

Modeling for Industrial Heat Exchanger Type Steam Reformer

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Abstract—In a heat exchanger type steam methane reformer, the temperature profiles and mole fractions along the axial distance from the top of the reformer can be predicted by using the channel model, considering radiation heat transfer. The cross-section of the reformer tube was divided into several channels as concentric circles and then heat transfer and mass transfer at the interfaces between adjacent channels were considered. Because the steam reformer is operated at high temperature, the radiation and convection were combined into one heat transfer coefficient to simplify the transfer analysis. This model predicts the industrial plant data very well; therefore, it may be used with confidence to design the industrial heat exchanger type reformer.

Key words : Heat Exchanger Type Reformer, Methane Steam Reforming, Convective Radiation Heat Transfer, Channel Model

INTRODUCTION

The steam reformer is widely used for the production of ammonia, methanol, hydrogen, acetic acid and fuel cells [Park et al., 1998]. The conventional furnace type reformer shows higher energy consumption because of the fuel combustion, though it produces export steam. In the conventional furnace type reformer, the reaction heat for steam reforming is supplied by radiation heat transfer from flame formed by the combustion of fuels such as hydrocarbons or plant off-gas. Therefore, currently, two types of reformers such as the Pd-Ru membrane reactor [Nam et al., 2000; Kim et al., 1999] as well as the heat exchanger type reformer [Schneider et al., 1992; Nirula, 1990] have been studied and applied, because they increase methane conversion and reduce energy consumption, respectively.

In the heat exchanger type reformer, the reaction heat of steam reforming is supplied by heat transfer of the hot gas generated from the secondary reformer. Therefore, the hydrocarbon consumption can be reduced by 20-30%.

In the heat exchanger type reformer, there are no serious hot spots due to indirect heat transfer from the heating gas temperature, unless carbon deposit takes place on the catalyst. Moreover, the heat exchanger type reformer has the advantage of an ecologically clean process because of no fuel combustion equipment except for the fired heater for HDS (Hydro-Desulphurization System). Since 1988 the heat exchanger type reformer has been developed and commercialized by licensors such as GIAP, ICI and M. W. Kellogg [Schneider et al., 1992; Nirula, 1990].

Xu and Froment [1989b] and Elnashaie et al. [1992] predicted profiles of design parameters such as temperature, reaction rates, effectiveness factor and partial pressure of each components for the industrial steam reformer, using the one dimensional heterogeneous model by Froment and Bishoff [1979]. Whereas Sosna et al.

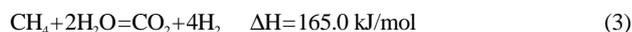
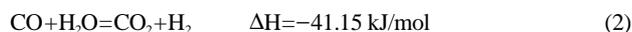
[1989] developed the channel model for the conventional type steam reformer using pilot plant data and well predicted the temperature and methane mole fraction along axial distance from the top. However, the modeling of heat exchanger type reformer, let alone an industrial scale design, has not yet been published.

In the present study, temperature profiles, mole fractions and reaction rates are predicted by using the channel model Sosna et al. [1989], which considers the counter-current heat transfer between hot gas and tube wall including radiation heat transfer. In order to predict the temperature profiles at the reformer tube surfaces, both the convection heat transfer and the radiation heat transfer are considered. The predicted results from this model are compared with the data from an industrial scale plant.

THE CHANNEL MODEL WITH COUNTERCURRENT HEAT TRANSFER

1. Reaction Kinetics

In the steam reforming reaction, the possible kinetic rate expressions considered are as follows: [Xu and Froment, 1989; Kim and Lee, 1991].



Kim and Lee [1991] summarized the kinetic equations of previous researchers and developed the rate equation using industrial catalyst when high hydrogen partial pressure interferes with the methane reaction. Xu and Froment [1989a] developed the rate equation of all the above reactions, but their equation is too complex and the effectiveness factor for reaction (2) has a minus value due to the switching of its direction of the reaction through the industrial reactor modeling. Though Elnashaie et al. [1992] simulated the industrial reformer using the equations by Xu and Froment [1989a],

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the effectiveness factor shows stiff variation along the axial distance from the top. Therefore, they showed the monotonic decrease of the effectiveness factor for reaction of CO₂ only after elimination of CO-shift reaction (2), but the effectiveness factor was still negative at the end of reformer tube.

