การประชุมวิชาการเสนอผลงานวิจัยระดับชาติและนานาชาติ ครั้งที่ 8
“Research 4.0 Innovation and Development SSRU’s 80th Anniversary”

Validity of the Non-Porous-Catalyst Assumption for Modeling of the Water-Gas-Shift Process

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Abstract

The water-gas-shift (WGS) is an important process for producing hydrogen. The catalyst for this process is porous while the mathematical model describing the WGS process often applied the assuming that the catalyst is non-porous. In this research, validity of the non-porous-catalyst assumption was investigated by numerical simulation for an isothermal plug flow reactor. The reactor performance calculated using the non-porous-catalyst assumption was compared to that using the porous-catalyst assumption. Calculation result shows that the reactor performances obtained from the two assumptions are closed to each other. The non-porous-catalyst assumption is therefore valid for describing the reactor performance.

Keywords: Water-Gas-Shift Process, Kinetic, Simulation

Introduction

Hydrogen is a strategic material that is used in various chemical processes. The most common process to produce hydrogen is steam reforming of methane (Hou & Hughes, 2001; Gallucci & Basile, 2008). A process that usually follows the steam methane reforming is the water-gas-shift (WGS) of which the reaction is described by

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H^{o}_{298} = -41.1\ \text{kJ/mol} \qquad (1)$$

This reaction produces additional hydrogen production to the whole process. It is a reversible and slightly exothermic reaction. Various catalysts are used to achieve high reaction rate. However, the catalyst is deactivated during operation. The catalyst deactivation in the WGS reactor can occur due to many causes involving formation of coke on catalyst surface, sintering, and poisoning (Kim & Thompson, 2005; Liu *et al.*, 2005; Ilinich *et al.*, 2007). The poisoning is the main cause of catalyst deactivation in the WGS reactor (González-Velasco *et al.*, 1962; Young & Clark, 1973; Schaidle *et al.*, 2010).

The WGS process has been investigated in order to determine the process characteristics that are required for operation and design of the reactor. The mathematical model describing the process that has been used for the investigation is usually based on the assumption that the catalyst is non-porous (Moe, 1962; González-Velasco *et al.*, 1962; Amadeo & Laborde, 1995; Ayastuy *et al.*, 2005; Adams & Barton, 2009). However, the catalyst is normally porous. In this research, we investigated whether the non-porous-catalyst assumption can be applied to describe the reactor performance.

Objective

The goal of this research is to investigate the validity of the non-porous-catalyst assumption for mathematically describing the WGS process.

Research Scope

1. The validity of the non-porous-catalyst assumption is to be investigated by numerical simulation.
2. Numerical simulation was performed to compare the reactor performance calculated using the non-porous-catalyst assumption with that calculated from the porous-catalyst case.
3. The reactor performance is indicated by the CO conversion at the reactor exit versus time.
4. An isothermal plug flow reactor was studied.
5. Catalyst deactivation is due to poisoning.

Literature Review

The kinetics reaction rate of the WGS process for the conditions that there is no mass transfer resistance has been reported for each of the four gases, including CO, H_2O, CO_2, and H_2, as follows (Moe, 1962):

$$-r_{CO} = \varphi\, k_{wgs}\, y_{CO} y_{H_2O}\, (1 - \frac{y_{CO_2} y_{H_2}}{K_{eq}\, y_{CO} y_{H_2O}}) \tag{2}$$

where $-r_{CO}$ is the rate of WGS reaction (mol gcat^{-1} s^{-1}), φ is the pressure factor, k_{wgs} is the rate constant of WGS reaction (mol gcat^{-1} s^{-1}), y_i is the composition of gas species i, and K_{eq} is the equilibrium constant.

The pressure factor (φ) is described by (Rase, 1977)

$$\varphi = 0.86 + 0.14P \qquad \text{for } P < 24.8 \text{ atm} \tag{3}$$

where P is the pressure (atm).

The equilibrium constant (K_{eq}) can be calculated using (Moe, 1962)

$$K_{eq} = \exp\,(\frac{4577.8}{T} - 4.33) \tag{4}$$

Young and Clark (1973) investigated the catalyst deactivation of the WGS process due to poisoning. The equations of the disappearance rate of the poison and the deactivation rate were described by

$$-r_p = k_p P_p a \tag{5}$$

$$-\frac{da}{dt} = k_d P_p a \tag{6}$$

where $-r_p$ is the rate of poisoning (mol gcat^{-1} s^{-1}), k_p is the rate constant of poisoning (mol gcat^{-1} Pa^{-1} s^{-1}), P_p is the partial pressure of poison (Pa^{-1}), t is the operation time (s), k_d is the rate constant of deactivation (Pa^{-1} s^{-1}), and a is the catalyst activity that is defined as (Levenspiel, 1999)

$$a = \frac{\text{rate at which the pellet converts reactant } j}{\text{rate of reaction of } j \text{ wiht afresh pellet}} = \frac{-r_j}{-r_{j,0}} \tag{7}$$

The value of the catalyst activity (a) ranges from 0 to 1. Eqs. (2) – (6) were used for numerical simulation in this work.

