# ESTIMATION OF PLATINUM GAUZES CATALYST FOR AMMONIA OXIDATION IN NITRIC ACID PRODUCTION

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## *ABSTRACT*

*This paper illustrates design aspects of a shallow bed reactor involving a very rapid reaction, which is a diffusion controlled reaction. The design of the bed composed of a small number of catalyst screens, is normally based on past experience, scale-up on the basis of equal velocity, and careful planning for good distribution. Methods needed to estimate the number of meshes, diameter, height and volume of catalyst bed are discussed. This design method can be useful for economic or operating studies.*

**Keywords :** *Ammonia Oxidation, Gauze, Kinetic, Nitric Acid, Shallow Bed Reactor*

## 1.0 INTRODUCTION

There were approximately 65 nitric acid (HNO) manufacturing plants in the U. S. with a total capacity of 11 million tons of HNO per year. The plants range in size from 6,000 to 700,000 tons per year. About 70 percent of the nitric acid produced is consumed as an intermediate in the manufacture of ammonium nitrate ($NH_4$ $NO_3$), which in turn is used in fertilisers. Another 5 to 10 percent of the nitric acid produced is used for organic oxidation in adipic acid manufacturing. Nitric acid is also used in organic oxidation to manufacture terephthalic acid and other organic compounds. Explosive manufacturing utilises nitric acid for organic nitrations. Nitric acid nitrations are used in producing nitrobenzene, dinitrotoluenes, and other chemical intermediates. Other end uses of nitric acid are gold and silver separation, military munitions, steel and brass pickling, photoengraving, and acidulation of phosphate rock.

Much of the nitric acid produced in the world is manufactured via a high-temperature catalytic oxidation of ammonia. This process consists of three main steps: ammonia oxidation, nitric oxide oxidation, and absorption. This process can be performed at one or multiple pressures. This paper focuses on the single pressure process. Newer processes typically operate at a low and a high pressure to favour the reactions.

In nitric acid production, first of all, ammonia is vaporised in a vaporiser before it is mixed with compressed air and send to a shallow bed reactor as shown in Figure 1. In the reactor, ammonia oxidation will occur, where nitrogen monoxide will be produced. The reaction in the reactor will take place at a temperature of 840-880°C. Due to the high temperature involved in the reactor, energy can be recovered by cooling the gaseous mixture in a waste heat boiler and cooler-condenser. Along waste heat boiler and cooler-condenser, the nitrogen monoxide will be oxidised to nitrogen dioxide, and dilute nitric acid will be condensed out at the condenser. The nitrogen dioxide will enter the absorber where absorption with water will take place and finally, nitric acid will be produced. Tail gas will be produced at the absorber, and the nitric acid produced from absorber will be mixed with the dilute nitric acid from condenser to produce the final product of nitric acid (Figure 2).

Generally, there are three steps involved in nitric acid production:

(i) Catalytic oxidation of ammonia with atmospheric oxygen to yield nitrogen monoxide:

$$4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(1)}$$

(ii) Oxidation of the nitrogen monoxide product to nitrogen dioxide or dinitrogen tetroxide:

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)} \quad \text{or}$$

$$2NO_{(g)} + O_{2(g)} \longrightarrow N_2O_{4(g)}$$

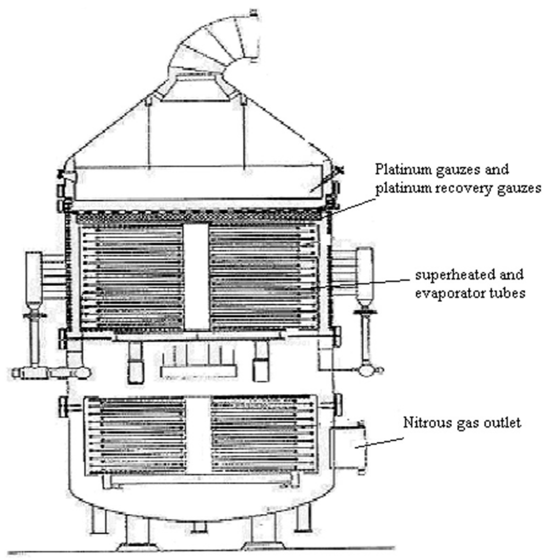


***Figure 1: Shallow bed reactor for catalytic ammonia oxidation with integrated waste-heat recovery system***

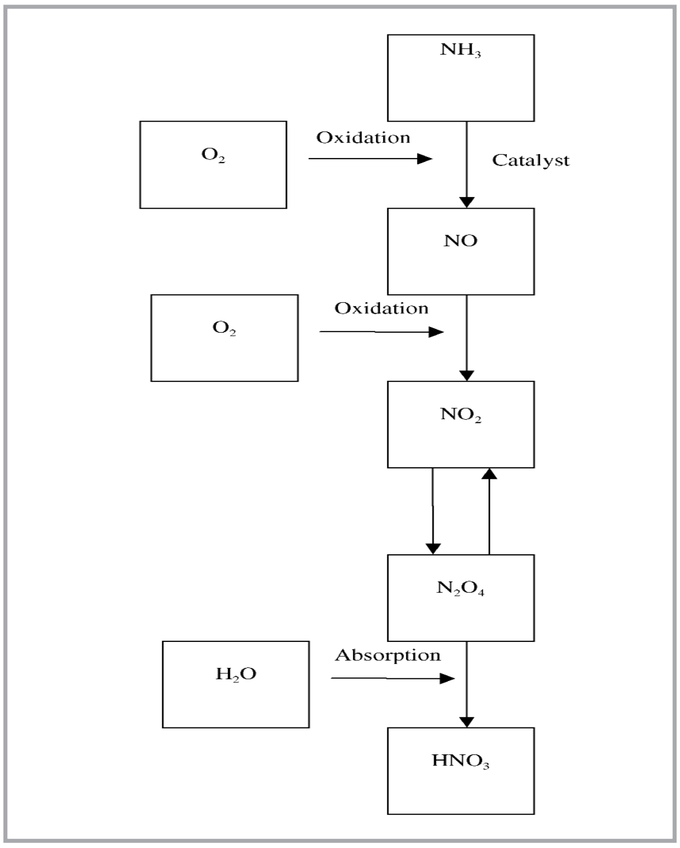


***Figure 2: Schematic diagram of nitric acid production***

(iii)Absorption of the nitrogen oxides to yield nitric acid:

$$3NO_{2(g)} + H_2O_{(l)} \longrightarrow 2HNO_{3(1)} + NO_{(g)}$$

## 2.0 AMMONIA OXIDATION

Ammonia oxidation that takes place in the reactor can be categorised as the reaction between gas phase and a solid catalyst. The most suitable type of reactor is the thin beds and wire gauzes. It is also known as shallow bed reactor. This kind of reactor is usually used in fast catalytic reactions that must be quenched rapidly. The materials to be reacted are in contact with wire screens or thin layers of fine granules. For example, ammonia in a 10% concentration in air is oxidised by flow through a fine gauze catalyst made of 2 to 10% Rh in Pt, 10 to 30 layers, and 0.075 mm diameter wire. Contact time is 0.0003s at 750ºC and 7 atm followed by rapid quenching [1].

## 2.1 REACTOR DESIGN

In the reactor, ammonia oxidation will occur, and for the reaction to happen at faster conversion rate, platinum catalyst is used. High temperatures and high velocities will produce essentially total conversion of ammonia. The catalyst is placed on wire gauzes and the parameters of the catalyst used and calculated will be discussed in detail in following sections.

On the basis of mass transfer control the rate of ammonia oxidation may be written in terms of a mass transfer coefficient with the ammonia partial pressure at the catalyst surface assumed to be zero for this rapid reaction.

$$-r_A = k_{gA}{}^s a_{WR} P_A \qquad (1)$$

where $P_A$ is the partial pressure of ammonia in bulk fluid and $a_{WR}$ is the surface area per unit volume of screen. For shallow beds reactors, axial diffusion must surely be important, however, at very high flow rates encountered in commercial equipment the effect of axial dispersion is less important than the problem of ensuring uniform flow distribution across the gauzes. The ammonia oxidation rate determining step in the reaction of NO is the transport of ammonia to the catalyst surface, and the reaction kinetic, $k^s_{gA}$ is given as [2]:

$$k^s_{gA} = \frac{0.865 N_{Re}{}^{-0.648} G}{P N_{sc}{}^{2/3} M_m \varepsilon_w} \qquad (2)$$

where $N_{Re}$ is the *Reynolds number, G* is the superficial flow rate (g/cm$^2$ .sec), $N_{Sc}$ is *Schmidt number*, $M_m$ is the molecular weight of mixture of gases and $\varepsilon_w$ is the porosity of gauzes.

