers of platinum gauze in an effort to obtain higher yields at the higher rates of gas flow.

Taylor² has shown that the theoretical temperature rise at 100 per cent conversion for a 10 per cent by volume of ammonia is 723° C. If 1.815 liters per square centimeter per minute (60 cubic feet per square foot) of a gas mixture are forced through one layer of a gauze catalyst, there will be left approximately a 3 per cent ammonia content to be oxidized by the subsequent layer of platinum. The heat evolved by the oxidation of such a small ammonia concentration is less than 300° C. and far too low for good oxidation efficiency, unless the gas is preheated.

Curtis³ observed that when separating two platinum gauzes about 6 mm. (0.25 inch) and applying electric heat to the first gauze, a much more efficient catalyst combination resulted than when a single gauze was used.

For a long time in the early experimental use of multi-layer gauzes, it was decided that the layers must be in close contact or decreased oxidation efficiency resulted. It was assumed that reactions 2, 3, and 4 might occur.



Baxter and Hickey⁵ actually considered reaction 2 as a possible means of preparing pure nitrogen. It appears that the speed of this interaction is also influenced by the presence of a platinum catalytic surface.⁶ Moreover, the burning of ammonia in air to nitrogen is an old-time experiment and involves no catalyst whatsoever. Ramsay and Young⁷ long ago discussed the ready decomposition of ammonia by heat

at 500° C. Still another possible loss is indicated in the work of Jellinek⁸ upon the nitric oxide equilibrium, where it was noted that nitric oxide is catalytically decomposed to nitrogen and oxygen in the presence of platinum at the relatively low temperature of 689° C. At any rate, when nitric oxide comes in contact with platinum below 1000° C., there must be some decomposition; yet the space velocity relations govern the degree. Shun-ichi-Uchida⁹ has pointed out that with such catalysts as fine platinum gauze or iron-bismuth mixed oxides we can neglect reaction 2 and consider the whole ammonia oxidation reaction as the result of reactions 1 and 4 occurring consecutively. He explains, by means of this viewpoint, the occurrence of a maximum in the nitric oxide yield *vs.* time of contact curve. He also points out that reaction 4 is probably quite slow, while reaction 1 takes place in the presence of platinum with a contact of 0.00087 second.

Experimental Procedure

This laboratory in 1925 studied the above known facts and deemed it wise to conduct a series of tests to determine whether it was possible to use a separated platinum gauze catalyst with increased efficiency. It seemed possible to employ the upstream gauze as a temperature stabilizer for the separated downstream gauze and thereby possibly to eliminate electrical heating or complicated heat exchangers in the design of ammonia oxidation equipment.

When the downstream gauze is located a suitable distance from the upstream gauze depending chiefly upon the gas velocities used, a sufficiently high temperature should be obtained upon the much diluted ammonia-gas mixture as to enable the downstream gauze to oxidize all of the residual ammonia. The only precaution to observe would be to maintain a sufficiently high gas velocity as to minimize reaction 2, 3, or 4.

Some of the heat of the reaction is lost from the gauze by conduction through the converter and catalyst holder, and the temperature gradient must be far more favorable for constant conditions on the downstream gauze than on the first or upstream gauze. It seemed to the authors that the more uniform the temperature gradient before and after the catalyst, the greater the uniformity of operation, and the use of separated gauzes would accomplish this. With a contact time of but 0.0002 second and a cold intake-gas mixture, it is difficult to expect that thermal equilibrium and resultant catalyst stability can be obtained at the contact surface.

The same equipment was employed as used for the data of the previous paper.⁴ The air flow was stabilized by passing it through large carbons. Synthetic ammonia as supplied by the Atmospheric Nitrogen Corporation, of Syracuse, N. Y., was used. The necessary indicator corrections were made on the intake and exit samples as previously indicated. Table I gives a summary of the data taken.

One series of tests was taken with a single piece of platinum gauze of 0.076 mm. (0.003 inch) diameter and 80 mesh. The active surface of this catalyst was 2.85 sq. cm. (0.442 square inch) per layer; a second series of tests was made with two pieces of gauze which were superimposed and in very intimate contact; another series was studied in which the two gauzes were separated 1.3 cm. (1/2 inch); a final series with the gauzes

¹ Received September 11, 1928.

² Taylor, *J. IND. ENG. CHEM.*, **11**, 1121 (1919).

³ Curtis, *Chem. Met. Eng.*, **27**, 699 (1922).

⁴ Perley and Smith, *IND. ENG. CHEM.*, **17**, 258 (1925).

⁵ Baxter and Hickey, *Am. Chem. J.*, **33**, 300 (1905).

⁶ Reinders and Cats, *Chem. Weekblad*, **9**, 47 (1912).

⁷ Ramsay and Young, *J. Chem. Soc.*, **45**, 88 (1884).

⁸ Jellinek, *Z. anorg. Chem.*, **49**, 229 (1906).

⁹ Shun-ichi-Uchida, *J. Phys. Chem.*, **30**, 1297 (1926).

separated 2.5 cm. (1 inch) was also carried out. The same mass velocity per gram of platinum was employed in all cases.