Methodology / Calculation Procedure

Numerical simulation was used to investigate the non-porous-catalyst assumption for mathematically describing the WGS process with poisoning deactivation. Due to the poisoning, the reactor performance indicated by the conversion of CO decreases with time. Therefore, we compare the CO conversion versus time curve obtained from the non-porous-catalyst model with that from the porous-catalyst model. If the two curves from the two models are close to each other, the non-porous-catalyst assumption is valid.

Porous-Catalyst Model

The porous-catalyst model has two mass balance equations which were applied in the inter-particle and intra-particle regions.

For the intra-particle region, a one-dimensional model is applied.

The mass balance for each of the four gas species, including CO, H_2O, CO_2, and H_2, is written as follows:

$$D_i\left(\frac{d^2C_i}{dx^2}\right) + \frac{aW_{cat}\left(R_{i|x}\right)}{\left(1-\varepsilon_b\right)V_{reactor}} = 0 \tag{8}$$

The mass balance equation for poison is written as

$$D_p\left(\frac{d^2C_p}{dx^2}\right) + \frac{W_{cat}\left(k_p P_p a\right)}{\left(1-\varepsilon_b\right)V_{reactor}} = 0 \tag{9}$$

where D_i is the diffusivity coefficient of gas species i (m^2 s^{-1}), D_p is the diffusivity coefficient of poison (m^2 s^{-1}), C_i is the concentration of gas species i (mol m^{-3}), C_p is the concentration of poison (mol m^{-3}), x is the coordinate along the thickness of catalyst (m), a is the catalyst activity, W_{cat} is the weight of catalyst (gcat), $V_{reactor}$ is the volume of reactor (m^3); the reactor volume is 0.005 m^3, ε_b is the void fraction that is defined by the ratio of the void volume to the reactor volume; the void fraction was assumed to be 0.5 for the catalyst pellet packed with the WGS reactor, and $R_{i|\,x}$ is the intrinsic reaction rate of gas species i (mol gcat^{-1} s^{-1}). The intrinsic reaction rate is the reaction rate without mass transfer resistance. Therefore, the WGS rate expression described by Eq. (2) is reasonably assumed to be the intrinsic reaction rates ($R_{i|\,x}$).

The boundary conditions for the intra-particle region for each of the five gases, including CO, H_2O, CO_2, H_2, and poison, are given by

$$x = Lp \qquad C_i = C_{i,\,bulk} \tag{10}$$

$$x = 0 \qquad \frac{\mathrm{d}\,C_i}{\mathrm{d}\,x} = 0 \tag{11}$$

where Lp is the half of the thickness of the catalyst pellet with a slab shape (m); the thickness of the catalyst pellet with a slab shape is 0.646 millimeters, and $C_{i,\,bulk}$ is the bulk concentration of gas species i (mol m^{-3}).

For the inter-particle region, the mass balance for each of the five gas species, including CO, H_2O, CO_2, H_2, and poison, is written as follows:

$$\frac{\mathrm{d}\,F_i}{\mathrm{d}\,z} + \left(1 - \varepsilon_b\right) A R_{avg,\ i,\,|z} = 0 \tag{12}$$

where F_i is the mole flow rate of gas species i (mol s^{-1}), z is the coordinate along the length of reactor (m), A is the cross sectional area of reactor (m^2); the cross sectional area of reactor (A) is 0.0177 m^2, and $R_{avg,\,i,\,|z}$ is the average reaction rate of gas species i (mol m^{-3} s^{-1}). The average reaction rate of the four gas species ($R_{avg,\,i,\,|z}$), including CO, H_2O, CO_2, and H_2, is calculated by

$$\left(R_{avg,\ i}\right)_z = \left(\frac{\int_{x=0}^{x=L_p} (a\,r_i)_x \quad \mathrm{d}\,x}{L_p}\right)_z \tag{13}$$

The average reaction rate of the poison ($R_{avg,\,p|\,z}$) is calculated by

$$\left(R_{avg,\ p}\right)_z = \left(\frac{\int_{x=0}^{x=L_p} \left(a\,k_p\,P_p\right)_x \quad \mathrm{d}\,x}{L_p}\right)_z \tag{14}$$

The boundary condition for the inter-particle region for each of the five gas species, including CO, H_2O, CO_2, H_2 and poison, is given by

$$z = 0 \qquad F_i = F_{i,\,0} \tag{15}$$

where $F_{i,\,0}$ is the inlet mole flow rate of gas species i (mol s^{-1}).