### 2.1.1 NUMBER OF GAUZES

From literature, at temperature, T = 900°C and pressure, P= 100 psig (7 bar), a quantity of 80 mesh gauze ($n_w$), with wire of 0.003 in. in diameter ($d_w$), equivalent to 2 Troy oz/ton of acid produced and a cross sectional area of 2.7547 sq ft/100 daily tons of $HNO_3$ produced is required [3]. The equations below are used in calculating the number of gauzes, after further deriving and simplifying from mass transfer concept as shown in equations (1) and (2):

$$\text{In}(1-X_A) = -K^s_{gA} P n_s f_w \frac{M_F}{G}) \qquad (3)$$

$$n_s = \frac{-\text{In}(1-X_A)\varepsilon_w{}^{0.352} d_w^{0.648}\, G^{0.648} \mu_f^{0.019}}{(5.81761 \text{ x } 10^{-5}) f_w T_i^{0.333} (28.85+11.82 y_{AO})^{0.667}} \qquad (4)$$

where $f_w$ is the wire area per gauze cross-sectional area for one gauze, $\varepsilon_w$ is porosity of mesh, $d_w$ is wire diameter, $\mu_f$ is viscosity, $y_{Ao}$ is initial gaseous mole fraction of A. Perfect plug flow model is assumed in calculating the number of gauzes, which is approached in the unit with a special gas distributor.

### 2.1.2 HEIGHT OF CATALYST BED

The height of catalyst bed needed in this detailed design project is calculated by:

$$h_c = 2 d_w n_s \qquad (5)$$

### 2.1.3 DIAMETER OF CATALYST BED

Gillespie and Kenson [3] proposed a method in determining the cross sectional area of catalyst bed. It is found that the area is 2.7547 sq ft/100 daily tons $HNO_3$.

The diameter can be determined using:

$$D = \sqrt{\frac{4A}{\pi}} \qquad (6)$$

### 2.1.4 WEIGHT OF CATALYST

From literature, weight of 80-mesh gauze is 1.71 troy oz/ft$^2$ and the catalyst needed is 2 troy oz/daily ton [3]. The following equation is used in calculating total weight of catalyst bed.

$$w_c = [1.71 \text{ x Area(ft}^2) \text{ x } n_s] + [2 \text{ x Daily production rate}] \quad (7)$$

## 2.1.5 VOLUME OF CATALYST BED

After calculating the height and diameter of the catalyst bed, the volume of the catalyst bed can be determined by:

$$\text{Volume of catalyst} = \frac{1}{4}\pi D^2(h_c) \quad (8)$$

Details of the example calculation are shown in Appendix and Table 1 is the summary of the calculated results.

## 3.0 CONCLUSION

It is always not easy to estimate the amount of catalyst used in ammonia oxidation. Conventional packed bed reactor design method is not suitable in estimating the catalyst needed. A simple estimation method of catalyst gauze thickness has been proposed in this work. These design method can be useful in economic or operating studies. ■

***Table 1: Result for chemical detailed design of reactor***

| Parameter | Value | Unit |
|---|---|---|
| Temperature | 840 | °C |
| Pressure | 8 | bar |
| Mesh size | 80 | $in^{-1}$ |
| Wire diameter | 0.003 | in |
| Porosity | 0.806 | - |
| Mass velocity of gasses | 2.126 | $g/cm^2.s$ |
| Superficial velocity of gases | 29.14 | g/cm.s |
| Number of gauzes needed | 21 | - |
| Height of catalyst bed | 0.32 | cm |
| Diameter of catalyst bed | 1.987 | m |
| Weight of catalyst and gauzes | 112.70 | kg |
| Volume of catalyst | 0.010 | $m^3$ |

## APPENDIX:
### Catalyst calculations

From literature [3]:

Mesh size, $n_w = 80 \text{ in}^{-1}$

Wire diameter, $d_w = 0.003$ in.