However, because the above reactions are known to be reversible, many researchers [Khomenko et al., 1971; Allen et al., 1975; Ko et al., 1995; Twigg, 1989] suggest that the reaction mechanism can be described with two simple equations. (1) and (2). Khomenko et al. [1971] developed the rate equation for methane conversion using 0.03 mm nickel foil in order to obviate any pore diffusion limitation. They concluded that the water shift reaction approaches equilibrium. Their equation can be considered to apply to any brand of nickel catalyst, compensated with an effectiveness factor.

Therefore, in this study, the reaction rate equation by Khomenko et al. [1971] was adopted for modeling the industrial scale methane steam reformer. The rate equation is as follows:

$$R_1 = \frac{k_1 P_{CH_4} P_{H_2O} [1 - P_{CO} P_{H_2} / (K_{p1} P_{CH_4} P_{H_2O})]}{P_{H_2O} + l_2 P_{H_2} + l_3 P_{H_2}^3} \quad (4)$$

Where, $k_1 = 2.38 \times 10^2 T^{-3} \exp[-33720/RT]$, cm³(STP)/(m²·h·atm)

$$l_2 = 8.12 \times 10^3 T^{-3} \exp[19520/RT], \text{ atm}^{-1}$$

$$l_3 = 1.82 \times 10^7 T^{-6.5} \exp[46700/RT], \text{ atm}^{-2}$$

According to the brochure of HTAS regarding the catalyst R-67-7H, the Ni surface area and bulk density of catalyst range from 3,500-5,000 m²/kg and 900-1,000 kg/m³. In order to convert the unit of k_1 into kmol/m³·h·atm, it is necessary to multiply the factor of 0.18 by average values of Ni surface area and bulk density in the above equation.

The rate equation for CO-shift reaction is as follows as Sosna et al. [1989].

$$R_2 = k_2 P_{CO} [1 - P_{CO_2} P_{H_2} / (K_{p2} P_{CO} P_{H_2O})] \quad (5)$$

2. Channel Model for Tubular Reformer

The schematic diagram for the heat exchanger type reformer is shown in Fig. 1. The feed (natural gas and steam mixture), which is introduced to the top of reformer, flows through the tubular reformer. The steam reforming reaction takes place through the catalyst bed inside the tube while the hot gas passes through the annular space between reformer tube and cover tube. The hot gas from the secondary reformer is introduced at the bottom of the reformer shell. The product gases from reformer tubes are collected in the header located at the top of the reformer and get out from the reformer. Because the reaction heat is supplied in the radial direction from the tube wall, temperature gradients may be developed in the radial direction due to the consumption of heat as the reaction is occurring. Whereas, the steam methane reaction rate depends on the temperature and a molar concentration gradient in the radial direction may develop. It is necessary to analyze the heat transfer and molar diffusion in the radial direction.

Therefore, the present model was developed under the concept that the cross-section of the reformer tube is divided into several concentric circles and the increase in radius of concentric has to be equal. The increment of radius, dr , is equivalent to the volumetric diameter of catalyst particle to have a physical meaning of channel size, because the reactions are performed inside of the catalyst par-

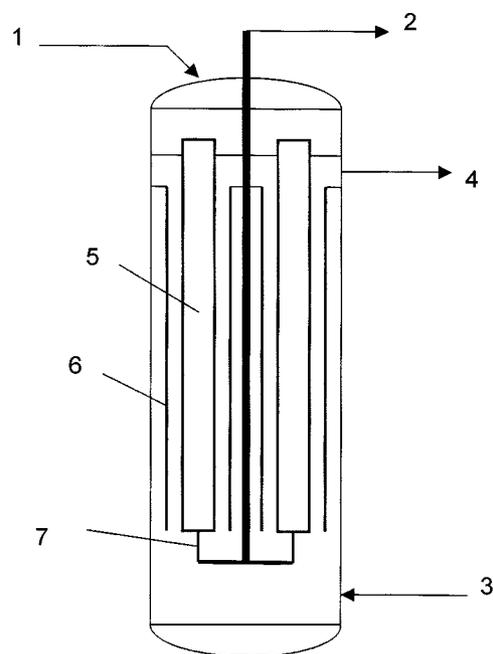


Fig. 1. Schematic diagram of heat exchanger type reformer.

