Control of a Single Process Unit: Dynamic Model of Ammonia Synthesis Reactor

PASCAL BOCK, 199368

JAKOB KÜBLER, 199197

CHRISTIAN WEIDELE, 200329

I. INTRODUCTION

The aim of the course *Process Control* is to control a multivariable process unit. To do so, we will follow four steps for control system design. First we will model the system (section II) before we will analyse the model in a second step. After that we will design and implement a controller as third and fourth step.

Our focus lays not on developing a model, so we need a well documented multivariable model which is not to complex. With [1] we found a good documented multivariable model of the ammonia synthesis. Other approaches of dynamic simulation of ammonia synthesis can be found in [3] using Soave-Redlich-Kwong equation and modeling a four-bed ammonia synthesis catalytic reactor and [4] using a three-bed ammonia synthesis catalytic reactor. In [5] a model based on the Arrhenius equation for for- and backward reaction is considered. But all these are not as good documented as [1] in which the Arrhenius equation is only used for the reverse reaction rate constant and the reaction rate for the forward reaction is based on the Gillespie-Beattie correlation. Ammonia is critical for production of fertilizers and one of the most produced chemicals in the world. The production of high amounts of ammonia made the fast growing world population of the last century possible. [6]

Despite the simplicity of the model it is possible to simulate the unnstable behaviour of the system and the oscillatory behaviour of the temperature when steady state is disturbed. A controller not only for feed temperature before heat exchanger also for feed flow rate and composition of feed is recommended in [1]. Using a simple PI-controller for temperature regulation is considered for a more complex model of ammonia synthesis in [5].

II. MODEL DEVELOPMENT

The model describes the Haber-Bosch process by focusing on the main reaction

$$N_2(g) + 3\,H_2(g) \xrightleftharpoons{\text{Fe}} 2\,NH_3(g) \cdot \tag{1}$$
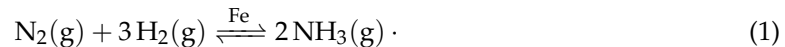
In addition to N_2 and H_2 Argon (Ar) is used as an inert gas. The reactor is using an iron (Fe) based catalyst. The same assumptions as in [1] are holding.

In this chapter we will show a short derivation of the model equation we used in Matlab. We will proceed in four steps. First we will derive the mole balances. For solving these we need to develop an equation for the accumulation term and derive the energy balance in a second and third step. And in a last step we will evolve the equations for the heat exchanger.
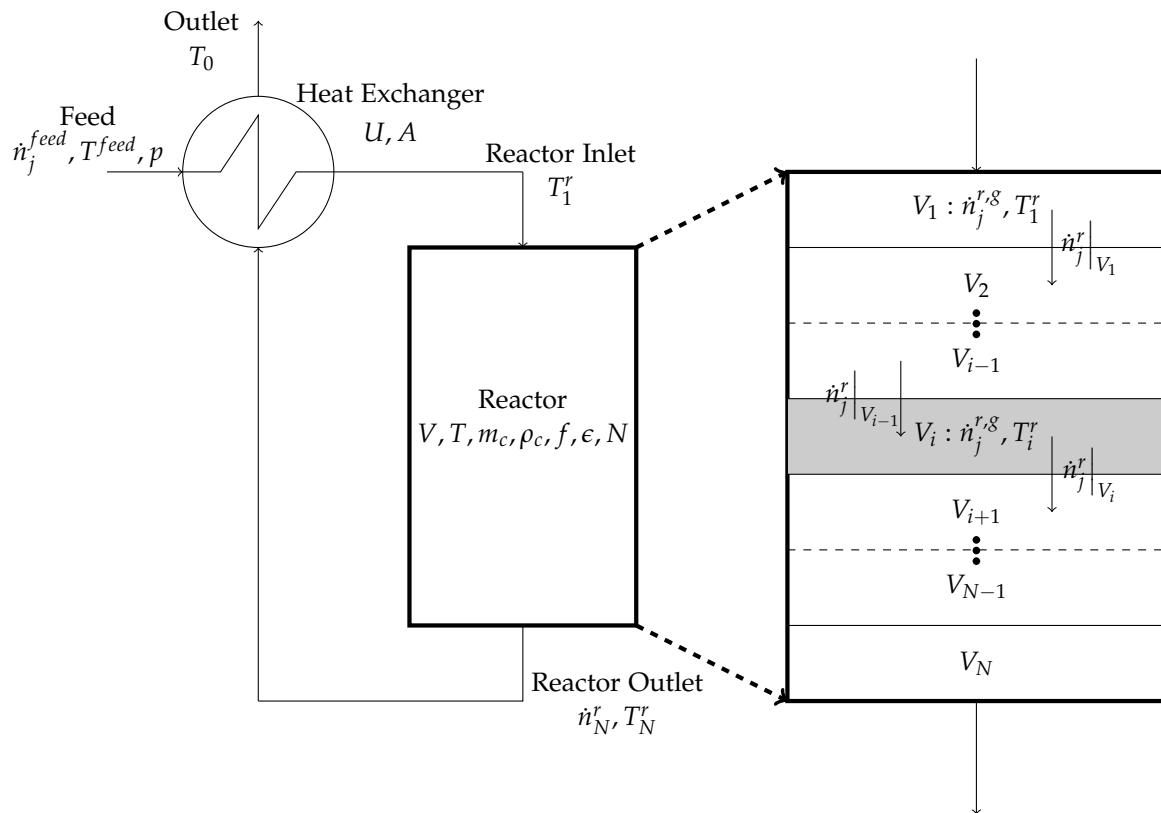
Figure 1: Flow sheet of reactor and heat exchanger (according to [1]) and volume compartments $V_i = \frac{V}{N}$

I.   Molar Balance of Volume Compartment

For a volume compartment $V_i = \frac{V}{N}, i = \{1, 2 \dots, N\}$ the mole balance equation is given as

$$\frac{d}{dt} n_j^r \Big|_{V_i} = \dot{n}_j^r \Big|_{V_{i-1}} - \dot{n}_j^r \Big|_{V_i} + \dot{n}_j^{r,g} \Big|_{V_i}. \tag{2}$$

At this, $\dot{n}_j^r \Big|_{V_{i-1}}$ is the molar stream coming from the volume compartment before, $\dot{n}_j^r \Big|_{V_i}$ is the molar outlet stream of V_i and $\dot{n}_j^{r,g} \Big|_{V_i}$ describes the moles generated of species $j \in \{N_2, H_2, NH_3, Ar\}$ in volume compartment V_i. For $i = 1$ the inlet stream is the molar feed stream, this also hold for the energy balance in subsection III.

II.   Accumulation Term $\dot{n}^{r,g}$

The production of species j can be expressed in dependence of the reaction rate r, the stoichiometry ν and the catalyst mass m_c by

$$\dot{n}_j^{r,g} \Big|_{V_i} = \nu_j r \Big|_{V_i} m_c \frac{\Delta V}{V} \tag{3}$$

For calculating the only unknown the Temkin-Pyzhev equation $r \Big|_{V_i} = f(k_+, k_-)$ is used and can be found in [1]. To derivate the rate constant for the reverse reaction an Arrhenius approach [2, p. 148] $k_- = k_0^- exp\left(-\frac{E_A}{RT}\right)$ is used. Via $k_+ = k_- K_p$ and the Gillespie-Beattie correlation for the equilibrium constant K_p it is possible to derive the rate constant for the forward reaction. The partial pressure is calculated like shown in [2].
The temperature in volume compartment V_i can be derived by using the ideal gas law $pV = nRT$ and considering the porosity of the catalyst bed (void fraction of catalyst ϵ).

$$T^r \Big|_{V_i} = \frac{p \Delta V}{\sum_j n_j^r R} \epsilon \tag{4}$$

III.   Energy Balances

After developing an equation for the accumulation term we will derive an equation for the molar stream from V_i to V_{i+1}. Considering a reactor without heat flow, no shaft work and constant pressure the energy balance for V_i will be

$$\frac{d}{dt} H \Big|_{V_i} = \dot{H} \Big|_{V_{i-1}} - \dot{H} \Big|_{V_i}. \tag{5}$$

Where, $\dot{H} \Big|_{V_{i-1}/V_i}$ are the enthalpy flow in (i) or out ($i - 1$) of V_i. The enthalpy can be written as a sum of the components j and the catalyst c $H \Big|_{V_i} = \sum_j n_j^r \tilde{H}_j \Big|_{V_i} + m_c \hat{H}_c \Big|_{V_i}$. $\tilde{H}_j$ is a molar enthalpy and $\hat{H}_c$ is the mass specific enthalpy of the catalyst. Using the equation before, Equation 2 and Equation 5 we will get

$$\sum_j n r_j \frac{d\tilde{H}_j}{dt} \Big|_{V_i} + m_c \frac{d\hat{H}_c}{dt} = -\sum_j \dot{n}_j^{r,g} \tilde{H}_j \Big|_{V_i} + \sum_j \dot{n}_j^r \left(\tilde{H}_j \Big|_{V_{i-1}} - \tilde{H}_j \Big|_{V_i}\right) \tag{6}$$

3

To simplify this equation we make the following assumption $d\tilde{H}_j \approx \tilde{c}_{p,j}dT$ and $\tilde{H}_1 - \tilde{H}_2 \approx \bar{\tilde{c}}_p(T_1 - T_2)$. $\tilde{c}_{p,j}$ is the molar heat capacity and $\bar{\tilde{c}}_p$ is the average molar heat capacity of a gas mixture. Plugging in the assumptions in Equation 6 and using the time derivative of the ideal gas law ($\frac{dp}{dt} = 0$) for changing the expression $\frac{dT}{dt}$ in Equation 6 we will get the following expression:

$$T_r C_p \dot{n}^{r,g}\Big|_{V_i} - \Delta\tilde{H}_r n_r r m_c\Big|_{V_i} = T_r C_p \dot{n}_r\Big|_{V_i} - \dot{n}_r\Big|_{V_{i-1}}\left[T_r C_p\Big|_{V_i} + \bar{\tilde{c}}_p\Big|_{V_{i-1}} n_r\Big|_{V_i}\left(T_r\Big|_{V_{i-1}} - T_r\Big|_{V_i}\right)\right] \quad (7)$$

This can be rewritten in a matrix form

$$b = A \cdot n_r. \tag{8}$$

where $A \in \mathbb{R}^{N \times N}$ and $\dot{n}_r, b \in \mathbb{R}^{N \times 1}$. The components of b and A can be written as

$$b_1 = T_r C_p \dot{n}^{r,g}\Big|_{V_1} - \Delta\tilde{H}_r n_r r m_c\Big|_{V_1} + \dot{n}_r^{feed}\left[T_r C_p\Big|_{V_1} + \dot{n}_r^{feed}\bar{\tilde{c}}_p n_r\Big|_{V_1}\left(T_1^r - T_r\Big|_{V_1}\right)\right] \quad (9)$$

$$b_i = T_r C_p \dot{n}^{r,g}\Big|_{V_i} - \Delta\tilde{H}_r n_r r m_c\Big|_{V_i}, \ i \in \{2,3,\ldots,N\} \tag{10}$$

and

$$A_{i,i} = T_r C_p\Big|_{V_i}, \ i \in \{1,2,\ldots,N\} \tag{11}$$

$$A_{i,i-1} = -T_r C_p\Big|_{V_i} - \bar{\tilde{c}}_p\Big|_{V_{i-1}} n_r\Big|_{V_i}\left(T_r\Big|_{V_{i-1}} - T_r\Big|_{V_i}\right), \ i \in \{2,3,\ldots,N\}. \tag{12}$$

Solving Equation 8 will give $\dot{n}_r$. To get the desired expression for $\dot{n}_j^r$ the mole fraction $x_j\Big|_{V_i} = \dfrac{n_j\Big|_{V_i}}{\Sigma_j n_j\Big|_{V_i}}$

is used.

$$\dot{n}_j^r\Big|_{V_i} = x_j^r \dot{n}_r\Big|_{V_i} \tag{13}$$

IV. Heat Exchanger

There are two streams of gas and respectively four relevant temperatures for a counter current heat exchanger. The inlet Temperature T_j^{feed} into the heat exchanger of the reactants and the outlet temperature of the heated up reactants T_1^r, which is also the inlet temperature of the reactor. The stream of Ammonia, by-products and inert gas leaves the reactor with T_N^r and enters the heat exchanger to heat up the inlet stream of the reactor. The gas mixtures leaves the heat exchanger with temperature T_o. In [1] you can find a short derivation for the equation of the temperature reactants entering the reactor

$$T_1^r = \frac{T^{feed} + \frac{UA}{\dot{m}_i \hat{c}_p^i}T_N^r}{1 + \frac{UA}{\dot{m}_i \hat{c}_p^i}} \tag{14}$$

and the outlet stream of the heat exchanger after heating up the reaction gas

$$T_o = \frac{T_N^r + \frac{UA}{\dot{m}_i \hat{c}_p^i}T^{feed}}{1 + \frac{UA}{\dot{m}_i \hat{c}_p^i}}. \tag{15}$$

Where $\dot{m}_i = \sum_j \dot{m}_j^i$ is the overall mass flow through volume compartment i.

V.   Possible Control Design

VI.   Degree of Freedom Analysis

III.   Simulation Results

IV.   Selection of a Control Structure for Linear Model

I.   Linearisation

II.   Selection of Best Control Structure

V.   Design Controller

I.   Testing on Nonlinear Model

References

[1] Asanthi Jinasena, Bernt Lie, and Bjørn Glemmestad. Dynamic model of an ammonia synthesis reactor based on open information. University College Southeast Norway, 9th EUROSIM Congress on Modelling and Simulation, September 2016.

[2] Hartmut Kamp. *Physikalische Chemie: Grundlagen für Biowissenschaftler*. Springer-Verlag, 1988.

[3] N. Kasiri, A.R. Hosseini, and M. Moghadam. Dynamic simulation of an ammonia synthesis reactor. *Computer Aided Chemical Engineering*, 14:695 – 700, 2003.

[4] Erasmo Mancusi, Pier Luca Maffettone, Francesco Gioia, and Silvestro Crescitelli. Nonlinear analysis of heterogeneous model for an industrial ammonia reactor. *Chemical Product and Process Modeling*, 4(2):5, 2009.

[5] John C Morud and Sigurd Skogestad. Analysis of instability in an industrial ammonia reactor. *AIChE Journal*, 44(4):888–895, 1998.

[6] Venkat Pattabathula and Jim Richardson. Introduction to ammonia production. `www.aiche.org`, September 2016. Online aviable at: `https://www.aiche.org/resources/publications/cep/2016/september/introduction-ammonia-production`; last accessed 15th April, 2017.