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SIMULATION OF THE FIXED-BED REACTOR FOR METHANOL SYNTHESIS

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Abstract. *The industrial process of methanol synthesis from synthesis gas is carried out in the presence of the high selective* $Cu/ZnO/Al_2O_3$ *catalyst. For the prediction of yield of crude methanol, produced at different operating conditions, it is necessary to derive mathematical model of the reactor which simulates its work, what is done in this paper. Reactor is fixed-bed type with four quench distributors. Modeling and simulation of the reactor is possible if the kinetics of the reaction system is known. Kinetic model proposed by Bussche and Froment is chosen. Simulation results are compared with design and plant data taken from industry. Calculated results are in a good agreement with design values, while better agreement with plant data is achieved when deactivation of the catalyst is taken into consideration.*

Key words: *simulation, reactor, fixed-bed, methanol, synthesis*

Introduction

The industrial process of methanol synthesis from the mixture of carbon oxides and hydrogen of an defined composition, i.e. from synthesis gas, is recently carried out mainly in the presence of the high selective $Cu/ZnO/Al_2O_3$ catalyst which permits operation at lower temperature and lower pressure than classic high-pressure process.

Both the modern and the earlier process use the fixed-bed reactor with the same principle of the recirculation loop. The use of low conversion per pass, together with the recycling of the unreacted gas around the loop, facilities the control of temperature in the catalyst bed. Nevertheless the highly exothermic nature of the reaction requires the use of special reactor design.

Quench reactor of the ICI'S standard is an example. Part of the circulating gas is preheated and fed to the inlet of the reactor. The remainder is used as quench gas and is admitted to the catalyst bed through distributors in order to control bed temperatures.

For that kind of reactor, modelling and simulation of its operation is done.

Modelling of the Fixed-Bed Reactor

For the prediction of quantity and composition of the crude methanol produced at different operating conditions, it is necessary to derive mathematical model of the reactor which would simulate its operation. That is possible if the kinetic behaviour of the reaction system is known. In this work, for modelling of the fixed-bed reactor for synthesis of methanol, the kinetic model reported by Bussche and froment is chosen /1/. They determined the model parameters for the same industrial copper-based catalyst as is used in the tested plant. Accepted model takes into consideration only reaction of the methanol synthesis from carbon dioxide and inverse water-gas shift reaction:

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \qquad \text{(I)}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad \text{(II)}$$

The model of the fixed-bed reactor with four quench distributors (ICIŚ type) is derived upon some simplifications: ideal plug flow and adiabatic operation of the reactor. Based on that assumptions, the equations for mass and heat balance are given as follows:

$$\frac{d\beta_1}{dz} = r_1 \rho_c \qquad (1)$$

$$\frac{d\beta_2}{dz} = r_2 \rho_c \qquad (2)$$

$$\frac{dT}{dz} = -\frac{\Delta H_1}{C_p N} r_1 \rho_c - \frac{\Delta H_2}{C_p N} r_2 \rho_c \qquad (3)$$

$$\frac{dP}{dz} = -\left[150\left(\frac{1-\varepsilon}{Re}\right) + 1.75\right]\frac{\rho_g U_g^2 (1-\varepsilon)}{d_e \varepsilon^3} \qquad (4)$$

where are:

β_i – extent of reaction i, kmol/m^2s
r_i – rate of reaction i, kmol/kg_{kat}s
ρ_c – catalyst bulk density, kg/m^3
ΔH_i – heat of reaction i, kJ/kmol
C_P – heat capacity of reaction mixture, kJ/kmol K
N – molar flow (flux) of reaction mixture, kmol/m^2s
P – pressure, Pa
ε – porosity
Re – Reynolds number, $Re = U_g d_e/\nu_g$
ρ_g – gas density, kg/m^3
U_g – gas apparent velocity, m/s
d_e – ekvivalent diameter of catalyst pellet, m
υ_g – kinematics gas viscosity, m^2/s
z – lenght of the reactor, m

For the rate of methanol synthesis and the inverse water gas shift reaction the following expressions are accepted /1/:

$$r_1 = \frac{k_4 p_{CO_2} p_{H_2}\left[1 - \frac{1}{K_{e,1}}\left(\frac{p_{H_2O}\, p_{CH_3OH}}{p_{H_2}^3\, p_{CO_2}}\right)\right]}{\left[1 + k_3\left(\frac{p_{H_2O}}{p_{H_2O}}\right) + k_1\sqrt{p_{H_2}} + k_2\, p_{H_2O}\right]^3} \qquad (5)$$