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|-------------------|-------------------|
| 1. Feed gas | 5. Reformer tubes |
| 2. Product gas | 6. Cover tubes |
| 3. Hot gas inlet | 7. Pigtaills |
| 4. Hot gas outlet | |

ticle. Therefore, if we divide the cross-section into $n-1$ concentric circles, n channels exist inside the tube. If we assume that good mixing occurs inside one channel and heat and mass transfer occur at the interface between channels, the mass and heat balances for the j component in i -th channel can be described by following equations, respectively:

$$\Delta N_j^i / \Delta Z = \sum_{k=1}^m \xi_{jk} \eta_k R_k S_i + 2\pi r_{i+1} De_j^{i+1} / \Delta r (C_j^{i+1} - C_j^i) - 2\pi r_i De_j^i / \Delta r (C_j^i - C_j^{i-1}) \quad (6)$$

$$C_p m \Delta T^i / \Delta Z = \sum_{k=1}^m Q_k (1 - \epsilon) R_k S_i + 2\pi r_{i+1} h^{i+1} / \Delta r (T^{i+1} - T^i) - 2\pi r_i h^i / \Delta r (T^i - T^{i-1}) \quad (7)$$

for $i=1, \dots, n$

where, n is defined as an integer value of $R/d_i + 0.5$

Boundary conditions are,

$$\text{At } Z=0, N_j^i = N_j^0 \text{ and } T^i = T_w^0 \text{ for } i=1 \dots n \quad (8)$$

$$\text{At } r=0, De_j^i = 0 \text{ and } h^1 = 0 \quad (9)$$

$$\text{At } r=D_i/2, T^{n+1} = T_w^n, h^{n+1} = h_w \quad (10)$$

The main parameters for estimating the mole flow and temperature along the axial distance from the top are mass transfer coefficients besides the reaction rate. The mass transfer coefficient, De_j for the j component between channels can be defined by the following equation of Sosna et al. [1989]:

$$De_j = 0.28 \times D_j^i + 0.01 Pr^i \times Re^i \quad (11)$$

Molecular diffusivity of j component to bulk phase, D_j^i , can be

obtained by the rule of Blanc's law calculation with the molecular diffusivity of one component j to the other component phases, which was predicted by Sherwood et al. [1975].

On the other hand, the heat transfer coefficient h^i in the catalyst bed can be defined by following equation:

$$h^i = h_v^i + v^i d_i C_p^i C^i / Bo \quad (12)$$

where h_v^i implies the thermal conductivity and radiation heat transfer coefficient.

$$h_v^i = k_g^i + h_r^i \quad (13)$$

Here, the radiation heat transfer coefficient can be calculated by the following equation as defined by Kulkarni and Doraiswamy [1980]:

$$h_r^i = 1.755 \times 10^{-7} T^3 \epsilon d_i + (1 - \epsilon) [1 / (10 k_g) + (1 / 1.755 \times 10^{-7} T^3 \epsilon d_i)] \quad (14)$$

Moreover, the second term of Eq. (12) means the convective contribution to the conductivity in the radial direction caused by flow in the catalyst bed as defined by Westerterp [1986]. According to his study, the Bodenstein Number, Bo can be predicted by the following equation as per the previous researcher.

$$Bo = 8 [2 - (1 - 2(d_i/D_i))^2] \quad (15)$$

In order to calculate the heat transfer coefficient between inside tube wall and catalyst bed, the following correlation equation was adopted.

$$Nu_w = 0.09 Re_w^{0.8} Pr^{1/3} \quad (16)$$

Where, $Re_w = 2\Delta r \rho_g V / \mu$

From the above Eq. (16), the heat transfer coefficient between tube wall and n -th channel can be calculated.

In order to supply the reaction heat by the hot gas from secondary reformer, a countercurrent double pipe heat exchanger was adopted. Therefore, the hot gas from secondary reformer passes upward through the annular space between cover tube and reformer tube and then is cooled down. However, for the sake of simplicity, the heating gas would be considered to be heated from the outlet gas temperature up to the inlet temperature of the hot gas from the secondary reformer. For the hot gas from the secondary reformer, the heat transfer can be considered as follows.

$$C_{p, hg} m_{hg} \Delta T_{hg} / \Delta Z = q_1 + q_2 \quad (17)$$

Where, q_1 means the heat transfer from hot gas to reaction tube.
 q_2 means the heat transfer from hot gas to cover tube.

