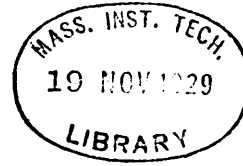


*Chem. eng'g
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thesis
1929*



A STUDY OF THE CONVERSION EFFICIENCY
OF AN AMMONIA OXIDATION UNIT

Submitted to the Chemical Engineering Department,
Massachusetts Institute of Technology, as partial
fulfillment of the requirements for the degree of
Bachelor of Science
in
Chemical Engineering.

May 1929.

FOREWARD

The authors feel very grateful to Professor F.W. Adams of the Chemical Engineering Department of the Massachusetts Institute of Technology for his suggestions in working out the method of analysis. They also wish to thank Messers Conklin and Healy of the Merrimac Chemical Company for their cooperation in arranging to run the test on the plant equipment, and the staff of the laboratory of the Everett plant for the helpful assistance they gave all during the time we were working there.

ABSTRACT

The method of analyzing nitrogen oxide gases leaving the convertor by absorbing them on asbestos covered with lead peroxide and regenerating the gases in a nitrometer, was found quite unsatisfactory. Absorption in a sodium peroxide solution followed by a permanganate bubbler, however, gave good results and furnishes a relatively simple method of plant analysis accurate to within about two per cent. On the two runs made on the plant equipment a conversion efficiency of about 95% was obtained.

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Conversion Efficiency of Ammonia Oxidation.

This thesis was run on the ammonia oxidation Subject unit in the Merrimac Chemical Company, Everett, Massachusetts.

The object of the thesis was to determine the conversion efficiency of the unit. Object

One of the most important chemicals in time Introduction of peace or war is nitric acid, as it is the basis of the fertilizer and munition industries. For this reason it is very important for a country to have a source of nitric acid which cannot be endangered by foreign powers. This led to the development of the ammonia oxidation process. Although the Merrimac Chemical Company does not use the process as a source of nitric acid - but as a source of nitrogen oxides for the sulphuric acid chambers - nevertheless the actual ammonia oxidation is the same as that used in the manufacture of nitric acid.

The principle of ammonia oxidation has been known for a long time, Kuhlman accomplishing the process by using platinum and other substances as catalyst in 1839. At that time, however, there was no commercial necessity for the process, and as a result, no development resulted from his discovery. As the demands for fertilizers and munitions became more pressing, the Germans realized the importance of a home supply of nitric acid.

To assure this supply, Ostwald developed the process on a commercial scale, establishing a small plant in 1909

at Gerthe in Westphalia. Another plant was erected by the English at Velvorde, Belgium. In the process developed by Ostwald, the ammonia-air mixture passed thru an outer tube of silica, and then thru an inner tube of nickel containing the platinum catalyst. Thus it served as a preheater and a converter. This process was not used by the Germans during the war.

The next development in the oxidation of ammonia was the Kaiser process in which Dr. Kaiser of the University of Heidelberg constructed a plant using a platinum gauze in an iron pipe. This was in 1912 and 1913, and marked the first use of gauze for a catalyst. The process cannot compete with modern methods.

Kaiser
Process

The process used by the Germans during the war was developed by Frank-Caro. In his method, electrically heated platinum gauze was used. From this point on, the development became quite rapid. In 1916, the American Cyanamid Company erected a plant at Warners, New Jersey, to supply a 60,000 ton sulphuric acid plant with nitrogen oxides. In the same year, the Bureau of Mines started work on the process, and soon found that the electrical heating of the gauze was unnecessary if three layers of platinum were superimposed upon one another. This point marked the change from the flat gauze to the cylindrical basket type. It was found that iron pipe could be used after the converter so long as the temperature of the gases remained above 170-200°F. Before the converter,

Later
Developments

(3)

it is necessary to use aluminum piping. Gauze temperature is another important feature in the proper operation of the plant, the best temperature being above 825°C, and it should never fall below 750°C.

