Modeling of ammonia three bed synthesis reactor

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Abstract
In this study, the heterogeneous modeling of the ammonia synthesis reactor is presented. Nitrogen and hydrogen gases react to produce ammonia through an exothermic reaction at high temperature and pressure. The ammonia synthesis reactor has several types in which the three-bed type is modeled with acceptable error. The rate of conversion of the nitrogen and the output temperature of the reactor reached 22.6% and 716.77 K respectively. Finally, using sensitivity analysis, the effect of input parameters such as temperature and velocity on the output conversion was investigated. The conversion decreased with increasing velocity and since the ammonia production is equilibrium and exothermic reaction at a certain temperature, the conversion of nitrogen reached a maximum.

Keywords: ammonia synthesis, reactor modeling, packed bed reactor, heterogeneous model.

Introduction
Ammonia is the second most valuable and widely used material in various industries including chemical and agricultural industry. It is also widely used in the manufacture of materials such as fertilizers, explosive materials, and other organic nitrogen compounds[1]. Ammonia is produced during the well-known Haber-Bush process as shown schematically in Fig 1. During this process, the nitrogen and hydrogen gases enter the catalytic reactor at high temperature and pressure react through a single reversivle reaction and no side reaction occurs significantly. The catalysts used in this process are iron, nickel and more recently ruthenium[2]. The reaction rate parameters also vary depending on the type of catalyst used[3]. Production of ammonia is associated with high heat generation. For temperature control, based on type of cooling, different types of reactors such as an internal direct cooling reactor, adiabatic quench cooling reactor and, adiabatic indirect cooling reactor have been provided [4]. In addition, many studies have been done on the ammonia synthesis process. In 2005, Babu et al. simulated the ammonia auto thermal reactor using the Quasi-Newton method and obtained the optimal amount of reactor length based on the reactor inlet temperature[5]. In 2014, Carvalho et al. proposed a method for optimizing the ammonia synthesis reactor by solving the BVP (boundary value problem) type differential equations and reported the optimization results [6]. In 2014, Farivar et al. modeled and simulated the ammonia reactor synthesis of urea and ammonia plant of shiraz petrochemical company and investigated the effect of operating pressure[7]. In this study, we modeled the three-bed adiabatic indirect cooling ammonia synthesis reactor and compared the results with the

khorasan petrochemical industry data. Then the parameters such as inlet temperature and inlet velocity were analyzed.

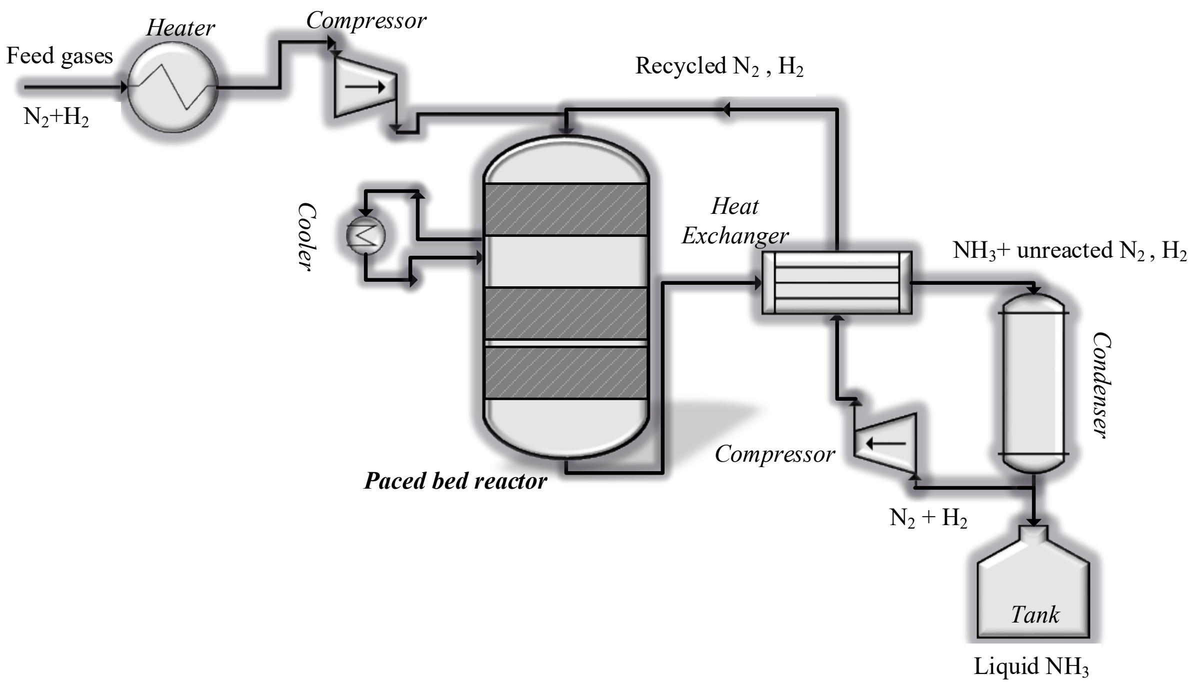

Fig.1 Haber-Bosch ammonia synthesis process[6]