Therefore, q_1 and q_2 can be defined by the following equations, respectively, considering radiation heat transfer:

$$q_1 = (h_{c,1} + h_{r,1}) \pi D_o (T_g - T_{w,o}) \quad (18)$$

$$q_2 = (h_{c,2} + h_{r,2}) \pi D_c (T_g - T_c) \quad (19)$$

It can be considered that all of the heat transfer from the hot gas to the cover tube by Eq. (19) is transferred to the reformer tube by radiation.

$$q_2 = (h_{c,2} + h_{r,2}) \pi D_o (T_g - T_c) = h_{r,3} \pi D_c (T_c - T_{w,o}) \quad (20)$$

Therefore, the equation can be expressed in terms of $T_{w,o}$, T_g and

heat transfer coefficients.

The convective heat transfer coefficient $h_{c,1}$ between the hot gas and the reformer tube wall and the convective heat transfer coefficient $h_{c,2}$ can be calculated by following equations [Bloch, 1967].

$$Nu_1 = 0.86 (Do/Dc)^{-0.16} 0.0186 Re_c^{0.8} \quad (21)$$

Where, $Nu_1 = (Dc - Do) h_{c,1} / 2k_g$

$$Nu_2 = [1 - 0.14(Do/Dc)^{0.6}] 0.0186 Re_c^{0.8} \quad (22)$$

Where, $Nu_2 = (Dc - Do) h_{c,2} / 2k_g$

The radiation heat transfer coefficients can be calculated with the emissivity as follows,

$$h_{r,1} = 4.9 \times 10^{-8} (\epsilon_w + 1) \epsilon_g T_g^3 [(1 - (T_{w,o}/T_g)^{3.6}) / 2(1 - T_{w,o}/T_g)] \quad (22)$$

$$h_{r,2} = 4.9 \times 10^{-8} (\epsilon_c + 1) \epsilon_g T_g^3 [(1 - (T_c/T_g)^{3.6}) / 2(1 - T_c/T_g)] \quad (23)$$

$$h_{r,3} = 4.9 \times 10^{-8} (1 - \epsilon_g) \epsilon_c \epsilon_g T_c^3 [(1 - (T_c/T_g)^{3.6}) / (1 - T_c/T_g)] \quad (24)$$

Throughout the above equations, the temperature profiles of the reformer tube, cover tube, reaction gas and hot gas can be obtained for tube length with an increase of length by 0.01 m.

RESULTS AND DISCUSSION

1. Model Verification

The model developed in this study includes all possible phenomena taking place in the heat exchanger type reformer through a rigorous heat and mass transfer analysis as well as the kinetic equation by Khomeiko et al. [1971].

In order to verify this model, data from an industrial scale heat exchanger type reformer, which was used in ammonia production in China, and predicted values by this model are presented in Table 1.

First, from the top of the catalyst bed, the mass and heat balance equations for each channel are numerically solved with an increase of length until the heating gas temperature, T_g is the temperature of heating gas from the secondary reformer, $T_{g,in}$.

The accuracy of the model is proved by the actual results as shown in Table 1. The predicted methane content in the product is very accurate, 25.97%, compared with the actual content, 25.71%, with a difference of 0.28%, and for CO_2 by 0.8%. This result is better than the results by Elnashaie et al. [1992].

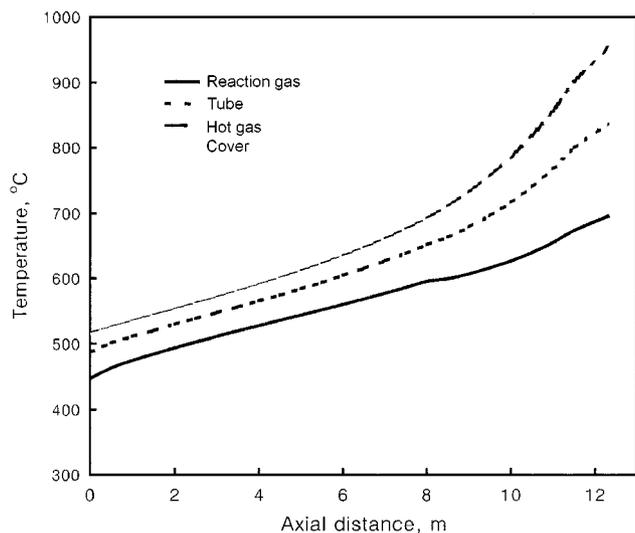
Though the steam reforming reaction tends to reach the equilibrium state, the actual product composition has a gap from its chemical equilibrium state at the outlet temperature. While the equilibrium constant can be calculated from the actual product composition, the equilibrium temperature can be deduced from the equilibrium constant because the equilibrium constant is a function of temperature. The approach temperature is defined as the difference between actual temperature and equilibrium temperature. Therefore, the approach temperature represents the catalyst activity. Throughout the operation results, the approach temperature to the equilibrium for methane conversion is 7.6 °C.

