2-D Homogeneous Modeling and Simulation of Catalytic WGS Reactor

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Abstract:

In this paper, a simulation of a fixed bed reactor for water gas shift reaction, which forms part of a hydrogen production, was carried out. A commercial CuO/ZnO/Al2O3 catalyst was employed and a two-dimensional homogeneous model was applied for the simulation. The kinetic information has been taken from literature for the WGS reaction. The distribution of concentration in fluid bulk as well as porous catalyst, rate of reaction, pressure profile and superficial velocity distribution were represented as results of study. The simulation results validated using pressure drop of the reactor obtained via Darcy’s law as well as equilibrium conversions. gPROMS, a general purpose modeling package, was used for modeling and simulation of the water-gas shift reaction.

Keyword: WGS Reaction, Homogeneous Modeling, Simulation, Fixed bed Reactor, gPROMS

1. Introduction

Water The water-gas shift (WGS) reaction is a crucial industrial reaction which is wildly used in ammonia, methanol, and hydrogen production, petroleum refineries for a variety of operations and Fischer-Tropsch process [1]. It is a reversible, exothermic and usually catalytic chemical reaction which refers to the reaction of carbon monoxide with steam to produce carbon dioxide and hydrogen [2, 3].

\[
\text{CO} + \text{H}_2\text{O} \xrightarrow{\text{Catalyst}} \text{CO}_2 + \text{H}_2; \Delta H_{298K} = -41.1 \text{ kJ/mole} \tag{1}
\]

The water-gas shift reaction is practiced over a wide variety of temperatures. In spite of very slow kinetics, the production of CO2 and H2 is favored at low temperatures (120–300ºC) due to thermodynamic equilibrium conditions at low temperatures (120–300ºC). On the other hand, the WGS reaction is kinetically satisfactory at high temperatures (300–450ºC) while the products are not thermodynamically favored. Iron-based catalysts are typically used in high temperature applications, whereas copper or aluminum-based catalysts are utilized at low temperatures [4]. Many experimental studies exist that attempted to seek the best performance of different catalysts in order to obtain a better conversion of CO in the low temperature water-gas shift reaction. A great review of low temperature WGS catalyst was published by Jacubs et al. [5].

Fixed bed catalytic reactors are frequently used for gas-solid and liquid-solid reactions. There are newer types of reactors such as fluidized bed reactors, but nevertheless the fixed bed reactors are commonly used for numerous operations in petrochemical industry. The continuum models are usually used to describe the fixed bed reactors. Moreover, mathematical feasible treatment of the model equations is an essential feature of any mathematical model. Consequently, the proposed model must represent the performance of a real reactor to give helpful information for its design and analysis [6].

Numerous models for the water gas shift reactors have been published to date. Choi and Stenger [7] studied methanol steam reforming which is linked with a low temperature water gas shift reaction. Giunta et al. [8] developed a steady-state 1D heterogeneous model to simulated low temperature water gas shift reactions in a fixed-bed reactor. The effects of some important parameters (e.g. catalyst pellet size, inlet temperature, operational time and reactor diameter) were also studied. Considering
temperature and concentration variations as a function of the reactor axial position, Wright and Edgar [9] developed a dynamic 1D homogeneous model that is appropriate for small reactor with crushed catalyst particles as well as for the system with no diffusion limitations and negligible pressure drop limitations. Francesconi et al. [10] described a steady-state 1D pseudo-homogeneous model like the model proposed by Guinta et al. [8]. Considering temperature and mass gradients in both the axial and radial directions of the reactor, the proposed model was compared to a 2D model. It is resulted that the differences due to radial variation were negligible. Also, the 1D model was accurate for steady-state considerations. Ding and Chan [11] described a 2D heterogeneous model indicated that variations in the reactor radius influenced conversion because of changes in the superficial velocity of the reactor, whereas changes in the internal radial profiles showed minor influences. Conversely, Chen et al. [12] proposed another 2D model that showed radial effects get intensified by increasing gas velocity.

In this paper, a 2D homogeneous, steady-state model suitable for use with small catalyst pellets is presented. The model implemented in gPROMS and simulated using orthogonal collocation finite element method. Then, the simulation results were validated by pressure drop of the reactor as well as mass concentration at equilibrium. The equation-oriented modeling system - gPROMS - has several features for parameter estimation and simulation tasks.