Mathematical model

Mathematical modeling is a good way to analyze and improve system performance. In this work, ammonia synthesis reactor modeling is performed based on a one-dimensional and heterogeneous model. Energy and mass balance equations for this reactor are also presented. The 4th order Runge-Kutta method is used to solve these equations. The following assumptions are considered for the modeling:

- Steady state condition
- Variable physical properties during the process
- The model is heterogeneous and one-dimensional
- Regardless of the heat dissipation of the reactor
- Constant pressure along the reactor

Mass balance:

The mass balance for a differential element in the catalyst bed gives:

$$\frac{u_z \varphi_i P}{R_g T}\frac{dy_i}{dz} = \upsilon_i \eta R_{NH_3}$$

The ammonia production rate presented by Temkin is as follow [8]:

$$R_{NH_3} = k_2\left[K_a^2 a_{N_2}\left(\frac{a_{H_2}^3}{a_{NH3}^2}\right)^{\alpha} - \left(\frac{a_{NH_3}^2}{a_{H_2}^3}\right)^{1-\alpha}\right]$$

where α is constant between 0.5 to 0.75 [8].

k_2 is estimated by an Arrhenius equation as follow[8]:

$$k_2 = 1.7698\times 10^{15} e^{-\left(\frac{40765}{R_g T}\right)}$$

K_a is the equilibrium constant and obtained from the following equation [8]:

$$\log_{10}^{K_a} = -2.691122\log_{10}^{T} - 5.519265\times 10^{-5}T + 1.848863\times 10^{-7}T^2 + \frac{2001.6}{T} + 2.6899$$

The activity of species is defined as [8]:

$$a_i = f_i = y_i \times \varphi_i \times P$$

$$\varphi_{H_2} = \exp(e^{\left(-8.8402T^{0.125}+0.541\right)}P - e^{\left(-0.1263T^{0.5}-15.980\right)}P^2 + 300e^{\left(-0.011901T-5.941\right)}\left(e^{-\frac{P}{300}}-1\right))$$

$$\varphi_{N_2} = 0.93431737 + 0.3101804\times 10^{-3}T + 0.295896\times 10^{-3}P - 0.2707279\times 10^{-6}T^2 + 0.477507\times 10^{-6}P^2$$

$$\varphi_{NH_3} = 0.1438996 + 0.2028538\times 10^{-2}T - 0.448762\times 10^{-3}P - 0.1142945\times 10^{-5}T^2 + 0.2761216\times 10^{-6}P^2$$

Effectiveness factor is calculated form following equation [8]:

$$\eta = -17.539 + 0.0769T + 6.9005X - \left(1.08279\times 10^{-4}\right)T^2 - 26.4247X^2 + \left(4.92765\times 10^{-8}\right)T^3 + 38.9373X^3$$

X is the conversion of the nitrogen component.

Energy balance:

The energy balance for the differential element in catalyst bed is as follows:

$$\rho u_z C_{p_{mix}} \frac{dT}{dz} = \Delta H_{rxn} R_{NH_3} \eta$$

The heat of reaction is calculated from the following equation [9]:

$$\Delta H_{rxn} = 9723.24\left[-23840.57 + (P-300)\left(1.08 + (P-300)\left(0.01305 + (P-300)\left(0.83502\times 10^{-5}\right) + (P-300)\times\left(0.65934\times 10^{-7}\right)\right)\right) + 4.5(1391-T)\right]$$

The operating condition and reactor specification described in Table 1.

Table 1 Reactor operating conditions

Parameter	value
Feed composition (mole fraction)	
H_2	0.6672
N_2	0.2297
NH_3	0.0222
Inlet temperature, K	640
Inlet pressure, atm	125.8
Total feed flow rate, kg hr^{-1}	189932.4
Reactor length, m	2.79

Result and discussion:

To determine the validity and correctness of the presented model for the ammonia synthesis reactor, the simulation results including the mole fraction, temperature, and the nitrogen conversion at the reactor's outlet are compared to the Khorasan petrochemical plant data in Table 2.

