https://erjm.journals.ekb.eg
ISSN: 1110-1180

DOI: ---------

ERJ
Engineering Research Journal
Faculty of Engineering
Menoufia University

Modelling of an Industrial Catalytic Ammonia Oxidation Reactor for Nitric Oxide Production in Nitric Acid Plant

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ABSTRACT
Modelling of an industrial catalytic ammonia oxidation reactor for nitric oxide production in nitric acid plant over gauzes of Pt/Rh catalyst presents the current study. Most of mathematical models of Catalytic ammonia oxidation process were developed for microreactors. Mathematical models were simulated for industrial ammonia oxidation reactor, describing the effect of external conditions such as, (inlet temperature, inlet pressure, inlet composition of gas mixture…) on the behavior of the reactor, but there aren't models describe the variation of concentration of gas species along the catalyst bed. In the current study, two basic models for mass balance and energy balance are used (after integration by new version of MATLAB (R2017b)) for an industrial ammonia oxidation reactor. The first model (mass balance) was used to predict the variation of the concentration of NH_3, O_2, NO and H_2O along the catalyst bed of the reactor (4.8m diameter, 1m height). The second model (energy balance) was used for the same reactor to predict temperature variation along the catalyst bed. The deviation in the 1st case didn't exceed 6.2 % for NO, 3.8% for H_2O, 5.6% for $O_2$and 1% for NH_3.Also, in case of energy balance the deviation was 0.4 %, so the mathematical models have shown quite high degree of accuracy to predict the operating values with minimum deviation. The rate of consumption/ formation for NH_3, O_2, NO and H_2Owere also calculated.
Keywords: *modeling; ammonia oxidation; Pt/Rh catalyst; industrial reactor.*

1. Introduction

Nitric acid production is one of the large-scale processes in chemical industry. It is one of the most important bulk chemicals to produce fertilizer, explosives, and dye [1]. Ammonia oxidation with air over platinum catalysts is one of the most important heterogeneously catalyzed reactions both in chemical technology as well as in environmental catalysis. The formation of NO at >800 K is the key step in the production of nitric acid known as Ostwald process [2]. To be able to analyze and optimize the operation of a plant, one must first have a mathematical model describing the real behavior of the process. The modelling of a plant can be done in many ways; one can use the physical and chemical relationships the process is based on, or one can try to find the model experimentally. So, we can have different models for the same process. The main reaction for catalytic ammonia oxidation is:

$$4NH_3 + 5O_2 = 4NO + 6H_2O \quad (1)$$

This reaction is very highly exothermic reaction; Uronen has shown that the overall oxidation rate is controlled by the transfer of NH_3 from the bulk gas phase to the platinum surface [3]. The total pressure during the combustion of NH_3 is the most important technological parameter of industrial oxidation of ammonia. Normally, the working temperature in the catalyst bed is about 890°C and increases with increasing pressure .

The ammonia concentration in its mixture with air is 9.5 to 11.5 vol. %, the time of contact with the catalyst is $10^{-3}$to 10^{-4} sec. The platinum catalyst, which is usually an alloy with rhodium (2 -10%), has the form of gauzes made up of wires [3].

2. Aim and Research Significance

Most of mathematical models of Catalytic ammonia oxidation process were developed for micro reactors. Mathematical models were simulated for industrial ammonia oxidation reactor, describing the effect of external conditions such as, (inlet temperature, inlet pressure, inlet composition of gas mixture…) on the behavior of the reactor, but there aren't models describe the variation of concentration of gas species

along the catalyst bed. So, the objective of the present work is to find an appropriate mathematical model for an industrial reactor for the oxidation of ammonia on Pt-Rh gauzes, which shows the variation of concentration for gas species, and temperature variation along the length of catalyst bed. The rate of consumption/ formation for gas species was also calculated.