The plant of the Merrimac Chemical Company has the latest development in ammonia oxidation units. The air is passed up thru a stripping column down which a carefully regulated stream of ammonia liquor descends. The bottom of the column is heated by the converted gases in a heat interchanger, thus driving out the last traces of ammonia. The ammonia-air mixture then passes thru a heat interchanger heated by the converted gases. This preheated mixture is then passed thru the converter, where it goes thru the platinum basket in the bottom of which is a silica plate. The converted gases then go thru the two heat interchangers mentioned above, and thus to the chambers. The platinum gauze used at the plant is made up of platinum wire 0.003 inches in diameter, containing not more than 0.1% iridium. The gauze is made up of 80 mesh wire in the form of a cylinder, the bottom being one layer, and the side four layers of wire superimposed on each other. Aluminum piping is used between the stripping column and the converter, the holder in the converter being made of nickel. After the converter, iron pipe is used. So it is seen that the plant uses the proper equipment as specified by the tests of the Bureau of Mines.

The Unit
at Merrimac

About a day before work was started Conditions at Merrimac at the plant, the platinum gauze burned out. Since the gauze had only been in operation two months, it was quite apparent that there was something wrong with the process. From a survey of the literature, it was readily seen that dust was very detrimental to the gauze, and would soon cause it to burn out. Mr. Conklin, who has charge of this unit, informed us that very dirty ammonia was being used in the process, due to storage of the ammonia in very dirty drums. It was quite logical to suppose that a similar destruction of the gauze would occur if this same ammonia were used. For this reason, the authors collaborated with Mr. Conklin in the development of a cleaning system. A settling tank followed by a filter was proposed, one filter for the clearer upper layer, and another for the dirty sludge in the bottom. The result was the installing of a settling tank, without a filter for the upper layer, but provision for filtering the sludge.

The most important and most difficult Method of Analysis of Gases part of the test was soon seen to be the development of an accurate method of analyzing the converted gases. Several methods were suggested in the literature and in former theses, so it was necessary to investigate these in the laboratory. One method used in a previous thesis and also at the plant for the analysis of gases leaving the Gay Lussac tower was recommended for the authors use. In this method, the gases are passed thru tubes containing lead peroxide on asbestos. PbO₂ Method
The nitrogen oxides react with the lead peroxide

to form lead nitrate. This is then leached out, and the solution introduced into a nitrometer. Upon the addition of concentrated sulphuric acid, and shaking, NO is formed. This gas is measured in the nitrometer, and thus the nitrogen oxide concentration of the gases determined. The method of operating the nitrometer was first checked by introducing a definite amount of lead nitrate into the nitrometer. This gave the required volume of NO. Several methods of generating a definite amount of NO and NO₂ from a weighed portion of Cu, were tried, but not all of the gas was absorbed by the lead peroxide. A definite volume of gas was next generated by using a weighed amount of sodium nitrite, which reacted with potassium ferrocyanide and sulphuric acid. This again would not give the proper amount of gas in the nitrometer to indicate complete absorption by the lead peroxide. Finally NO was generated in the nitrometer from lead nitrate as was done above, and this passed thru the absorption system, but complete absorption could not be obtained when the NO was passed thru pure or when the NO was first passed thru a bulb to dilute it with air. The asbestos sludge was leached again, but no gas was given off in the nitrometer from this washing, thus showing the method of leaching to be satisfactory. Two absorption bulbs were put in series, but the second bulb did not absorb any gas, which indicated that the first bulb was sufficient, no gas escaping into the second bulb.