Table 2 the model results and plant data

	Plant data	Modeling result	Relative errors (%)
Mole fraction			
H_2	0.5684	0.4943	13.03
N_2	0.1967	0.1781	9.45
NH_3	0.1435	0.1386	3.41
Temperature, K	723	716.77	0.86
Nitrogen conversion	0.237	0.226	4.64

The temperature profile along the reactor is presented in Fig 2. At first, the temperature is increased rapidly due to the high concentration of reactants and the high exothermic reaction rate. The outlet temperature of the first bed decreases from 745.94 to 640 K after heat transfer with coolant. Then it enters the second bed. Due to the equilibrium approach and the decrease in reaction rate in the second and third bed, its temperature increase is less than that of the first bed.

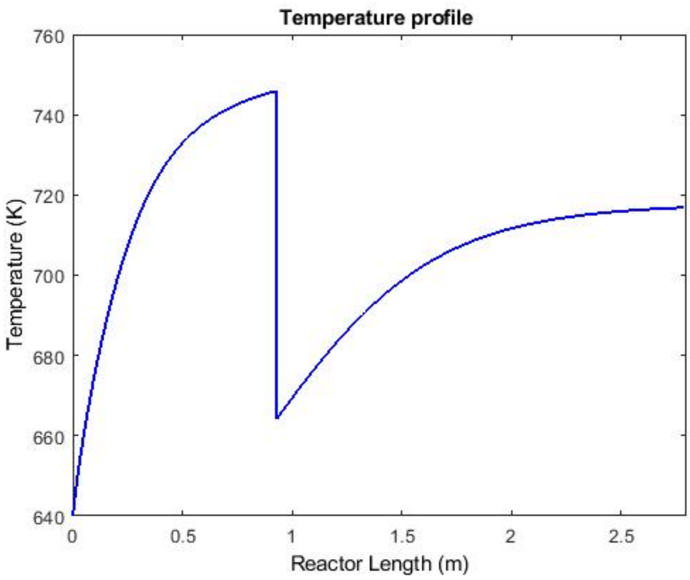

Fig. 2 Temperature profile along reactor

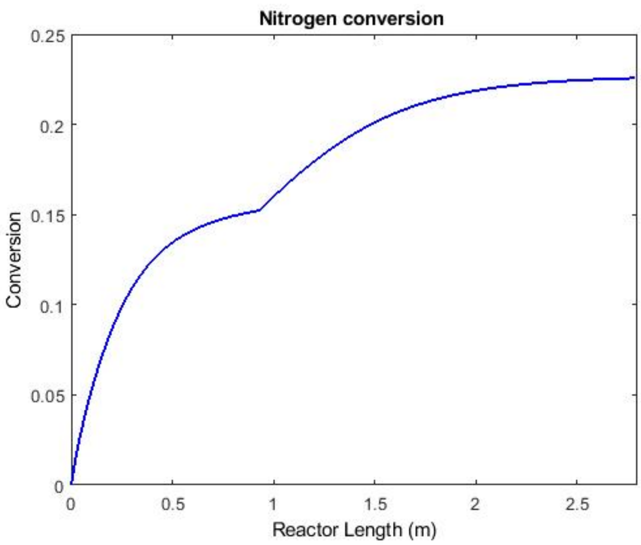

Fig. 3 Nitrogen conversion along reactor

Fig.3 demonstrate the variation of nitrogen conversion along the beds. is constantly increasing because the equilibrium and exothermic reaction is occurs, the reaction moves to greater nitrogen consumption.
Sensitivity analysis is an effective way to check the effect of parameters on each other. In this work, the effects of the inlet temperatures and the flow velocities on the reactor performance are determined. The inlet temperature and inlet velocity are considered to change in range of 560-660 K and 5-9 m/s respectively. During these ranges, the highest nitrogen conversion was obtained 0.2501 at temperature 587.49 K and velocity 5 m/s. The rate of nitrogen conversion decreases with increasing velocity due to reduced residence time. But with increasing temperature due to equilibrium occurrence, the ammonia production reaches a maximum value then decreases.

Conclusion

In this work, one-dimensional heterogeneous modeling was used to simulate the ammonia paced bed reactor. The effectiveness factor was calculated using the empirical relation in the literature. In the proposed model, simulation results with a 6.28% average relative error was obtained.

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