2. Mathematical Modeling

The According to the mathematical models that were represented in the literature [6-12], a 2-D homogeneous mathematical model designed to represent the steady state behavior of a fixed-bed catalytic reactor were developed according to the following considerations and assumptions: (1) steady-state condition, (2) no radial velocity, (3) negligible radial pressure drop, (4) no gravitational effects, (5) neglecting kinetic energy in momentum balance, (6) neglecting energy of viscose forces in momentum balance, (7) isothermal operation, (8) gases have an ideal behavior, (9) reaction takes place only on the catalyst surface and (10) negligible external and internal heat-transfer resistances. In this model, the flow has a contribution by both convection and diffusion while radial dispersion is considered. The following model was developed by simplifying governing equations:

Species equation:

\[
\frac{\partial}{\partial z} (u_s C_i) = \frac{\partial}{\partial z} \left( D_{ax,i} \frac{\partial C_i}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r D_{rad} \frac{\partial C_i}{\partial r} \right) + v_i r_i \rho_{cat} (1 - \varepsilon_b)
\]  

(2)

where corresponding boundary conditions:

\[-\varepsilon_b D_{ax,i} \frac{\partial C_i}{\partial z} |_{z=0} = u_s |_{z=0} \big( C_i |_{z=0} - C_{i,ln} \big) \]  

(3)

\[\frac{\partial C_i}{\partial z} |_{z=L_R} = 0 \]  

(4)

\[\frac{\partial C_i}{\partial r} |_{r=0} = \frac{\partial C_i}{\partial r} |_{r=R_t} = 0 \]  

(5)

Momentum equation:

\[- \frac{dp}{dz} = \int \rho g C_0^2 \frac{z_0}{D_p} \]  

(6)

where \(f\) is friction factor that is calculated using well-known Ergun equation[6]:

\[f = \left( \frac{1-\varepsilon_b}{\varepsilon_b^2} \right) \left( \frac{150}{Re_p} + 1.75 \right) \]  

(7)

where \(Re_p\) is the particle Reynolds number, defined as:

\[Re_p = \frac{\rho u_s \sigma D_p}{(1-\varepsilon_b) \mu} \]  

(8)
where \( \rho_g \) is density of gas mixture, \( u_{x,0} \) is initial superficial velocity, \( D_p \) is catalyst particle diameter and \( \mu \) is viscosity of gas mixture.

Superficial velocity is related to the volumetric flow rate as follow:

\[
u_s = \frac{Q}{A_c}
\]

\( u_s \) is the reactor superficial velocity that depends on the pressure drop according to [13]:

\[
u_s = u_{s,0} \frac{c}{c_{in}} \frac{P_{in}}{P}
\]

The boundary condition at the inlet of the reactor is:

\[
P|_{x=0} = P_{in}
\]

For the low temperature reaction using a commercial Cu/ZnO/Al\(_2\)O\(_3\) catalyst and the by means of CO conversion experimental data extracted from Mendes et al. studies [14, 15], a simple power-law model was developed for kinetic rate expression. Following model gives excellent results at atmospheric pressure. Details are given in our previous publication [16].

\[
(-r_{CO}) = 4.887043 \exp\left(-\frac{3.948231 \times 10^4}{RT} \right) \rho_{CO}^{2.57} \rho_{H_2O}^{2.02} \rho_{CO_2}^{0.59} \rho_{H_2}^{-3.4}(1 - \beta)
\]

where \( \beta \), approach to thermodynamic equilibrium to account for the backward reaction, is defined as:

\[
\beta = \frac{P_{CO_2} \rho_{H_2O} \frac{1}{R}}{K_p}
\]

The thermodynamic equilibrium constant, in the temperature range 315°C to 480°C, was given by Ratnasamy et al. [1] through Eq. (14):

\[
K_p = \exp\left(\frac{4577.8}{T} - 4.22\right)
\]

In the temperature range over 298 Kelvin, thermodynamic equilibrium constant which decreases with increasing temperature is calculated [17, 18] by Eq. (15) and Eq.(16):

\[
K_p = 104366.9372 \exp\left[\frac{-\Delta H_f}{R} \left(\frac{1}{T} - \frac{1}{298}\right)\right]
\]

\[
\Delta H_f \left[\frac{1}{mol}\right] = -4.193164204 \times 10^8 + 15464.04 \times T - 2.24478 \times T^2 + \frac{9.677496 \times 10^8}{T}
\]

Physical properties and correlations that used in model are extracted from literature [4].