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Other methods suggested in the literature, although they might have been satisfactory, were discarded because they were not practical for plant operation. Finally a method suggested by the British ministry of Munitions Na₂O₂ Method in a pamphlet "The Oxidation of Ammonia applied to Vitriol Chamber Plants", published (revised edition) March 1921 was tried. In this method, the gas is aspirated thru two Drechsel absorption bottles containing a sodium peroxide solution, and then thru a ten bulb tube containing acidulated potassium permanganate. The first two bottles are titrated at the end of the run with standardized acid, using litmus as an indicator, a light purple end-point being obtained instead of the usual one. The potassium permanganate is titrated with standardized oxalic acid to a colorless endpoint. When tests were made on this method of analysis, by generating a definite volume of NO in the nitrometer, 98.5 to 99% of the gas was accounted for in the absorption train. To make the conditions similar to those encountered in the plant, the pure NO was passed thru a bulb placed in the system, thus bringing it into contact with air, producing NO₂. This method of analysis having been found sufficiently accurate, the plant investigation was ready to be started.

The amounts of solution used in the various bottles are as follows:-

- (1) A Drechsel bottle containing:-
 - 100 cc. distilled water
 - 20 cc. N/Na₂O₂ solution
 - 40 cc. H₂O₂ solution (3%)

(7)

- (2) A Drechsel bottle containing:-
50 c.c. distilled water
10 c.c. N/Na₂O₂ solution
20 c.c. H₂O₂ solution (3%)

The N/Na₂O₂ solution is prepared by adding 78 grams of sodium peroxide solution to 1 kilograms of powdered ice in small quantities with stirring, and then adding 1 liter of distilled water and filtering through glass wool. It is kept in a bottle with a capillary tube through the cork to allow the traces of O₂ given off to escape.

- (3) A 10-bulb tube containing:-
5 c.c. N/10 KMnO₄ solution
10 c.c. 50% sulfuric acid

This train of three bottles is followed by the aspirator and graduate.

When the apparatus was installed in place in the plant several precautions were found necessary to obtain satisfactory results. Condensation in the gas sampling lines gave considerable trouble. The NO sampling pipe was lagged to prevent this until the gases had entered the glass tubes from ^{which} any condensate could be washed out at the end of a run. The ammonia percentage determination was carried out rapidly several times during an hour run with the same end in view, and an average of these taken. To correct for the partial vacuum present in the NO aspirator bottle, a manometer was installed to give a measure of this. In the titration of the Na₂O₂ solution, a light purple end-point was obtained with litmus rather than the usual one, but this was found quite satisfactory.

Precautions
in Analysis

(8)

Although over half a dozen runs were made in the Results day and a half available for experimentation, only two of these were successful due to difficulties of a minor nature which were encountered. The first of these, which was run several hours after the new gauze had been installed gave an efficiency of 92.6% at the low rate of feed of 5.81# of ammonia per hour. The gas entering the convertor in this case had an ammonia content of 9.9%. In the second successful run, which took place the following day, an efficiency of 96.3% was calculated, feeding ammonia at the rate of 8.54#/hour and at a strength of 9.2%.

In the two runs mentioned the following data Data was recorded:-

Run #1

Reading on air gauge	.25
Ammonia feed	5.81#/hr.
Exit gas temperature	425 C
Gas aspirated thru ammonia absorber	1000 c.c.
" " " NO "	945 c.c.
M.e.'s of Na ₂ O ₂ disappearing	4.45
M.e.'s of KMnO ₄ "	.263
M.e.'s of HCl neutralizing ammonia	4.423

Run #2

Reading on air gauge	.55
Ammonia feed	8.54#/hr.
Exit gas temperature	520 C
Gas aspirated thru NO absorber	1010 c.c.
Pressure of gas aspirated	23mm. vac.
Per cent ammonia in gas entering absorber	(a) 9.2 (b) 9.2
M.e.'s of Na ₂ O ₂ disappearing	4.44
" " KMnO ₄ "	.514
Gauze Temp.	854°C

The results of the work done indicate that the sodium peroxide method of analysis is quite practicable if the proper precautions are taken, the method being simple enough for plant use. Its accuracy is within two percent. The experimental work performed on the plant equipment is too limited to warrant any general conclusions, although the two runs indicate a conversion efficiency of approximately 95%.