2. Temperature Profiles

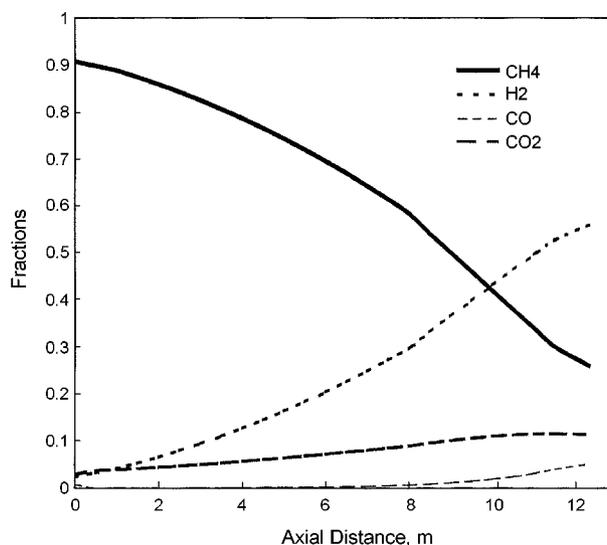
The temperature profiles of the reaction gas, tube temperature, hot gas and cover tube are shown in Fig. 2. Even though the temperature of the cover tube is close to that of hot gas, the radiation heat transfer from cover tube to reformer tube for total heat flux is

Table 1. Comparison between plant data and model predictions

Reformer tubes:	Effective tube length=12.3 m Number=168 Inner/outer diameter=0.102/0.114 m	
Cover tubes:	Inner diameter=0.135 m	
Process gas:	Natural gas with following composition (vol% dry basis): CH ₄ 83.66%, C ₂ H ₆ 11.76%, C ₃ H ₈ 0.95%, C ₄ H ₁₀ 0.11%, C ₃ H ₁₂ 0.01%, N ₂ 3.51%	
Feed conditions:	Feed temperature, T ^m =439 °C Feed pressure, P ^m =2.5 Mpa Natural gas flow rate=10,877 Nm ³ /h S/C ratio=2.78	
Hot gas data:	Inlet temperature=955 °C Outlet temperature=515 °C Composition (vol%, wet basis) CH ₄ 0.29%, CO 7.75%, CO ₂ 6.69%, H ₂ 35.73%, N ₂ 14.42%, H ₂ O 35.12% Flow rate=83,226 Nm ³ /h Pressure=2.2	
Outlet condition	Plant data	Model predictions
Temperature, °C	694	696.5
Pressure, MPa	2.40	2.44
Product composition (dry basis), %		
CH ₄	25.71	25.97
CO	4.73	5.21
H ₂	55.43	56.01
CO ₂	12.26	11.46
N ₂	1.85	1.35

**Fig. 2. Temperature profiles along the axial distance from the top of reformer tube.**

15% at the bottom of the tube and 5.5% at the top of the tube of heat flux according to the calculation results. Therefore, radiation heat transfer should not be ignored for modeling of the heat exchanger type reformer because of high temperature operation. The temperature difference at the bottom of the reformer is higher than

**Fig. 3. Profiles of mole fractions along the axial distance from the top of reformer.**

that at the top of the reformer, which means that the much more methane steam reaction (1) takes place at the bottom of the reformer of the high temperature region. The temperature profile is a typical one for a countercurrent exchanger system with reaction. Furthermore, the predicted temperature of the product gas is accurate compared with the actual data; therefore, this model can be considered as reasonable.

From this temperature profile both of the cover tube and reformer tube, the thickness of the reformer tube can be determined for the purpose of cost reduction.

3. Mole Fraction Profiles

The predicted mole fractions of CH₄, H₂, CO₂, CO along the axial distance are shown in Fig. 3. The methane fraction decreases gradually by 6 meters and its decrease becomes greater over 8 meters. This trend is different from the result by Xu and Froment [1989b]. Because they calculate the heat transfer with the constant flame temperature and overall heat transfer coefficient, the conversion rate of methane along the axial distance is different. As can be seen in this figure, the CO content is very low up to 8 meters, because the shift reaction goes to equilibrium easily as reported by Khomenko et al. [1971]. However, the CO₂ fraction would not increase further over 11 meters, because the CO-shift reaction is exothermic, while the hydrogen content increases further because the methane steam reaction is endothermic.