Table I—Experimental Data
(Preheat temperature, 470° C.; 9 to 10 per cent ammonia)

GAUZE ARRANGEMENT	TOTAL GAS IN GAUZE			
	0.636 liter per sq. cm. 21.6 cu. ft. per sq. ft.	1.610 liters per sq. cm. 52.4 cu. ft. per sq. ft.	2.44 liters per sq. cm. 80.0 cu. ft. per sq. ft.	3.51 liters per sq. cm. 114.5 cu. ft. per sq. ft.
	No. Effi- tests ciency	No. Effi- tests ciency	No. Effi- tests ciency	No. Effi- tests ciency
	%	%	%	%
Single	5 90.2	8 90.0	6 89.7	3 81.9
Double close contact	8 91.5	7 95.5	7 94.3	6 91.1
1.3 cm. (0.5 inch) separated	14 90.6	5 95.3	13 94.0	9 91.3
2.5 cm. (1 inch) separated	12 90.7	9 95.0	12 93.2	6 90.0

Results

The quantitative results of the laboratory tests were not entirely those anticipated. With a preheated gas mixture, the results of the three series of tests using two gauzes are essentially the same for a given ammonia content irrespective of the arrangement of the gauzes. It was expected that with high gas-flow rates on a separated gauze the capacity and efficiency should be higher than for the close layer type of

catalyst owing to the greater temperature stability of the ammonia-gas mixture oxidized by the second gauze. Apparently reactions 2, 3, and 4 tend to offset any advantage gained by speeding up reaction through increased gas temperature. The accurate measurement of the gas temperature between the gauze layers is a very difficult task and hence an estimate of this temperature was not made.

In each instance where a double flat gauze was employed, the highest efficiencies were secured with a gas-flow rate of about 1.6 liters per square centimeter per minute (52 cubic feet per square foot) of total gauze in both layers.

Conclusions

1—A multi-layer platinum gauze catalyst has a greater capacity at a higher efficiency than a single gauze, irrespective of whether the layers are in direct contact or not.

2—The use of separated platinum gauze layers on a preheated gas mixture gives nearly as high oxidation efficiencies as if the catalyst layers were in close contact, but no greater capacities.

3—An intake gas flow of approximately 1.6 liters per square centimeter per minute (52 cubic feet per square foot) and preheated to 470° C. gives the highest oxidation efficiencies, irrespective of whether the layers are in close contact or not. This gives a catalyst contact time of approximately 0.00019 second.

A Complete Sludge-Washing Plant in a Single Unit¹

A. Anable

THE DORR COMPANY, 247 PARK AVE., NEW YORK, N. Y.

THE countercurrent principle is well known in chemical engineering practice, particularly in connection with the washing of precipitates free from contaminating solutions or, when the solution is the material of value, for recovering the valuable solution from the residue or precipitate. Advanced forms of the application of mechanical means to the simplification of washing are countercurrent decantation plants, in which the material to be washed is continuously settled from weaker and weaker solutions in a series of continuous mechanical thickeners. The advantages of continuous washing plants are well known and need no elaboration. Suffice it to say that continuous countercurrent washing in conjunction with continuous agitation has shown marked advantages over older batch methods for the production of caustic soda, sulfate of alumina, phosphoric acid, barium sulfide, and blanc fixe, to mention only a few of the better known applications.

Countercurrent Decantation in Caustic Soda Manufacture

The conventional type of plant of this sort is shown in flow sheet form in Figure 1, this particular flow sheet representing the manufacture of caustic soda by the lime-soda process. Causticizing is carried out on a continuous basis in three agitators, arranged in series and equipped with steam coils so that the milk of lime and soda ash may be kept at an elevated temperature during the entire time of agitation required for effective causticization. In the first thickener the clear, hot, and strong caustic solution overflows continuously to evaporation or other further treatment, while the settled lime mud is moved to the center and pumped to No. 2 thickener, and so on through the remaining thickeners, in each of which it

comes in contact with weaker and weaker solutions. As a result this lime is progressively impoverished in dissolved values and is eventually discharged from the last thickener virtually free from caustic solution. The wash water added in the last thickener cascades as an overflow product from one thickener to the next, always moving in a direction countercurrent to that of the solids. It finally overflows No. 2 thickener and is used for making up fresh milk of lime, after which it reenters the system via the agitators.

Caustic soda is widely used in amounts from 1 ton up at plants manufacturing gases; producing phenol, creosote, mineral oils, etc.; reclaiming rubber from old stock; and making artificial silk, to mention only a few cases. Some of these companies purchase caustic in drums or tank cars, while others causticize soda ash with lime by the batch method without taking any particular pains to secure a high chemical recovery through efficient sludge-washing. The accompanying table lists some of these operations which require a small amount of caustic soda and gives the use of the caustic in each case.

MATERIAL MANUFACTURED
Gases, such as helium for dirigible balloons, oxygen for welding, and hydrogen and nitrogen for manufacture of synthetic ammonia
Phenol, creosote, mineral oils and tar oils
Soda and sulfate pulp
Reclaimed rubber
Artificial silk

USE OF CAUSTIC SODA
Circulated in gas scrubbers for absorption of carbon dioxide
Purification of tar acid
Digestion of wood chips
Old rubber stock digested with caustic for destruction of fiber
Various neutralization operations

Washing Thickener

To meet the requirements of such cases, where floor space is at a premium but where sludge-washing is essential in order

¹ Received September 25, 1928.