3. Nitric Acid by The Ammonia Oxidation Process

The ammonia oxidation process makes essentially all of the nitric acid produced. With the proper catalyst, ammonia (NH3) can be oxidized with air to yield nitric oxide (NO) and water. The chemical equation is as follows:

$$4NH_3 + 5O_2 = 4NO + 6H_2O \quad (1)$$

The nitric oxide is further oxidized with excess air to yield nitrogen dioxide (NO_2).

$$2NO + O_2 = 2NO_2 \quad (2)$$

The nitrogen dioxide may then be absorbed in water to form an aqueous solution of nitric acid.

$$3NO_2 + H_2O = 2HNO_3 + NO \quad (3)$$

In general, the process for nitric acid manufacture consists of preheating the air, mixing it with ammonia gas, passing it over a platinum catalyst, extracting the heat produced from this reaction by using it to preheat the incoming air and then cooling further, adding secondary air and then absorbing the nitrogen dioxide in water to form nitric acid. In more detail, air is compressed, filtered, and preheated to about 300°C by passing it through a heat exchanger. Ammonia gas is continuously vaporized from anhydrous liquid ammonia in a steam-heated evaporator. The compressed air at T=233˚C, P=4.8 bar and ammonia at T=60˚C, P=6.4 bar are mixed in a mixing chamber to produce a mixture containing 8 to 10% ammonia by volume. The ammonia-air mixture is then passed through the reactor, which contains the platinum-rhodium (2 to 10% rhodium) catalyst. The reaction is very exothermic. The catalyst temperature may range from 800°C to 925°C. The temperature of the gases from the converter is above 600°C. The converter gases are a mixture of nitric oxide, water, oxygen, and nitrogen. It is necessary to cool these gases so that they may be absorbed [4].

4. Ammonia Oxidation Industrial Reactor

Catalytic reactors containing catalyst in the form of gauze are used in the production of nitric acid (Ostwald process).The industrial reactor for ammonia oxidation is shown in figure (1), it is composed of : (1) Catalyst layer, (2) Layer for catchment of the escaped catalyst, (3) cooling area. The rapid cooling helps in minimizing the loss from decomposition of generating NO. In this case the dimensions of the reactor are 1m in height and an effective diameter of 4.9 m. The inlet ammonia concentration is typically 9.5 to 11.5 vol. %, the time of contact with the catalyst is$10^{-3}$to 10^{-4}sec. The platinum catalyst, which is usually an alloy with rhodium (2-10%), has the form of gauzes made up of wires. The catalyst life time for the process is about 6 months [3].

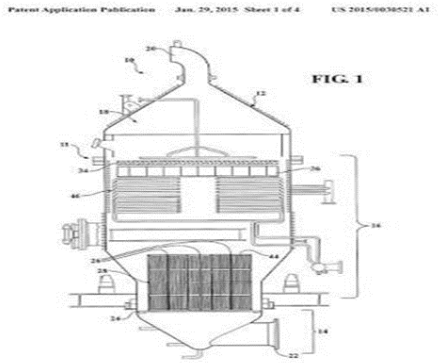

Figure 1- Ammonia Oxidation Industrial Reactor

5. Industrial Catalyst for Ammonia Oxidation

The oxidation of ammonia is carried out over platinum / rhodium gauzes. The ammonia-air mixture is passed through the reactor, which contains the platinum-rhodium (2 to 10% rhodium) catalyst. This is in the form of sheets of very fine wire gauze, packed in layers. In some plants, the composition of the catalyst is (90% Pt- 10 %Rh). The effective gauze diameter is 4600 mm, the wire diameter is 0.0076 mm. The NO yield increases with increasing the surface area of catalyst. The reaction is very exothermic. The working temperature in the catalyst bed is about 890˚C. As the gauze temperature increases, the rate of Pt losses increases. This is the main reason of the limitation on gauze temperature [3].

5. Model Development

Assumptions used for modeling reactor for ammonia oxidation are:[٥]

- One- dimensional steady state mathematical model.
- The radial temperature gradient in the reactor is minimized.
- The number of gauzes is enough high for full ammonia conversion, so catalytic reactions take place on Pt gauzes only.

- A very steep temperature gradient may develop within the pack, when a highly exothermic creation takes place on the Pt/Rh gauzes

Heat and mass balance equations like ones in Equations (4) and (5) with some differences are used. MATLAB 2017 is used to solve heat and mass balance equations for ammonia oxidation reactor, where ammonia oxidation reaction occurs as in Eq. (1).