$$r_2 = \frac{k_5\, p_{CO_2}\left[1 - \frac{1}{K_{e,2}}\left(\frac{p_{H_2O}\; p_{CO}}{p_{H_2}^3\; p_{CO_2}}\right)\right]}{\left[1 + k_3\left(\frac{p_{H_2O}}{p_{H_2}}\right) + k_1\sqrt{p_{H_2}} + k_2\, p_{H_2O}\right]} \tag{6}$$

where are:

p_{CO2}, p_{H2},... – partial pressure of the CO_2, H_2,...
k_1 = $0.499\ e^{17197/RT}$
k_2 = $6.62{*}10^{-11}\ e^{124119/RT}$
k_3 = = 3453.38
k_4 = $1.07\ e^{36696/RT}$
k_5 = $1.22{*}10^{10}\ e^{94765/RT}$
$K_{e,1}$ = $10^{3066/T\ -\ 10.592}$
$K_{e,2}$ = $10^{-2073/T\ +\ 2.029}$

Fourth order Runge-Kutta method is used for solution of differential eqaution system (1) – (4), separately for each layer of catalyst in the reactor, as after each layer the reaction mixture is got cold with quench – part of the feed mixture of the lower temperature. The consequence of quenching is change on composition and temperature of the reaction mixture. Temperature after cooling is calculated on the bases of the adiabatic heat balance. Calculated temperature and composition are the initial values for integration of mass and heat balance equations for the next layer of catalyst.

Molar flow of components is calculated as:

$$N_k = N_k^o + \sum_{j=1}^{2} \nu_{kj}\, \beta_j \tag{7}$$

where are:
N_k^o, N_k – initial molar flow (flux) of component k, kmol/m^2 s
ν_{kj} – stoichiometric coefficient of component k in j reaction (for products is positive, for reactants is negative)

The assumption that reaction mixture is mixture of the ideal gases is accepted, since the same hypothesis is taken for derivation of the reaction rate equations [1]. That fact is also used for calculation of heat capacity of reaction mixture.

Temperature dependence of heat of reaction is given by the Kirchoff equation.

Equilibrium composition of reaction mixture is determined from the equilibrium constants for reactions (I) and (II).

Simulation Results

In the present paper, for each simulation, flow, temperature, pressure and composition of main and quench streams are used as input data. Composition, temperature and pressure at reactor outlet are calculated and compared with both design and plant data taken from industry. Comparatively, there are also given calculated data for equilibrium composition of the reaction mixture.

Simulation results for each catalyst bed in the reactor for

Table 1. Simulation results along catalyst beds in the reactor for methanol synthesis for design data

Bed	Main flow kg/h	Quench kg/h	Quench temp °C	Inlet			Outlet		
				T, °C	P, bar	CH_3OH vol %	T, °C	P, bar	CH_3OH vol %
1.	103301	46324	110	240.0	51.2	0.692	298.8	51.2	3.091
2.	149625	46324	110	240.3	51.2	2.107	288.2	51.2	3.988
3.	195948	46324	110	245.8	51.2	3.003	283.2	51.1	4.500
4.	242272	46324	110	249.7	51.1	3.591	280.3	51.0	4.827
5.	288595			252.5	51.0	4.002	278.2	50.9	4.932

Table 2. Comparison of different results for outlet composition of the reaction mixture, conversions, temperature and pressure for design data

Component	Inlet mol %	Outlet, mol %		
		Design	Simulation	Equilibrium
H_2	60.525	57.172	56.895	54.844
H_2O	0.043	0.363	0.374	0.426
CO	14.417	11.955	11.769	10.014
CO_2	4.146	4.172	4.165	4.326
CH_3OH	0.692	4.594	4.932	7.502
CH_4	2.205	2.376	2.389	2.501
N_2	17.973	19.369	19.476	20.387
CO conversion, mol %		23.058	24.668	38.768
CO_2 conversion, mol %		6.635	7.303	8.017
Temperature, °C		270.0	278.2	270.0
Pressure, bar		50.9	50.9	50.9

Table 3. Simulation results for catalyst beds in the reactor for plant data

Bed	Main flow kg/h	Quench flow kg/h	Quench temp. °C	Inlet			Outlet		
				T, °C	P, bar	CH_3OH vol %	T, °C	P, bar	CH_3OH vol %
1.	96156	11523	94.2	219.0	49.0	0.000	293.5	49.0	2.671
2.	107679	25573	94.2	272.2	49.0	2.372	289.4	49.0	2.981
3.	133252	25573	94.2	251.8	49.0	2.381	283.1	48.9	3.500
4.	158825	25573	94.2	252.4	48.9	2.904	279.0	48.8	3.865
5.	184398			253.1	48.8	3.294	276.1	48.7	4.135

Table 4. Comparison of different results for outlet composition of the reaction mixture, conversions, temperature and pressure for plant data

Component	Inlet mol %	Outlet, mol %		
		Plant	Simulation	Equilibrium
H_2	78.208	76.633	75.863	73.237
H_2O	0.000	0.400	0.543	0.919
CO	8.452	6.612	5.559	1.645
CO_2	2.545	2.282	2.213	2.099
CH_3OH	0.000	2.696	4.135	9.297
CH_4	6.869	7.239	7.437	8.146
N_2	3.926	4.138	4.251	4.656
CO conversion, mol %		25.772	39.256	83.585
CO_2 conversion, mol %		14.924	19.698	30.442
Temperature, °C		234.7	276.1	234.7
Pressure, bar		48.4	48.7	48.5

Table 5. Simulation results for catalyst beds in the reactor for plkant data and catalytic activity of 0.1583

Bed	Main flow kg/h	Quench kg/h	Quench temp. °C	Inlet			Outlet		
				T, °C	P, bar	CH_3OH vol %	T, °C	P, bar	CH_3OH vol %
1.	96156	11523	94.2	219.0	49.0	0.000	242.6	49.0	0.929
2.	107679	25573	94.2	226.8	49.0	0.828	255.9	49.0	1.814
3.	133252	25573	94.2	224.9	49.0	1.456	248.3	48.9	2.275
4.	158825	25573	94.2	223.4	48.9	1.894	243.0	48.8	2.588
5.	184398			222.2	48.8	2.213	235.9	48.8	2.701

Table 4. Comparison of different results for outlet composition of the reaction mixture, conversions, temperature and pressure for plant data and catalytic activity of 0.1583

Component	Inlet mol %	Outlet, mol %		
		Plant	Simulation	Equilibrium
H2	78.208	76.633	76.575	73.237
H2O	0.000	0.400	0.455	0.919
CO	8.452	6.612	6.662	1.645
CO2	2.545	2.282	2.227	2.099
CH3OH	0.000	2.696	2.701	9.297
CH4	6.869	7.239	7.240	8.146
N2	3.926	4.138	4.138	4.656
CO conversion, mol %		25.772	25.214	83.585
CO2 conversion, mol %		14.924	16.968	30.442
Temperature, °C		234.7	235.9	234.7
Pressure, bar		48.5	48.8	48.5

design data are presented in Table 1. Comparison of design, simulation and equilibrium results for outlet composition of the reaction mixture and conversions of CO and CO for design data are given in Table 2.

Calculated results, given in Tables 1 and 2, are in a good agreement with design values.

Simulation results are also compared with plant data. Results calculated for the catalyst bed in the reactor are presented in Table 3.

Plant, simulation and equilibrium data for composition of the reaction mixture at outlet of the reactor are compared in Table 4. It is evident that calculated values of outlet composition and conversions of CO and CO considerably deviate from plant data.

Deviation may be explained by reduction of catalytic activity which is not taken into consideration during the modelling of the reactor. To introduce an function of catalytic deactivity into model, which simulates reactor operation, it means to multiply expressions for reaction rates with that function. Function of catalytic deactivity would defined drop of catalytic activity in time. For evaluation of that kind function, i.e. to determine the form and parameters of function, plant data for whole period of catalyst "life" is necessary.

Because of lack of that data in our work, it is possible, by repeated simulation, to determine just an value of catalytic deactivity function which the best fit plant data. That value would then made possible to adjust control parameters of the reactor for changed operating conditions, for the purpose of optimal synthesis of methanol.

Determined value of catalytic deactivity function which the best fit plant outlet concentration of methanol for actual plant data is 0.1583. In Tables 5 and 6 are presented simulation results calculated by the model which takes into consideration catalytic activity of 0.1583.

Simulated outlet temperature from the reactor is just for 1.2 C higher than plant one. The same, good agreement of outlet concentration of methanol, as well as other compared parameters, with plant data is obvious when the value of catalytic deactivity function is applied during the stimulation.

By determination of value of catalytic deactivity function for the other sets of plant data on the explain way (by adjustment of the outlet methanol concentration), the similar values, which decrease in time, are obtained. This is also point out the need to take into consideration some function of catalyc deactivity during modelling the reactor for methanol synthesis.

Conclusions

Simulation results, calculated by derived mathematical model which simulates the operation of the fixed-bed reactor for methanol synthesis, are compared with design and plant data. That results are in a good agreement with design values. Better agreement of the simulation results with plant data is achieved when deactivation of the catalyst is taken into consideration.

References

[1] Vanden Bussche, M.K. Froment, F.G. "A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al_2O_3 Catalyst", Journal of Catalysis, 161, pp. 1–10, 1996