2.1. Integration Strategy

Using the differential method as equation 14, the experimental reaction rates were obtained by calculating the CO conversion. The model equations were implemented in the equation-based process modeling system gPROMS. The corresponding PDEs were then discretized and solved using orthogonal collocation finite element method. The Simulation of proposed model was executed by mesh size of \( N_z=25 \) and \( N_r=10 \) along the fixed bed axial and radial directions, respectively. The parameters used in the numerical modeling of the fixed bed reactor for the WGS can be found in Table 1.
Table 1: Operating Conditions and Parameters Used in this study

<table>
<thead>
<tr>
<th>parameters</th>
<th>unit</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature range</td>
<td>[K]</td>
<td>453.15 – 573.15</td>
</tr>
<tr>
<td>Feed Pressure</td>
<td>[bar]</td>
<td>1.20</td>
</tr>
<tr>
<td>Mass of Catalyst</td>
<td>[mg]</td>
<td>70 – 2400</td>
</tr>
<tr>
<td>Feed Composition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow Rate in the Feed</td>
<td>[mL·min⁻¹]</td>
<td>270</td>
</tr>
<tr>
<td>Bed Density</td>
<td>[kg·m⁻³]</td>
<td>1173.1</td>
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<tr>
<td>Reactor Length</td>
<td>[cm]</td>
<td>5</td>
</tr>
<tr>
<td>Reactor Diameter</td>
<td>[cm]</td>
<td>0.775</td>
</tr>
</tbody>
</table>

3. Results and Discussion
3.1. Simulation Results

Considering The model is a system of elliptic PDEs coupled with an IVP which have been solved using gPROMS DASOLV solver. The equations of the model have been previously described via equations 2 through 16. As results of the model, the two dimensional molar concentration profile of CO at 200 ºC as well as CO molar concentration profiles under different process temperatures are presented in Figures 1 and 2, respectively. As is shown in Figures 1 and 2, due to CO consumption, its concentration decreases along the bed. Furthermore, negligible variations are seen in concentration profile through the reactor radius. Moreover, increases in the process temperature lead to increasing of kinetic constant which results in more conversion and less concentration of CO at reactor outlet.

![Figure 1: Two dimensional CO concentration at 200 ºC](image1)

![Figure 2: CO concentration in gas phase down through the reactor at center line](image2)
The rate of reaction under different process temperatures are presented in Figure 3. According to Figure 3, the rate of reaction decrease along the bed length as a result of consumption of reactant. Also, more increase in process temperature, more decrease in rate of reaction.

![Figure 3: Rate of reaction through the reactor at center line](image)

The pressure profile in addition to the superficial velocity under different process temperatures are represented in Figures 4 and 5, respectively. Moreover, as is shown in Figures 4 and 5 pressure decreases along reactor length whereas superficial velocity increases along reactor length. It should be noted that deviations in both of pressure and superficial velocity are minor or negligible.

![Figure 4: Pressure profile across the catalyst bed at center line](image)

![Figure 5: Superficial Velocity Distribution across the catalyst bed at center line](image)
Normally, the pressure drop have no significant effect on the overall model performance because of inaccuracies in the reaction rate expressions as well as the uncertainties in the transport parameters. The pressure drop in the reactor is comparatively trivial so that in most cases an average value for the total pressure is used in the calculation. It was estimated that the maximum pressure drop is approximately 1.25% which is less than 5% of the total operational pressure in the reactor. As a consequence of this reason, were negligible pressure drop across the bed assumed, it would be significant. Although, simulation could be executed by means of inlet superficial velocity for all nodes through bed, it modified via equation 10. As presented in Figure 5, there was a minor increase along the bed length in the superficial velocity due to minor decrease in the pressure.

### 3.2 Model Validation

Validity of the simulation can be checked through CO conversion at equilibrium state [19]. Using equation 13 and equilibrium constant for different reaction temperature i.e. Equations 15 and 16, CO conversions are calculated which are compatible with the simulation result. The corresponding results are represented by Figure 6.

![Figure](Error! No text of specified style in document.: CO conversion at reactor outlet)

Furthermore, the validity of the simulation can be checked by calculations of pressure drop in the reactor using Darcy’s law as expressed by Equation 17 as well as Equation 18 [19]:

\[
\frac{Q}{A} = -\frac{K}{\mu} \frac{\Delta P}{L}
\]

\[
K = \frac{\varepsilon d_p^2}{72(1-\varepsilon)^2 \tau}
\]

where \(\mu\) is dynamic viscosity, \(K\) is permeability, \(L\) is the length of the reactor, \(\varepsilon\) is bed porosity, and \(\tau\) is tortuosity [20]. The pressure gradient, \(\Delta P/L\), was calculated for different process temperatures which are represented by Figure 7. As can be seen from figure, the pressure gradient obtained via Darcy’s law is less than the atmospheric pressure and approximately congruent with the pressure differences between the inlet and the outlet, for different process temperatures.
Moreover, it was estimated that the maximum pressure variation is about 1.25%. It should be noted that pressure drop less than 5% of the total operational pressure in the reactor guarantees that process is performed isobar. Also, it must be less than 120% of the total operational pressure in the reactor to satisfy safety considerations. The results are represented by Figure 8. As shown, the pressure variation in the reactor is relatively small so that to grante isobar conditions as well as safety.