3.1 Mass Balance Equation for an Industrial Ammonia Oxidation Reactor

The main governing equation for the gas phase species is [6]:

$$\frac{W}{A_{tot}} \frac{dX_{g,i}}{dz} = -K_{m,i}\, S\left(X_{g,i} - X_{s,i}\right) \qquad (4)$$

Where w is molar flow rate (mole/s), A_{tot} Cross-sectional area of catalyst (m^2), $X_{g,i}$Mole fraction of gas for specie i, z axial position (m) , $k_{(m,i)}$ mass-transfer coefficient for specie i (mole/m^2.s), S surface area per reactor volume (m^2) , $X_{s,i}$mole fraction of gas specie i at the surface of the catalyst .

The film model is used to describe the mass-transfer between the gas and the catalyst surface, which is the second term in Eq. (4) above. This model is based on one-dimensional SteadyState condition, Km and Xs were assumed to be constants .

This model can be solved using Matlab 2017, Where A_{tot} = 18.4 m^2, w=3419.6 mole /sec , S= 0.6 $m^{(-1)}$, Xs value for NH_3 , O_2 , NO and H_2O are listed in table 1 [7], and the value of the mass-transfer coefficient $k_{(m,i)}$ values shown in table 1 were adjusted to obtain reasonable predicted values at the outlet of the reactor for each specie :

Table 1- The values of $X_{s,i}$ and $K_{m,i}$ for NH_3 , O_2, NO and H_2O

Gas specie	$K_{m,i}$ (mole/m^2.s)	$X_{s,i}$ value[7]
NH_3	1.6×10^3	0
O_2	1.2×10^3	0.057
NO	1.8×10^3	0.095
H_2O	1.35×10^3	0.17

The following flow chart shows the steps of model solving:

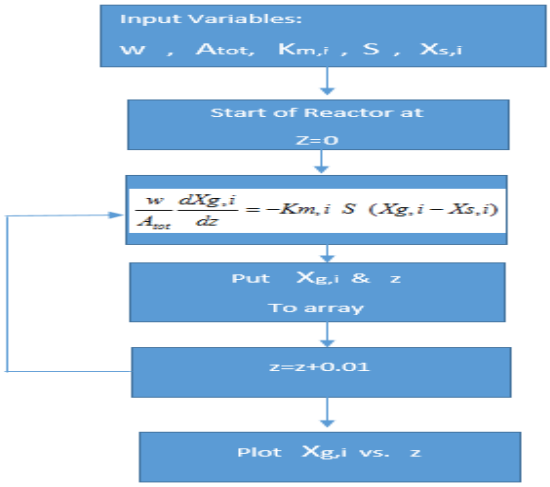

Figure 2- Flow Chart of the Steps of Mass Balance Model Solving

So, four graphs will result to show the concentration gradient of NH_3 ,NO ,H_2O and O_2 the length of catalyst bed.

3.1 Energy Balance Equation for an Industrial Ammonia Oxidation Reactor

The model of typical monolithic reactor [8] has been used for the simulation of catalytic ammonia oxidation process. It is represented by the following equation:

$$\rho\, Cp\, \frac{dT}{dt} = -v\, \rho\, Cp\, \frac{dT}{dz} - K_h(z)\, \frac{a}{\varepsilon}\, (T - T^*) \qquad (5)$$

Where ρ gas phase density (kg/m^3), Cp gas phase heat capacity (J/mole.k),T gas phase temperature(k), t time(s), v linear velocity (m/s), z axial coordinate(m) , k_h heat transfer coefficient (w/m^2.k) a specific surface area(m^{-1}), ε void fraction and T^* solid phase temperature (K). One-dimension SteadyState condition, constant solid phase temperature and heat-transfer coefficient, k_h are assumed, so the equation becomes as follow:

$$\frac{dT}{dz} = \frac{-K_h\, a}{\varepsilon\, v\, \rho\, Cp}\, (T - T^*)$$

The value of ρ is taken as the average value between the values of gas mixture density at the inlet and the outlet conditions of catalyst bed, where

$$\rho = \frac{P M_{mix}}{RT}$$

The Cp value is also assumed as the average value between the Cp values of gas mixture at the inlet and the outlet conditions of catalyst [9], the value of the heat-transfer coefficient, k_h is taken from literature