Eq. (6) describing the catalyst deactivation rate is also included in the set of differential equations to be solved with the initial condition given by

$$t = 0 \qquad a = 1 \tag{16}$$

The simulation involves determination of the gas composition (y_i) for each of the four gas species, including CO, H_2O, CO_2, and H_2, which is calculated by

$$y_i = \frac{F_i}{F_{total}} = \frac{P_i}{P} \tag{17}$$

The set of Eqs. (6), (8) – (12), (15), and (16) were solved by numerical method for the porous-catalyst model. The WGS operating conditions and parameters were selected to be comparable to those for commercial operation (Chocron *et al.*, 1996) as listed in Table 1. The diffusivity coefficients for the five gas species are shown in Table 2.

Table 1: Operating conditions and parameters used in simulation study

Variable/ Parameter	**Value**
P (Pa)	1,723 x 10^3
T (K)	490
Catalyst weight (g)	4,000
Density of catalyst (kg m^{-3})	700
Chlorine (ppm)	0.0005
Steam feed flow rate (mol s^{-1})	0.2083
Dry gas feed flow rate (mol s^{-1})	0.3389
Feed composition $CO/H_2/CO_2/N_2$ (vol %)	3.2/76.8/18.16/1.84
k_1 WGS rate constant (mol $gcat^{-1}$ s^{-1})	7.778 x 10^{-4}
k_p Poisoning rate constant (mol $gcat^{-1}$ Pa^{-1} s^{-1})	2.742 x 10^{-9}
k_d Deactivation rate constant (Pa^{-1} s^{-1})	4.935 x 10^{-4}

Table 2: Diffusivity coefficients for the five gas species (Chocron *et al.*, 1996)

Gas species	**CO**	**H_2O**	**CO_2**	**H_2**	**Poison***
D_i (m^2 s^{-1})	4.32 x 10^{-7}	5.21 x 10^{-7}	3.50 x 10^{-7}	1.98 x 10^{-6}	3.00 x 10^{-7}

*The poison is chlorine gas in this case.

Simulation was performed to calculate the CO conversion versus time curve which will be compared with that calculated from the non-porous-catalyst model.

Non-Porous-Catalyst Model

For the non-porous-catalyst model, the mass balance for each of the four gas species, including CO, H_2O, CO_2, and H_2, is written as follows:

$$\frac{\mathrm{d}F_i}{\mathrm{d}z} + \frac{aW_{cat}(-r_i)}{L} = 0 \qquad (18)$$

The mass balance equation for poison is written as follows:

$$\frac{\mathrm{d}F_p}{\mathrm{d}z} + \frac{W_{cat}(-r_p)}{L} = 0 \qquad (19)$$

where F_i is the mole flow rate of gas species i (mol s^{-1}), F_p is mole flow rate of poison (mol s^{-1}), z is the coordinate along the length of reactor (m), a is the catalyst activity, W_{cat} is the weight of catalyst (gcat), L is the reactor length (m); the reactor length (L) is 1 meter, r_i is the reaction rate of gas species i for non-porous-catalyst model (mol $gcat^{-1}$ s^{-1}), and $-r_p$ is the reaction rate of poisoning for the non-porous-catalyst model (mol $gcat^{-1}$ s^{-1}).

The boundary condition for each of the five gas species i, including CO, H_2O, CO_2, H_2, and poison, is given by

$$z = 0 \qquad F_i = F_{i,0} \qquad (20)$$

where $F_{i,0}$ is the inlet mole flow rate of gas species i (mol s^{-1}).

The reaction rate for the non-porous-catalyst model is the apparent reaction rate which is different from the intrinsic reaction rate applied in the porous-catalyst model. The involved apparent reaction rate expressions are needed to be determined. The apparent rate expression for the WGS reaction is described by

$$-r_{CO} = \varphi k_{wgs}\, y_{CO}{}^{m} y_{H_2O}{}^{n}\left(1 - \frac{y_{CO_2} y_{H_2}}{K_{eq}\, y_{CO} y_{H_2O}}\right) \qquad (21)$$

where m and n are the order of gas composition of CO and H_2O respectively.