4. Effectiveness Factor

Many researchers [Namaguchi and Kikuchi, 1988; Twigg, 1989; Xu and Froment, 1989b; Elnashaie et al., 1992] have reported the effectiveness factor for industrial nickel catalysts. Namaguchi and Kikuchi [1988] reported that the effectiveness factor has a value of 0.05-0.065. Twigg [1989] reported that the effectiveness factor may, depending on condition, only be as high as 0.3 at the inlet region and as low as 0.01 at the exit. However, Xu and Froment [1989b] and Sosna et al. [1989] reported that the effectiveness factor for methane conversion has a value of 0.015-0.025. The effectiveness factor for CO₂ reaction has discontinuity and shows minus values due to the reverse direction of this reaction. However, Elnashaie et

al. [1992] reported that the effectiveness factor has values ranging from 0.045 to -0.08 along the axial distance after they eliminated the CO-shift reaction.

The effectiveness factor for methane reaction in this study can be obtained as 0.04 by 8 meters from the top of the reformer tube and 0.12 over 8 meters, using the wolf algorithm with initial guess in order to match all calculated values with industrial data.

This value enables one to predict the inlet and outlet data of industrial plant. It can be considered the reason why the effectiveness factor increase at the bottom of reformer is induced from the different heating system compared with conventional fired heater type reformer. Moreover, the effectiveness factor for methane steam reforming is close to its definition because the kinetic equation of Khomeenko et al. [1971], which is applied to this model, is based on no mass transfer effect.

CONCLUSIONS

The model developed in this study was verified with the data from an industrial scale reformer that is operating in the ammonia industry. This model is accurate and reasonable for predicting the profiles of each temperature and mole fractions along the axial distance. Furthermore, radiation heat transfer is important for predicting accurate temperature profiles as well as the heat transfer rate. This model can be used with high confidence to design an industrial heat exchanger type reformer.

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NOMENCLATURE

Bo	: Bodenstein Number [$C C_p V d_p / \epsilon k_g$]
C	: molar concentration [kmol/m^3]
C_p	: heat capacity of gas mixture [$\text{kcal}/^\circ\text{C}\cdot\text{kg}$]
D	: molecular diffusivity to bulk phase [m^2/h]
De	: effective diffusivity in radial direction [m^2/h]
Dc	: inside diameter of cover tube [m]
Di	: inside diameter of reformer tube [m]
Do	: outside diameter of reformer tube [m]
d_v	: volumetric diameter of catalyst particle [m]
h	: heat transfer coefficient between channels [$\text{kcal}/\text{m}^2\cdot^\circ\text{C}\cdot\text{h}$]
h_r	: radiation heat transfer coefficient [$\text{kcal}/\text{m}^2\cdot^\circ\text{C}\cdot\text{h}$]
h_c	: convection heat transfer coefficient [$\text{kcal}/\text{m}^2\cdot^\circ\text{C}\cdot\text{h}$]
k	: intrinsic rate constant of reaction [$\text{kmol}/\text{m}^3\cdot\text{h}\cdot\text{atm}$]
k_g	: thermal conductivity of gas [$\text{kcal}/\text{m}^\circ\text{C}\cdot\text{h}$]
K_p	: equilibrium constant of reaction
N	: mole flow rate [kmol/h]
Nu	: Nusselt Number
Q	: reaction heat [kcal/m^3]
Pr	: Prandtl Number
q	: heat transfer rate [$\text{kcal}/\text{m}\cdot\text{h}$]
r	: channel radius [m]
R	: reaction rate [$\text{kmol}/\text{m}^3\cdot\text{h}$]

Re	: Reynolds Number in channel, $2 \Delta r \rho_g V/\mu$
Re_c	: Reynolds Number for double pipe, $(D_c - D_o) \rho_g V/\mu$
S	: cross-sectional area of channel [m^2]
T	: temperature [K]
Z	: axial distance from the top [m]

Greek Letters

ζ_{jk}	: stoichiometric coefficient of component, j in the k-th reaction
ϵ	: catalyst bed porosity or emissivity
η	: effectiveness factor

Subscripts and Superscripts

c	: cover tube
g	: gas
i	: i-th channel number
j	: j-th component
k	: reaction number
w	: tube wall
1	: from hot gas to reformer tube
2	: from hot gas to cover tube
3	: from cover tube to reformer tube

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