Surface area per unit volume, $a_{wr} = \pi l_w n_w^2$,

where $l_w = [(1/n_w)^2 + d_w^2]^{0.5}$

Therefore, $a_{wr} = \pi n_w^2[(1/n_w)^2 + d_w^2]^{1/2}$
$= \pi(80)^2[(1/80)^2 + 0.003^2]^{1/2}$
$= 258.5 \text{ in}^{-1}$

Wire area per gauze cross sectional area,
$f_w = a_{wr} 2d_w$
$= (258.5)(2)(0.003)$
$= 1.55$

Porosity, $\varepsilon w = 1 - \frac{a_{wr}d_w}{4}$

$= 1 - \frac{258.5(0.003)}{4}$

$= 0.806$

i) Calculating mass velocity, G:

$$G = \frac{\text{Flowrate of gases}}{\text{Cross sectional area of catalyst needed}}$$

$$= \frac{237286.50}{3600 \text{ x } 3.10}$$

$= 21.26 kg/m^2.s$

$= 2.126 g/cm^2.s$

ii) Calculating superficial velocity based on outlet conditions:

$u_s = g/\rho_{mixture}$

***Table A-1: Mass flowrate, molar flowrate and mole fraction of components in reactor feed***

| Components | Mass flowrate (kg/hr) | Molar flowrate (kmol/hr) | Mole raction |
|---|---|---|---|
| $NH_3$ | 14,450.00 | 850.00 | 0.10 |
| $O_2$ | 51,952.02 | 1,623.50 | 0.19 |
| $N_2$ | 170,884.05 | 6,103.00 | 0.71 |
| Total | 237,286.07 | 8,576.50 | 1.00 |

Average molecular weight,
$M = 0.10(17) + 0.19(32) + 0.71(28)$
$= 27.67$ kg/kmol

Operating pressure, P = 8 bar

Operating temperature, $T$ = 840ºC = 1113K

$\rho_{mixture} = MP/RT$

$$= \frac{27.63(8 \text{ x } 10^5)}{8.314(1113)}$$

$= 2,391.92 \text{ g/m}^3$

$= 2,391 \text{ x } 10^{-6} \text{ g/cm}^3$

Therefore, $u_s = \frac{2.126}{2,391 \text{ x } 10^{-6}}$

$= 888.33$ cm/s
$= 29.14$ ft/s

Thus $u_s = 29.14$ ft/s constitutes a more general criterion based on these reported data.

iii) Calculating number of gauzes needed:

$$n_s = \frac{-\ln(1-x_A)\varepsilon^{0.352} d_w^{0.648} G^{0.648} \mu_f^{0.019}}{(5.81761 \text{ x } 10^{-5}) f_w T_i^{0.333}(28.85 + 11.82 y_{AO})^{0.667}}$$

Where, $X_A$ = conversion of ammonia feed
$y_{Ao}$ = mole fraction of ammonia in feed
$\mu_f$ = viscosity of mixture

$\mu_f = (12.5 + 29.20 \times 10^{-3}T) \times 10^{-5}$ g/cm.s
$= [12.5 + 29.20 \times 10^{-3} (1113)] \times 10^{-5}$
$= 4.5 \times 10^{-4}$ g/cm.s

Therefore, $n_s$

$$= \frac{[-\ln(0.04)](0.806)^{0.352}(0.0076)^{0.648}(2.126)^{0.648}(4.5\times10^{-4})^{0.019}}{(5.81761\times10^{-5})(1.55)(1113)^{0.333}(28.85+1.17)^{0.667}}$$

= 20.17
= 21 gauzes

iv) Calculating height of catalyst bed:

Height of catalyst bed = $2d_w$

For 21 gauzes, height of catalyst bed, $h_c$ = 21 x 2 x 0.003
= 0.126 in
= 0.32 cm

v) Calculating diameter of catalyst bed:

From literature, cross sectional area
= 2.7547 sq ft/100 daily tons $HNO_3$

Since the daily production rate is 1,212.12 tons/day,

Therefore, cross sectional area = 2.7547(12.12)
= 33.39 sq ft (= 3.10 $m^2$)

Diameter of catalyst bed, D = $\sqrt{\dfrac{4(3.10)}{\pi}}$

= 1.987m

vi) Calculating weight of catalyst:

From literature, weight of 80-mesh gauze = 1.71 troy oz/$ft^2$, catalyst needed = 2 troy oz/daily ton.

Weight of one gauze = 1.71(33.39)
= 57.10 troy oz

Weight of 21 gauze = 21(57.10)
= 1,199.05 troy oz

Weight of catalyst needed = 2(1212.12)
= 2,424.24 troy oz

Total weight of catalyst and gauze = 1,199.05 + 2,424.24
= 3,623.29 troy oz
= 112,696.87
= 112.70kg

vii) Calculating volume of catalyst:

Volume of catalyst $= \frac{1}{4}\pi D^2 (h_c)$

$= \frac{1}{4}\pi(1.987)^2(0.0032)$

= 0.010 $m^3$

= 3.97 m

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