[5].This model solved using Matlab 2017, where ε=0.03 (ε= mesh length –wire diameter Mesh length = 1 / (mesh number/cm), Where mesh number = 1024 mesh / cm^2 , wire diameter = 0.0076 mm [7]) , a= $0.6m^{-1}$,v=3m/s,T^*=1163K[7], K_h=0.2×10^4(W/m^2.K)[5],Cp=1.2×10^3(J/mole.K)[9] , ρ=2.5 (kg/m^3) , and the following flow chart shows the steps of model solving:

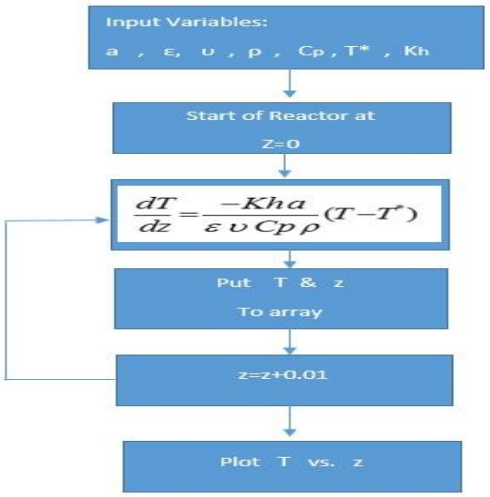

Figure 3- Flow Chart of the Steps of Energy Balance Model Solving

So, the graph will result to show the temperature gradient along the length of catalyst bed.

Kinetics of Ammonia Oxidation:

For the main reaction of catalytic ammonia oxidation:

$4NH_3 + 5O_2 = 4NO + 6H_2O$

The rate of reaction is very rapid, it depends on contact time and reaction mixture composition, and it is controlled by transfer of ammonia from the bulk gas to the platinum surface.[٢]

The rate of consumption / formation for reactants and products is calculated and are shown in table 2:

The rate was calculated as follow:

$$Rate\ expression = \frac{moles\ in - moles\ out}{residence\ time}$$

$$The\ residence\ time\ (\tau) = \frac{volume\ of\ reactor\ (v)}{volumetric\ flow\ rate\ for\ gas\ mixture(v^{\circ})}$$

Where v= 18.1 m^3 and v°= 30.346 m^3/ s [7]. So, residence time for ammonia oxidation reaction = 18.1/ 30.346 = 0.59s

Table 2- The rate of consumption/formation for NH_3, O_2 , NO andH_2O.

Gas specie	Process	Rate value (mole/s)
NH_3	Consumption	5.87×10^2
O_2	Consumption	7.34×10^2
NO	Formation	5.87×10^2
H_2O	Formation	8.81×10^2

7. Results and Discussion

The developed model predictions for catalytic ammonia oxidation reactor are investigated and compared with the industrial data. The figures are simulated using Matlab2017.

7.1The Concentration Gradient of NH_3 along The Length of Catalyst Bed

Figure (4) shows the concentration gradient of NH_3 along the length of catalyst bed, it is clear that the concentration of ammonia decreases from the inlet to the outlet of the reactor (this decrease is expected as a result of the reaction shown in equation (1)), and we can predict the concentration of ammonia at any point of the reactor. The plot demonstrates that model data agrees with an industrial data as the deviation= 1 %.

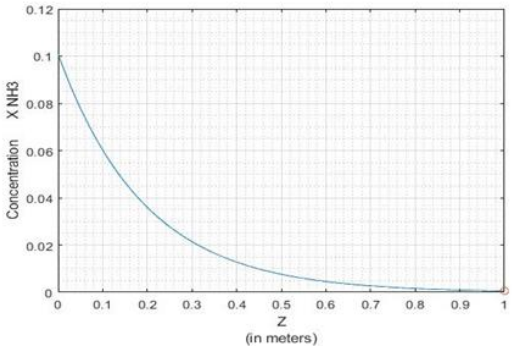

Figure (4): The concentration gradient of NH_3along the length of catalyst bed.

