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Modelling in methanol synthesis

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Recently, methanol synthesis with CO2-rich feed has drawn a lot of attention and research is currently aimed at finding a suitable catalyst for such a task. This paper presents a short description of methanol synthesis and different uses of process models. The paper also provides a mass balance based model for methanol synthesis in a continuous reactor. A sensitivity analysis is applied for the model in order to find the most significant parameters for the further use of the model. The model utilises the kinetic equation proposed by Vanden Bussche and Froment in 1996. The results from the sensitivity analysis reveal the significant parameters and show that the sensitivity of the parameters is higher with lower temperatures and higher pressures. The later utilisation of the model will benefit from this information when new data sets are used.

1. Introduction

Models are mathematical representations of processes describing the underlying process as precisely as possible. With models, the output variables of the process can be predicted based on the set of input variables and the set of model parameters. Process models can be applied to many fields of chemical engineering: research and development, process design and plant operation. Models expand the knowledge about the process behaviour and are useful in process optimisation. Steady-state or dynamic behaviour of the process can be studied with different kinds of models. Steady-state models do not tell us about the evolution of the process with time. They provide information about the future steady-state values given the set of input variables. Dynamical models describe the process behaviour over time. (Luyben, 2001)

Methanol synthesis is a widely studied process but still there is no mutual agreement about the reactions occurring within the process. Nowadays, the interest is in the production of methanol from CO_2-rich feed gas, instead of the traditional CO-rich feed. The economic operation of methanol synthesis from CO_2 requires an efficient catalyst allowing high enough methanol yields. The kinetics of methanol synthesis has also been studied widely. Many different kinds of kinetic equations have been derived based on different assumptions about the limiting phenomena. Maybe the most profound model is derived by Vanden Bussche and Froment (1996). Vanden Bussche and Froment (1996) and Setinc and Levec (2001) review some of the proposed kinetic equations in their articles.

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This paper reports the use of the sensitivity analysis to study the influence of model parameters to the output variables of the methanol synthesis process within certain temperature and pressure ranges. The significance of each parameter is determined and the results show that there are differences in parameter sensitivities depending on the operational conditions. There are also differences in sensitivities between parameters. The knowledge obtained from the sensitivity analysis can be used when identifying model parameters for data sets resulting from laboratory experiments. The results can also be used when simplifying the model. A dynamical process model based on the kinetics proposed by Vanden Bussche and Froment (1996) is derived in this study. This study is a part of the "CO2UTIL" research project funded by the Academy of Finland.

2. Methanol synthesis

Methanol is very commonly used as a feedstock in the chemical industries. It is also used as a fuel and as a solvent. (Løvik, 2001) It is produced commercially from synthesis gas ($CO/CO_2/H_2$) under high pressure and temperature. The used catalyst is mainly the copper/zinc based oxide catalyst. (Yang, 2008) Used oxide additives include, for example, Al_2O_3, Cr_2O_3 and ZrO_2 (Raudaskoski et al., 2007). Methanol is used when producing for example formaldehyde, acetic acid, and methyl tertiary butyl ether (MTBE). (Løvik, 2001) The use of CO_2 as a feedstock in methanol synthesis has drawn a lot of attention and is nowadays widely studied. The research has focused mainly on the search for the most suitable catalyst, as the performance of the process is highly dependent on the used catalyst. In methanol synthesis, either CO or CO_2 or both hydrogenates to methanol. The reactions (Klier, 1982) together with the water gas shift reaction (Skrzypek, 1995) are

$$CO + 2H_2 \Leftrightarrow CH_3OH \quad (1)$$
$$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O. \quad (2)$$
$$CO + H_2O \Leftrightarrow H_2 + CO_2. \quad (3)$$

The production of methanol is strongly influenced by thermodynamics. The thermodynamic equilibrium limits the process to a low conversion and thus the recycling of the outlet is required if a high conversion is desired. The overall reaction is also strongly exothermic and thus a significant cooling is required. The recycling and the cooling are the main causes of the investment costs. Methanol synthesis reactors have been designed based on three principles: the high cooling demand, the low pressure drop, and the favourable economy of scale. (Lange, 2001)