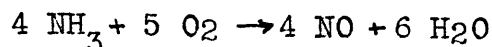
The ratio of ammonia to air in the gas Sample
Calculation entering the converter is given directly from the volume of air aspirated and the ammonia absorbed. If there were no change in volume of the air after the converter ~~it~~ would be possible to make a direct comparison of the weight of oxides of nitrogen corresponding to the volume of air aspirated, and the ammonia associated with an equal volume of air.

The aspirated volume after the converter, however, does not represent the volume of air which was associated with the ammonia corresponding to the oxides of nitrogen collected, because a portion of this air was used up in the oxidation. This consumed oxygen consist of two parts:

(1) a portion used in burning the ammonia to NO in the converter, and

(2) a further portion used in oxidizing the NO to higher oxides, which are then absorbed.

The first portion is the same in all cases, and is calculated as follows:-



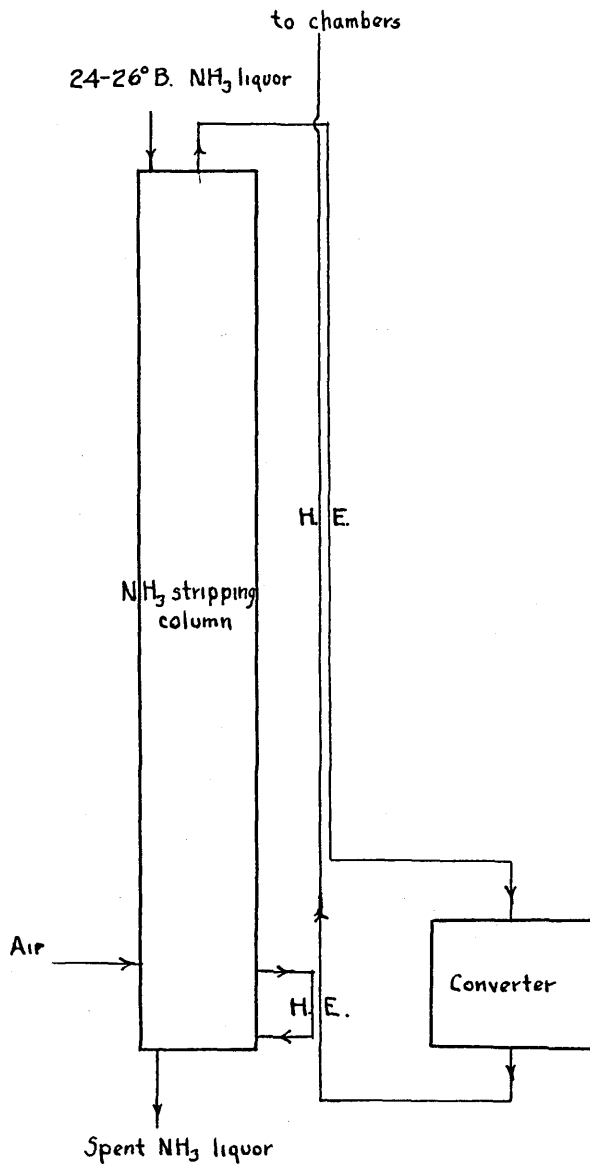
If ammonia percentage is 9.2%

$$\frac{0.092 \times 17}{(1 - .092)} \times \frac{1071}{22,400} = 0.0823 \text{ g. NH}_3 / 1071 \text{ cc. air}$$

$$\text{Efficiency} = 100 \times .0783 / .0823 = 95.1\%$$

$$\text{Average efficiency} = 96.3\%$$

N.B. By a consideration of the percentages of NO and O₂ in the gas before it reached the first absorption bottle, and the time of contact of these at room temperature, a rough calculation of the amounts going to NO₂ was made. This showed that approximately 85% of the NO was transformed to NO₂. The time of contact of the gases was figured from the size and length of the glass tubing before the first absorption bottle. The rate of reaction constant was obtained from page 136 of Noyes and Sherrill's "Chemical Principles".



AMMONIA OXIDATION UNIT
Everett, Mass.

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