7.2 The Concentration Gradient of O_2 along The Length of Catalyst Bed

Figure (5) shows the concentration gradient of O_2 along the length of catalyst bed, it is clear that the concentration of oxygen decreases from the inlet to the outlet of the reactor (this decrease is expected as a result of the reaction shown in equation (1)), and we can predict the concentration of oxygen at any point of the reactor. The plot demonstrates that model data agrees with an industrial data as the concentration of oxygen value at the outlet of the reactor in calculated

results approaches the experimental value (deviation=5.6%).

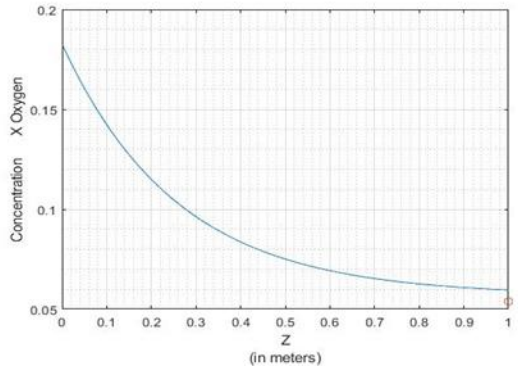

Figure (5): The concentration gradient of O_2 along the length of catalyst bed.

7.3 The Concentration Gradient of NO along the Length of Catalyst Bed

Figure (6) shows the concentration gradient of NO along the length of catalyst bed, it is clear that the concentration of NO increases from the inlet to the outlet of the reactor (this increase is expected as a result of the reaction shown in equation (1)), we can predict the concentration of NO at any point of the reactor. The plot demonstrates that model data approaches with industrial data as the concentration of NO value at the outlet of the reactor (deviation = 6.2%).

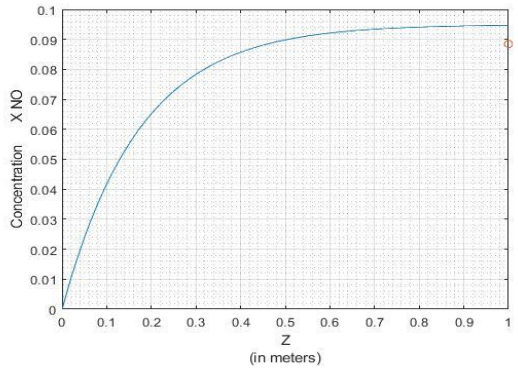

Figure (6): The concentration gradient of NO along the length of catalyst bed.

7.4 The Concentration Gradient of H_2O along The Length of Catalyst Bed:

Figure(7) shows the concentration gradient of H_2Oalong the length of catalyst bed, it is clear that the concentration of H_2O increases from the inlet to the outlet of the reactor (this increase is expected as a result of the reaction shown in equation (1)) , we can predict the concentration of H_2O at any point of the reactor. The plot demonstrates that model data agrees with industrial data outlet of the reactor (deviation = 3.8 %).

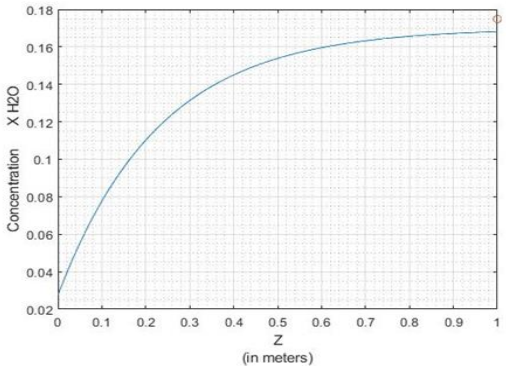

Figure (7): The concentration gradient of H_2O along the length of catalyst bed.

7.5 Temperature Gradient along the Length of Catalyst Bed

Figure (8) shows the temperature gradient along the length of catalyst bed, it is clear that the temperature increases from the inlet to the outlet of the reactor, as the ammonia oxidation reaction is highly exothermic. We can predict the temperature at any point of the reactor. The plot demonstrates that model data agrees with industrial data (deviation= 0.4 %).