4. Conclusions

Applying the two-dimensional homogeneous model, the simulation of the WGS reactor was performed in this work. The CO molar concentration within fluid bulk has been estimated. As shown previously, the CO molar concentration within fluid bulk is decreased along catalyst bed. Additionally, the variations in the reactor radius are negligible. Also the rate of reaction and pressure across the bed under different process temperatures are slightly decreased while the superficial velocity is slightly increased. By means of pressure drop of the reactor as well as concentration at equilibrium, the results were acceptably validated.
Acknowledgements
The authors kindly acknowledge the scientific association of Petroleum University of Technology.

<table>
<thead>
<tr>
<th>Nomenclature</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Cross-sectional Area of The Reactor</td>
</tr>
<tr>
<td>i</td>
<td>Species Involved in The Reaction (CO, H2O, CO2, or H2)</td>
</tr>
<tr>
<td>C_i</td>
<td>Concentration of Component i [mol·m⁻³]</td>
</tr>
<tr>
<td>D_ax,i</td>
<td>The Effective Axial Mass Diffusivity of Species i in The Bulk Phase [m²·s⁻¹]</td>
</tr>
<tr>
<td>D_rad</td>
<td>The Effective Radial Mass Diffusivity in The Bulk Phase [m²·s⁻¹]</td>
</tr>
<tr>
<td>D_p</td>
<td>Catalyst Particle Diameter [m]</td>
</tr>
<tr>
<td>f</td>
<td>Friction Factor</td>
</tr>
<tr>
<td>K_p</td>
<td>Equilibrium Constant for The WGS Reaction</td>
</tr>
<tr>
<td>L_R</td>
<td>Reactor Length [m]</td>
</tr>
<tr>
<td>P_i</td>
<td>Partial Pressure of Component i [Pa or bar]</td>
</tr>
<tr>
<td>Q</td>
<td>Volumetric Flow Rate [mL·min⁻¹]</td>
</tr>
<tr>
<td>P</td>
<td>Total Pressure [Pa or bar]</td>
</tr>
<tr>
<td>R</td>
<td>Ideal Gas Constant [J·mol⁻¹·K⁻¹]</td>
</tr>
<tr>
<td>Re_p</td>
<td>Particle Reynolds Number</td>
</tr>
<tr>
<td>R_t</td>
<td>Reactor Tube Radius [m]</td>
</tr>
<tr>
<td>r_i</td>
<td>Rate of Consumption or Formation of Species i [mol·g_cat⁻¹·h⁻¹]</td>
</tr>
<tr>
<td>r</td>
<td>Radial Coordinate of The Reactor [m]</td>
</tr>
<tr>
<td>T</td>
<td>Absolute Temperature [K]</td>
</tr>
<tr>
<td>u_s</td>
<td>Superficial Velocity [m·s⁻¹]</td>
</tr>
<tr>
<td>z</td>
<td>Axial Coordinate of The Reactor [m]</td>
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<table>
<thead>
<tr>
<th>Greek letter</th>
<th>Description</th>
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<tbody>
<tr>
<td>β</td>
<td>Term for The Backward Reaction or Approach to Equilibrium</td>
</tr>
<tr>
<td>ΔH₂₉₈</td>
<td>Standard Heat of Reaction [J·mol⁻¹]</td>
</tr>
<tr>
<td>K</td>
<td>Permeability [m²]</td>
</tr>
<tr>
<td>ε_b</td>
<td>Bed Porosity</td>
</tr>
<tr>
<td>μ</td>
<td>Dynamic Gas-mixture Viscosity [kg·m⁻¹·s⁻¹]</td>
</tr>
<tr>
<td>ν_i</td>
<td>Stoichiometric Coefficient of Species i</td>
</tr>
<tr>
<td>ρ_b</td>
<td>Catalyst Bulk Density [kg·m⁻³]</td>
</tr>
<tr>
<td>ρ_g</td>
<td>Gas Mixture Density [kg·m⁻³]</td>
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<tr>
<td>τ</td>
<td>Catalyst Tortuosity Factor</td>
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</table>

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTS</td>
<td>High Temperature Shift</td>
</tr>
<tr>
<td>LTS</td>
<td>Low Temperature Shift</td>
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<tr>
<td>WGS</td>
<td>Water-Gas Shift</td>
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5. References: