



Article A Computational Analysis of a Methanol Steam Reformer Using Phase Change Heat Transfer

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Abstract: A methanol steam reformer converts methanol and steam into a hydrogen-rich mixture through an endothermic reaction. The methanol reformer is divided into a reaction section and a heat supply section that transfers thermal energy from 200 to 300 °C. This study presents the behavior of the methanol steam reforming reaction using the latent heat of the steam. A numerical analysis was separately conducted for two different regimes assuming constant heat flux conditions. A methanol steam reformer is an annulus structure that has a phase change heat transfer from an outer tube to an inner tube. Different from the steam zone temperature in the tube, the latent heat of steam condensation decreases, and there is a gradual between-wall temperature decrease along the longitudinal direction. Since the latent heat of steam condensation is very sensitive to the requested heat from the reformer, it is necessary to consider a refined design of a methanol reformer to obtain a large enough amount of heat by steam condensation.

Keywords: computational analysis; high-pressure methanol steam reformer; phase change heat transfer; high pressure steam condensation; hydrogen production

1. Introduction

The exhaust gases from hydrocarbon fuel exacerbate global warming, which has triggered an economy based on hydrogen. Since global warming can be reduced with highly efficient power plants, new types of power plants have also been introduced in the world. Hydrogen energy has the advantage of having a high energy density, low pollutants emission, and fuel flexibility via various sources.

As of yet, the mass production of hydrogen is done by a chemical reaction requiring hydrocarbons. Hydrocarbon-based fuel-producing methods are the steam reforming process, partial oxidation process, and autothermal reforming process. Among them, the steam reforming process is not only economical but also relatively high efficient. The methanol reformer is known for its high energy density per volume, safety, and long-term durability through proper maintenance [1,2]. Various applications are examined such that the methanol reformer is applied to the fuel cell vehicle in the Necar 3 (1997) and Necar 5 (2000). Another application of methanol reformers is a portable fuel cell as a micro-reformer that is used for laptop computers and military robots. Different from the above, the methanol reformer is also used for a high-temperature stationary PEMFC(Proton Exchange Membrane Fuel Cell), which is known to be more tolerable to CO poisoning [3].

The methanol reformer is also applied to an air independent power propulsion system for submarines [4]. Since methanol is safer than hydrogen, it is very attractive to satisfy the requirements of military operations. Prior to methanol reformers, metal hydride was used to store hydrogen for fuel cells. Compared with metal hydride, methanol reformers have longer durability and a larger capacity of energy storage. Since the methanol is reformed for submarines, the operating pressures are very high. Even though the high pressure prevents a highly efficient conversion operation, it is necessary to work the reformer at that pressure to conceal the submarine from an external signature.

Several studies have been done in the field of the methanol steam reforming reaction. Amphlett et al. performed experiments on methanol conversion and reported that methanol conversion increased as the molar number of water vapor increased [5]. Reiyu Chein et al. conducted a numerical study on the steam reforming reaction and identified the mole fractions of methanol, hydrogen, and carbon monoxide in the reforming process [6]. This confirms the validity of numerical analysis for the methanol steam reforming reaction. Additionally, Ataallah et al. developed a three-dimensional model using CFD to study some parameters and features that affect the performance of a methanol steam reforming reaction at constant inlet mass flow rates and velocities varies with the channel dimensions and operating conditions. Shuji et al. investigated the behavior of catalyst materials, sheet paper containing SiC fibers, catalyst powders, and catalyst pellets, under different space velocities (SV) in the methanol steam reforming reaction [8].

On the other hand, Ji et al. reported on the steam reforming of methanol using phase change heat transfer [9,10]. Since the methanol steam reforming temperature ranges from 200 to 300 °C, they had to select an appropriate phase change medium for the temperature range. The phase change medium of their methanol steam reformer was deionized water, and the temperature and pressure of the phase change process were determined by the operating condition of the methanol steam reforming process. This idea is novel, and they experimentally evaluated the performance of the methanol reformer; however, the operating mechanism still needs to be examined. They also show that the high-pressure operation of the methanol steam reforming reaction produces a high concentration of carbon monoxide. They also pointed out that the concentration of carbon monoxide can be significantly reduced with the increasing SM (Steam to Methanol) ratio [11].

In particular, since the reaction mechanism comprises important parameters, the reaction kinetics are widely studied and reported [1–8]. However, most of the methanol steam reforming processes in literature are heated by the combustion of fuel or hot gases. There are scarce reports about the methanol reforming process with phase change heat transfer. Additionally, since the phase change of water around 200 to 300 °C requires very high vapor pressure, it is very difficult to find an experimental or numerical study of the methanol steam reforming process with phase change heat transfer.

In this study, a computational analysis was performed to investigate the behavior of a high-pressure methanol steam reforming process with phase change heat transfer. The water vapor condensation and the methanol steam reforming reaction take place in a hollow tube. Since the temperature of the phase change medium in the radial direction is varied and in the longitudinal direction as well, the methanol steam reforming reaction is closely linked to those temperature distributions. The computational sections are divided into two different regimes: one for phase change heat transfer and the other for the methanol steam reforming process.

2. Simulation Model

The methanol steam reforming process with phase change heat transfer is conducted in annulus tubes that layer two different sizes of tubes in the same center. The methanol and the steam flow into the inner tube, and superheated steam flows into the outer tube. The flow arrangement is a parallel flow. The methanol steam reformer has two compartments, which require two different analysis schemes. One is dominated by a two-phase flow, and the other is dominated by the methanol steam reforming process in porous media. Figure 1 shows the geometric information of the computational

analysis. There is a methanol steam reforming zone inside of the hollow tube, and heat is supplied from the outer tube to the reaction zone by the phase change of the steam. The flow direction of the reformer zone and phase change zone is parallel. The total height of the tube is 700 mm, and the thickness between the inner shell and outer shell is 2.1 mm. Since heat is transferred from the outer shell to the inner shell, it is observed that the outer surface of the inner shell has condensed vapors on it. The other conditions are summarized in Table 1.



Parameters	Dimension	Unit	Expression
T1	280	°C	Inlet temperature
Ts	279.9616	°C	Saturation temperature
P1	64.1646	bar	Inlet pressure of steam condensation zone
P2	30	bar	Inlet pressure of reaction zone
L	70	mm	Total length
Lt	2.1082	mm	Tube thickness
r1	2.9464	mm	Inlet radius of heat source zone
r2	10.5918	mm	Inlet radius of reaction zone
R	15.6459	mm	Total radius
ρ	8055	kg/m ³	Density of solid tube
C _p	480	J/kgK	Specific heat of solid tube
k	15.1	W/mK	Thermal conductivity of solid tube

Figure 1. Geometry of methanol steam reformer for numerical computation.Table 1. Geometric and operating parameters of numerical computation.

Since the vapor flow goes down by gravity, water vapor condenses on the inner surface of the outer tube. When the temperature of the water vapor meets a vapor saturation state, water droplets cover the outer tube, which act as heat transfer resistance.

2.1. Reaction Kinetics

The reaction kinetics of the methanol steam reforming process have been widely investigated. The following three processes are known to be the main reactions of the methanol steam reforming reaction [10–16]. The methanol steam reforming reaction is described by three elementary reactions:

methanol steam reforming reaction (SR), methanol decomposition (MD), and water gas shift (WGS) reaction.

Methanol steam reforming reaction (SR)

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \tag{1}$$

Water gas-shift reaction (WGS)

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

Methanol decomposition reaction (MD)

$$CH_3OH \rightarrow CO + 2H_2$$
 (3)

The Arrhenius equation is applied to calculate the chemical reaction rate. The basic form of the Arrhenius equation is as follows:

$$\mathbf{k} = A \times exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

where E_a is the activation energy, A is the pre-exponential factor, and k is the reaction rate constant. The kinetics constants of the methanol steam reforming reaction at 200 to 300 °C are shown in Table 2 [14–17].

Table 2. Constants of the Arrhenius equation for methanol steam reforming reaction.

Reaction Step	A [kmol/m ³ s]	E _a [kJ/mol]	Reaction Name
$\rm CH_3OH \rightarrow \rm CO + 2H_2$	1.43×10^9	1.22×10^8	Methanol decomposition reaction
$CO + H_2O \rightarrow CO_2 + H_2$	5.115×10^7	8.77×10^{7}	Water-gas shift reaction
$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$	2.002×10^{9}	9.27×10^7	Steam reforming reaction

2.2. Governing Equations

The gas mixture of the methanol and steam flows through the inner tube, and the steam reforming reaction is progressed. The governing equations are as follows:

Continuity equation

$$\nabla \cdot (\rho \nu) = 0 \tag{5}$$

Momentum equation

$$\nabla \cdot (\rho \nu \nu) = -\nabla \rho + \nabla \cdot (\overline{\tau}) + \rho g \tag{6}$$

Energy balance equation

$$\nabla \cdot (v(\rho E + p)) = \nabla \cdot K_{eff} \nabla T - \sum h_i J_j + S_h$$
(7)

$$E = h - \frac{p}{\rho} + \frac{v^2}{2}, \ h = \sum_i Y_i h_i$$
 (8)

$$h_j = \int_{T_{ref}}^T C_p \, dT, \ \overline{J_j} = -\left(rD_{j,m} + \frac{\mu_t}{Sc_t}\right) \nabla Y_j, \ k_{eff} = k + \frac{c_p\mu_t}{Pr_t}, \ S_h = -\sigma_j \frac{h_j^0}{M_i} R_j.$$
(9)

The reforming zone is filled with a catalyst. The reaction zone is set up to be porous media, and the catalytic reaction on the surface of the pellet is simulated by chemical kinetics. It is assumed that the porous media is charged homogenously, and the flow is laminar. Darcy's law is used to determine the internal velocity.

$$\Delta p = C_2 \frac{1}{2} \rho \Delta nv^2 + \frac{1}{\alpha} \Delta nv\mu \tag{10}$$

Darcy's law is represented by the sum of the inertial resistance and the viscous resistance. In addition, the porosity should be set and expressed as r in the following equation.

$$k_{eff} = \gamma k_f + (1 - \gamma)k_s \tag{11}$$

The porosity (*r*) is the ratio of the fluid volume to the total volume. The effective heat transfer coefficient (k_{eff}) is determined by the sum of k_f , the heat transfer coefficient in the fluid zone, and k_s , the heat transfer coefficient in the solid zone. On the other hand, saturated steam flows into the empty space in the outer tube, and the condensation condition is determined by the steam pressure and temperature. When the steam is induced, the pressure is set as 64.16 bar and the saturation temperature is set to 279.96 °C (553.11 K). When the endothermic reaction takes place in the reaction zone, the heat absorption results in the condensation of the steam. The vapor condensation is calculated by the Eulerian Lee model [14]. The liquid–vapor mass transfer (evaporation and condensation) is governed by the vapor transport equation.

$$\frac{\partial}{\partial t}(\alpha_v \rho_v) + \nabla \cdot \left(\alpha_v \rho_v \vec{v_v}\right) = \dot{m}_{lv} - \dot{m}_{vl} \tag{12}$$

Here, \dot{m}_{lv} and \dot{m}_{vl} are the rates of mass transfer due to evaporation and condensation, respectively. In the evaporation–condensation problem, mass transfer from the liquid to vapor is a positive mass transfer, and the units of Equation (11) are in kg/s/m³. The mass transfer rate on the right hand side of Equation (11) is defined as follows:

If
$$T_l > T_{sat}(evaporation), \ \dot{m}_{lv} = coeff \times \alpha_l \rho_l \frac{(T_l - T_{sat})}{T_{sat}}$$
 (13)

If
$$T_v < T_{sat}(condensation), \ \dot{m}_{vl} = coeff \times \alpha_v \rho_v \frac{(T_{sat} - T_v)}{T_{sat}}.$$
 (14)

Here, α and ρ are the phase volume fraction and density, respectively. *coeff* is a coefficient that must be tuned finely and can be interpreted as a relaxation time. The volume fractions represent the space occupied by each phase. The volume V_c of phase q is defined as follows.

$$V_q = \int \alpha_q dV \tag{15}$$

$$\sum_{q=1}^{n} \alpha_q = 1. \tag{16}$$

The effective density of *q* is expressed as follows.

$$\hat{\rho}_q = \alpha_q \rho_q. \tag{17}$$

In the above expression, ρ_q is the physical density of phase *q*. In addition, the governing equation on *q* is as follows.

Continuity equation

$$\frac{\partial}{\partial t} (\alpha_q \rho_q) + \nabla \cdot (\alpha_q \rho_q \vec{v_q}) = \sum_{p=1}^n (\dot{m}_{pq} - \dot{m}_{qp}) + S_q$$
(18)

Here, v_q is the velocity of phase q, \dot{m}_{pq} characterizes the mass transfer from the *p*th to *q*th phase, and \dot{m}_{qp} characterizes the mass transfer from phase q to phase p.

