

## Study of a CO<sub>2</sub> hydrogenation reactor for a methanol production plant based on CO<sub>2</sub> recycling and H<sub>2</sub>O electrolysis

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### 1. Introduction

The aim of the present work is to obtain a kinetic scheme for a CO<sub>2</sub> hydrogenation reactor that can be implemented in the model of a methanol production plant developed in Aspen Plus®. The power-law form was selected for its simplicity and compatibility with the simulation software. A two-step procedure was implemented to obtain the kinetic scheme. In the first step, a one-dimensional axial heterogeneous steady-state model for a mono-tubular plug-flow reactor was developed. The model allowed simulating the reactor under different conditions of temperature, pressure, feeding composition and gas spatial velocities. In the second step, the obtained data set was used as input for a non-linear fitting procedure, which solved, in the different conditions, the plug flow reactor (PFR) defining ordinary differential equation. The result was the set of kinetic parameters of power-law equation for CO and CO<sub>2</sub> hydrogenation and reverse water gas shift (RWGS).

### 2. Methods

In the first step of the work, the 1D axial steady-state model of a tubular plug-flow reactor was developed in MATLAB®. Main assumptions were: ideal gases with uniform properties in each axial section of the tube, neglecting the radial gradient of the physical quantities and axial dispersion and to impose isothermal reactor without pressure drops. Three reactions were considered: CO, CO<sub>2</sub> hydrogenation reactions and RWGS. The continuity equation was applied to the fluid phase in the axial direction, while for a single pellet it was considered as a boundary condition in each axial section of the reactor. The pellet was approximated as one-dimensional in the radial direction. Spherical catalyst pellets were assumed for the packed bed, with a diameter uniform along the reactor, with volume, bulk density, void fraction and porosity characteristics from the literature [1-3]. The intrinsic kinetics of a commercial Cu-Zn-Al catalyst [4], expressed as Langmuir-Hinshelwood-type equation form, were implemented in the model. The length of the reactor was assumed to be 8 m [5] and the diameter was chosen in such a way as to be equal to 15 times that of the pellet to avoid channelling phenomena. Boundary conditions imposed were the initial values of the concentrations of the chemical species, the continuity of the heat flux at the pellet interface and the symmetry of the concentration profile at the centre of the pellet. Simulation were performed by changing four parameters: temperature (240-300 °C), pressure (20-95 bar), spatial gas velocity (2-10 h<sup>-1</sup>) [5] and H<sub>2</sub>/CO, H<sub>2</sub>/CO<sub>2</sub> ratios. The last parameter was varied around the stoichiometric value per each of the three reactions: H<sub>2</sub>/CO<sub>2</sub> ∈ (1-5) for CO<sub>2</sub> hydrogenation, H<sub>2</sub>/CO<sub>2</sub> ∈ (1/3-3) for RWGS and H<sub>2</sub>/CO ∈ (0.5-4) for CO hydrogenation.

The data set obtained from simulations performed in the first part of the work was used as the reference for the second part of the study, the aim of which was to determine the parameters of the rates of reactions

expressed as power-laws accounting for the kinetic limitations related to transport phenomena. In order to find these quantities, the reactor was simulated, in the different conditions abovementioned, by solving the PFR ordinary differential equation:

$$\frac{d\dot{n}_{j,i}}{dM_{cat}} - v_{j,i}r_{i,mc} = 0$$

In the equation,  $\dot{n}_{j,i}$  is the molar flow rate of the specie  $j$  when considering only the reaction  $i$  and  $r_{i,mc}$  are the power-law reaction rates, where  $R_1$  and  $R_2$  are the involved reactants ( $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2$ ):

$$r_{i,mc} = k_{\infty,i} e^{-\left(\frac{E_{a,i}}{R_u T}\right)} p_{R1}^{a_i} p_{R2}^{b_i} \left(1 - \frac{\prod_{j=1}^{ns} p_j^{v_{j,i}}}{K_{P,i}^0}\right)$$

The conversions of reactants obtained by solving PFR equation were compared to those given by the 1D model inside a fitting procedure implemented in MATLAB®. The rate equation parameters were thus found from the minimization of the sum of the square errors calculated on the gas conversions.

### 3. Results and discussion

The results of the 1D axial steady-state heterogeneous model showed the expected trends for the concentrations of reactants and products along the axis of the reactor, as depicted in Figure 1 for the  $\text{CO}_2$  hydrogenation. To verify the reliability of the constructed model in terms of order of magnitude of the results, the obtained reaction rates at section level were compared to those resulting by a one-dimensional axial homogeneous steady state model. As expected, the rates obtained by the heterogeneous model were lower due to the species diffusion limitations. The kinetic scheme obtained from the fitting of heterogeneous model results was validated by means of parity plots calculated on the conversion of reactants at the outlet of the reactor. The reaction rates obtained through the solution of the PFR defining equation were used to calculate the conversion, that was compared with the one obtained from the heterogeneous model, for each of the three reactions considered. The parity plots showed a linear relation between the results of the models, thus demonstrating the reliability of the power-law kinetic scheme.

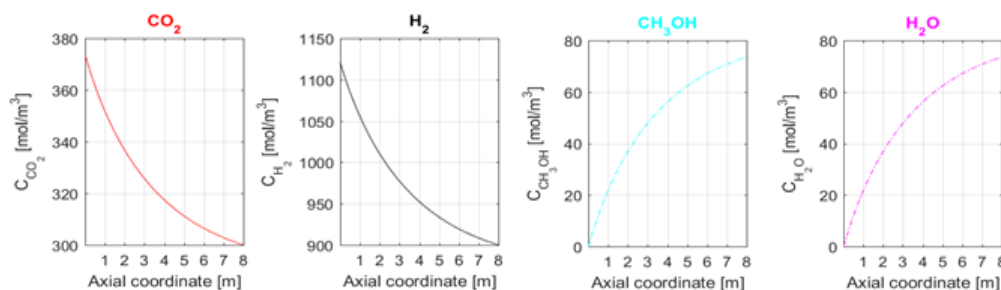


Figure 1.  $\text{CO}_2$  hydrogenation: concentration profiles for gas velocity =  $2 \text{ h}^{-1}$ ,  $T = 250 \text{ }^\circ\text{C}$ ,  $p = 65 \text{ bar}$ , stoichiometric compositions.

### 4. Conclusions

The work presented a two-step model-based procedure developed to obtain a kinetic scheme (power-law type) for a  $\text{CO}_2$  hydrogenation PFR reactor suitable for the implementation in an Aspen Plus® model. A heterogeneous reactor model was developed and the simulation results allowed to obtain the parameters of the kinetic scheme by a fitting procedure. The parity plots of conversions (heterogeneous vs. kinetic models) obtained demonstrated the reliability of the kinetic scheme. The kinetics obtained can be implemented in an Aspen Plus® reactor model that includes all the technological aspects (ie., thermal and pressure losses, etc.) not accounted for in the heterogeneous model and that can be also integrated in a full-plant simulation.

### References

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