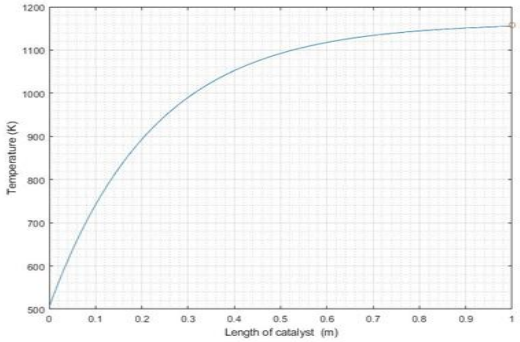

Figure (8): The temperature gradient along the length of catalyst bed.

8- Conclusions:

Two basic models including mass balance and energy balance were applied for an industrial ammonia oxidation reactor. Estimated ammonia and oxygen concentration variation along catalyst bed show ammonia and oxygen concentration decrease along the bed with deviation of 1% and 5.6 respectively between estimated and actual industrial data. Estimated NO and H_2O concentration variation along catalyst bed show NO and H_2O concentration increase along the bed with deviation of 6.2% and 3.8% between estimated and actual industrial data. Estimated

Temperature variation along catalyst bed shows temperature increase along the bed with deviation of 0.4% between predicted and actual industrial data. The rate of consumption/ formation of NH_3, O_2, NO and H_2O was calculated.

Recommendations:

make mathematical models for (oxidation of nitric oxide equation (2) and absorption of nitric dioxide equation (3)) which represent the remaining of the process of nitric acid production.

Nomenclature:

Atot : Cross sectional area of catalyst (m^2)

a : specific surface area(m^{-1})

Cp : gas phase heat capacity (J/mole.K)

k_h : Heat transfer coefficient (W/m^2. K)

$K_{m,i}$: mass-transfer coefficient for specie i(mole/m^2.s)

M_{mix} : The average molecular weight of gas species.

P : total pressure of gas mixture (atm)

R : general gas constant (atm. L / g-mole. K)

S : surface area per reactor volume (m^2)

T : gas phase temperature (K)

T^* : Solid phase temperature (K).

t : time (s)

V : volume of reactor (m^3)

$\dot{v}$: Volumetric flow rate for gas mixture (m^3/s)

w : molar flow rate (mole/s)

$X_{g,i}$: Mole fraction of gas for specie i

$X_{s,i}$: mole fraction of gas species i at the surface.

z : axial position (m)

ρ :gas phase density(kg/ m^3)

v : linear velocity (m/s)

ε :void fraction

τ :residence time (s)

9- References

[1] Abbasfard H., Ghanbari M., Ghasemi A., Ghahraman G. , Jokar S. M., Rahimpour M. R.**,"** CFD modelling of flow mal-distribution in an industrial ammonia oxidation reactor: A case study", Applied Thermal Engineering, 67, 223-229, (2014).

[2] Scheibe A., Hinz M., Imbihl R.," Kinetics of ammonia oxidation on stepped platinum surfaces II. Simulation results", Surface Science, 576, 131-144, (2005).

[3] Salam M. A., Nassef E., Elkheriany E., El Tawel Y.,"Modelling and Simulation of Gauze Reactor of Ammonia Oxidation " American Journal of Chemical Engineering, 4(1), 16-22, (2016).

[4] Burditt G.F. and Pournaras D.T.," Nitric Acid Manufacture ", Journal of the Air Pollution Control Association ,14(3),(1964).

[5] Vernikovskaya N.V. , Pinaeva L.G. ,. Isupova L.A.,"Oxidation of ammonia to NOx in a two bed reactor (Pt gauzes + oxide monolytic layer): Experimental studies and mathematical modeling",Chemical Engineering Journal,238,140-147,(2014).

[6] Olsson L. , Sjo¨vall H. , Blint R. J.," A kinetic model for ammonia selective catalytic reduction over Cu-ZSM-5",Applied Catalysis B: Environmental,81,203–217, (2008).

[7] Industrial data from an ammonia oxidation plant in Egypt.

[8] Jirát J., Kubíˇcek M., Marek M., "Mathematical modelling of catalytic monolithic reactors with storage of reaction components on the catalyst surface", Catalysis Today, 53, 583–596, (1999).

[9] Peters M.S. and Timmerhaus K.D. ,"PLANT DESIGN AND ECONOMICS FOR CHEMICAL ENGINEERS ", 4^{th} ed, McGraw-Hill,1991.