Similarly, for the poison, the reaction rate and the deactivation rate must be changed to be applicable to the non-porous-catalyst model. The reaction rate of poisoning for the non-porous-catalyst model (r_p) is the apparent poisoning rate which is described by

$$-r_p = k_p P_p{}^{u} a^{v} \qquad (22)$$

Where u is the order of partial pressure of poison, and v is the order of catalyst activity.

The apparent rate of the deactivation is similar to the apparent poisoning rate that was investigated and reported by Fogler (2006). Therefore, the apparent rate of the deactivation can be described by

$$-\frac{\mathrm{d}\,a}{\mathrm{d}\,t} = k_d P_p{}^u a^v \tag{23}$$

The initial condition for the apparent rate of the deactivation is given by

$$t = 0 \qquad\qquad a = 1 \tag{24}$$

The set of Eqs. (18) - (20), (23), and (24) were solved by numerical method for the non-porous-catalyst model. The parameters (k_{wgs}, m, n, k_p, u, v, k_d) in Eqs. (21) – (23) were determined by regression analysis or matching the CO conversion versus time curves between the two models.

Results

The obtained rate expressions for the non-porous-catalyst model are described by

$$-r_{CO} = 1.145\,\varphi\, y_{CO}{}^{0.911} y_{H_2O}{}^{0.631}\left(1 - \frac{y_{CO_2} y_{H_2}}{K_{eq}\, y_{CO} y_{H_2O}}\right) \tag{25}$$

$$-r_p = 1.945\, P_p{}^{0.988} a^{1.721} \tag{26}$$

$$-\frac{\mathrm{d}\,a}{\mathrm{d}\,t} = 5.011 \times 10^9\, P_p{}^{0.988} a^{1.721} \tag{27}$$

Figure 1 shows the CO conversion versus time curve obtained from the porous-catalyst model (circle symbol) comparing to that from the non-porous-catalyst model (solid line symbol).

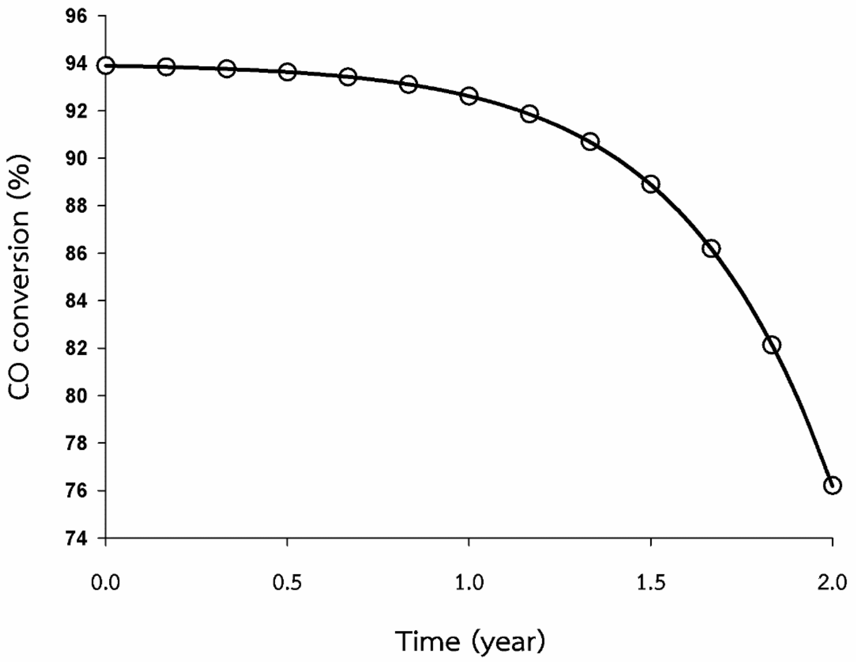

Figure 1: The CO conversion versus time curve obtained from the porous-catalyst model (circle symbol) compared with that from the non-porous-catalyst model (solid line symbol). Figure 1 shows that the two models give almost the same calculation results. The difference of the CO conversions between the two models is less than 0.03%. Consequently, the non-porous-catalyst assumption is valid.

Conclusion and Discussion

We have investigated the validity of the non-porous-catalyst assumption to describe the reactor performance for the WGS process by numerical simulation. It was found that the CO conversion versus time curve obtained from the non-porous-catalyst model are closed to that from the porous-catalyst model. Consequently, the non-porous-catalyst assumption is valid, and can be used to describe the reactor performance.

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