The production of methanol from synthesis gas may take place under the low or high pressure. The high pressure process operates typically at 200 atm and 350°C while the low pressure process operates at 50 - 100 atm and 220 - 250°C. The low pressure process has such economical and operational benefits that almost all the methanol plants built after year 1967 operate at the low pressure. The hydrogenation of carbon monoxide and carbon dioxide favours higher alcohols over methanol as products and dimethylether may also form in methanol synthesis. Thus, an efficient and selective catalyst is required to produce methanol. (Klier, 1982)

3. Dynamic model

In chemical and biochemical applications, macroscopic models are based on the assumed reaction scheme and the flow conditions. The development of an accurate model needs some a priori knowledge especially in selecting a valid reaction scheme and kinetic model structure. If no process knowledge is available, black-box modelling tools must be used. (Grosfils et al., 2007) The mass balances for methanol synthesis can be written based on the reactions given in (1)-(3). The mass balances are

$$\begin{aligned}
\frac{dC_{CO}}{dt} &= \frac{F}{V}(C_{CO_{in}} - C_{CO}) - R_1 - R_3 \\
\frac{dC_{H_2}}{dt} &= \frac{F}{V}(C_{H_{2in}} - C_{H_2}) - 2R_1 - 3R_2 + R_3 \\
\frac{dC_{CO_2}}{dt} &= \frac{F}{V}(C_{CO_{2in}} - C_{CO_2}) - R_2 + R_3 \\
\frac{dC_{H_2O}}{dt} &= \frac{F}{V}(C_{H_2O_{in}} - C_{H_2O}) + R_2 - R_3 \\
\frac{dC_{CH_3OH}}{dt} &= \frac{F}{V}(C_{CH_3OH_{in}} - C_{CH_3OH}) + R_1 + R_2
\end{aligned} \quad . \tag{4}$$

Above, the reaction rates, R_i, are given by some kinetic equation. In this study, the kinetic equation proposed by Vanden Bussche and Froment 1996 is used. That equation is based on equation (2) and (3) and thus the reaction rate R_1 is neglected. The kinetic equation is (Vanden Bussche and Froment, 1996)

$$\begin{aligned}
r_{CH_3OH} &= \frac{k_1 p_{CO_2} p_{H_2} \left(1 - p_{CH_3OH} p_{H_2O} / K_2^{eq} p_{CO_2} p_{H_2}^3\right)}{\left(1 + k_3 p_{H_2O} / p_{H_2} + \sqrt{k_4 p_{H_2}} + k_5 p_{H_2O}\right)^3} \\
r_{RWGSR} &= \frac{k_2 p_{CO_2} \left[1 - K_3^{eq} \left(p_{H_2O} p_{CO} / p_{CO_2} p_{H_2}\right)\right]}{\left(1 + k_3 p_{H_2O} / p_{H_2} + \sqrt{k_4 p_{H_2}} + k_5 p_{H_2O}\right)}
\end{aligned} \tag{5}$$

All the constants (k_j) in the above equation follow the general Arrhenius equation given by

$$k_j = A_j \, exp\left(\frac{B_j}{RT}\right) \tag{6}$$

4. Sensitivity analysis

Through sensitivity analysis, information about the importance of the input variables and model parameters can be obtained. Such information is useful while assessing the modelling results. The input variables and model parameters include a lot of uncertainty arising from different sources. This uncertainty passes through the model to the output

variables. Understanding the sensitivity of the model outputs to uncertainty is essential while developing reliable models. (Campolongo and Braddock, 1999)

The sensitivity analysis used in this study is presented earlier by Correa et al. (2005). It can be used to study the sensitivity of the model parameters in different operating conditions. In this study, the sensitivities are studied in different temperatures and pressures. The general steps of the analysis are

- Selection of the N parameters for testing (A and B in (6)).
- Select the studied values for the variables (temperature and pressure).
- Define the ranges of the parameters.
- Generate a random (uniform distribution) testing set with I experiments for each parameter within the defined range.
- Execute the tests with the model and calculate the value of the objective function (J_k), equation (7).
- Determine the sensitivity of the parameters with different values of the studied variable (δ_k), equation (8).
- Evaluate the overall sensitivity (γ) of each parameter, equation (9).

The equations for the objective function, the sensitivity of the parameters with different levels of the studied variable and the overall sensitivity are, respectively (Correa et al., 2005)

$$J_k = \sum_{i=1}^{I} \left[y_k - \hat{y}_{i,k} \right]^2 , \tag{7}$$

$$\delta_k = \frac{J_k}{y_k} \text{ and} \tag{8}$$

$$\gamma = \sum_{k=1}^{K} \delta_k . \tag{9}$$

In the equations above, y_k is the output of the model with the k:th value of the studied variable (temperature or pressure) and $\hat{y}_{i,k}$ is the predicted output for the i:th experiment. Both values are obtained with the simulator.

5. Results and discussion

The sensitivity of the A and B terms of the parameters in the kinetic equation are studied (k_3 has only the A term). The equilibrium constants are excluded from the analysis. The ranges for each parameter are set to ± 15 % and 100 experiments are carried out. Some preliminary analysis was performed and it was noticed that by studying the reaction rate R_2 conclusions of the parameter sensitivity can be made. The overall sensitivities (γ) of the studied parameters with varying temperature and pressure are presented in Figure 1. The histogram in Figure 1a) reveals four significant parameters. All significant parameters are the B terms of the Arrhenius' equations. Similarly Figure 1b) reveals two

significant parameters: the B terms of k_1 and k_2. These parameters are further studied in order to reveal if significant changes in the parameter sensitivities occur with different temperatures or pressures. The sensitivities (δ_k) of the significant parameters from Figure 1 with different levels of temperature and pressure are presented in Figure 2. The figure shows that the sensitivities are higher with lower temperatures and higher pressures. This indicates that with lower temperatures and higher pressures the changes in model parameters lead to greater changes in the model outputs.

The information obtained from the sensitivity analysis can be used later when identifying model parameters with a new data set. The most sensitive parameters (Figure 1) are those which contribute most to the model outputs and thus they can be used instead of identifying the whole model again. Attention must also be paid to the fitting with lower temperatures and higher pressures (Figure 2) because the erroneous parameter identification will lead to greater errors in such conditions. The obtained results may also indicate that the fitting in lower temperatures and higher pressures are accurate but the predictions in other conditions are not as accurate. In such situations, it may be advantageous to identify separate models for different operating conditions.

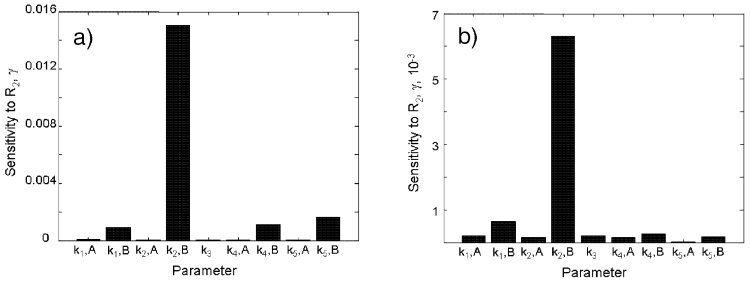

Figure 1. The overall sensitivities of the parameters with varying a) temperature and b) pressure.

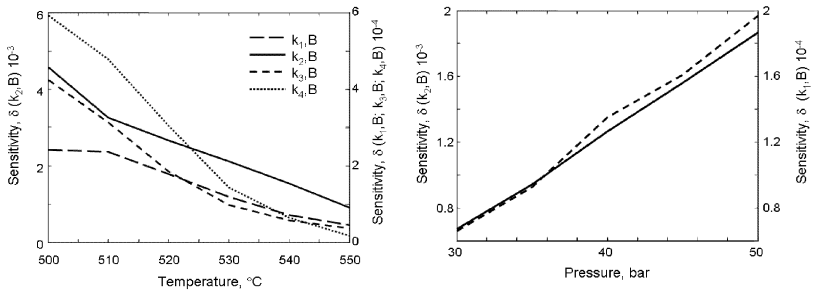

Figure 2. The sensitivities of the parameters in certain temperatures and pressures.

6. Conclusions

This paper presented a short description of methanol synthesis and different uses of process models. The paper also provided a mass balance based model for methanol synthesis in a continuous reactor. The model utilised the kinetic equations proposed by Vanden Bussche and Froment (1996). A sensitivity analysis was applied for the model in order to find the most significant parameters for the further use of the model. The results from the sensitivity analysis revealed the significant parameters, some activation energy terms in Arrhenius' equations. The sensitivity of the parameters is higher with lower temperatures and higher pressures. This result may also propose that different model parameters should be used in different operating points.

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