The momentum balance equation for phase *q* yields

$$\frac{\partial}{\partial t} \left(\alpha_q \rho_q \vec{v}_q \right) + \nabla \left(\alpha_q \rho_q \vec{v}_q v_q \right) = -\alpha_q \nabla p + \nabla \tau_q + \alpha_q \rho_q \vec{g} + \sum_{p=1}^n \left(\vec{R}_{pq} + \dot{m}_{pq} \vec{v}_{pq} - \dot{m}_{qp} \vec{v}_{qp} \right) + \vec{F}_q + \vec{F}_{lift,q} + \vec{F}_{vm,q}.$$
(19)

This is the momentum balance equation for phase *q* where τ_q is the *q*th phase stress–strain tensor.

$$\tau_q = \alpha_q \mu_q \left(\nabla \vec{v}_q + \nabla \vec{v}_q^T \right) + \alpha_q \left(\lambda_q - \frac{2}{3} \mu_q \right) \nabla \cdot \vec{v}_q I \tag{20}$$

Here, τ_q and μ_q are the shear and bulk viscosity of phase q; \vec{F}_q is an external body force; $\vec{F}_{lift,q}$ is a lift force; $\vec{F}_{vm,q}$ is a virtual mass force; \vec{R}_{pq} is an interaction force between the phases, and p is the pressure shared by all the phases.

Lift forces act on a particle mainly due to velocity gradients in the primary phase flow field. The lift force will be more significant for larger particles, but the ANSYS Fluent[®] model assumes that the particle diameter is much smaller than the inter-particle spacing [14]. Thus, the inclusion of lift forces is not appropriate for closely packed particles or for very small particles. The lift force acting on a secondary phase p in a primary phase q can be calculated by the formula below.

$$\vec{F}_{lift} = -C_l \rho_q \alpha_p \left(\vec{v}_q - \vec{v}_p \right) \times \left(\nabla \times \vec{v}_q \right)$$
(21)

The inertia of the primary-phase mass encountered by the accelerating particles (or droplets or bubbles) exerts a "virtual mass force" on the particles. The virtual mass force is as follows.

$$\vec{F}_{vm} = C_{vm} \alpha_p \rho_q \left(\frac{d_q \vec{v}_q}{dt} - \frac{d_p \vec{v}_p}{dt} \right)$$
(22)

 \vec{R}_{pq} depends on the fiction, pressure, cohesion, and other effects. \vec{v}_{pq} is the interphase velocity, which is defined as follow. If $\dot{m}_{pq} > 0$, then $\vec{v}_{pq} = \vec{v}_p$, If $\dot{m}_{pq} < 0$, then $\vec{v}_{pq} = \vec{v}_q$. Likewise, If $\dot{m}_{qp} > 0$ then $\vec{v}_{pq} = \vec{v}_q$. If $\dot{m}_{qp} < 0$ then $\vec{v}_{pq} = \vec{v}_q$.

2.3. Computational Methods and Boundary Conditions

Meshes are shown in Figure 2. The solver is a pressure-based solver, and a transient analysis was conducted. Additionally, axisymmetric computation was used to facilitate the analysis. The condensation/evaporation model is a Eulerian Lee Model which is provided by ANSYS Fluent[®]. At the wall of the outer tube, the adiabatic condition was applied for the heat transfer, and wall conditions were also selected for the momentum. Another adiabatic condition was set up along the symmetric axis. At the inter-wall between the inner tube and outer tube, a boundary condition was set up.



Figure 2. Meshes and domains for computational analysis.

Generally, the inner tube and outer tubes were set up to be two computational domains. However, because it is very difficult to solve the computation of two different physics simultaneously in the commercial software ANSYS fluent[®], this study separated the computation of those physics one by one by selecting coupling boundary conditions.

The Eulerian Lee model requires fine tuning of the parameters, which is known as a frequency factor [18]. The frequency factor affects the condensation or evaporation mass transfer rate that is empirically determined. Accordingly, it is necessary to tune the frequency factor so that the phase change mass transfer rate is reasonably determined. This is a clue to tune the model so that the proper heat flux determines the heat transfer coefficients and surface temperature.

At first, the constant heat flux conditions were the boundary condition of the inner tube side of the inter-wall. The first domain was the steam reforming zone, and the second domain was the solid tube. When the methanol steam reforming reaction progresses through the inner tube, it is assumed that a constant heat flux is absorbed from the steam condensation zone.

When the constant heat flux is acting on the surface of the inner wall, the inter-wall temperatures is T_s which is the surface temperature of the phase change zone, and the inner wall temperature is T_i which is the surface temperature of the steam reforming zone. Those notations are also found in Figure 1. The constant heat flux boundary conditions were set up to be 1, 2.5, and 5 kW. Equation (22) explains the heat transfer correlation with the induction of the constant heat flux from the wall. T_s , T_i , and h are unknowns, and h is a function of T_s . The methanol and steam mixture temperature through the inner tube and steam temperature through the outer tube were varied in the longitudinal direction. The heat transfer rate should be calculated by the log mean temperature difference (LMTD). It is assumed that the steam is not fully condensed throughout the outer tube. Then, the steam temperature of the outer tube should be maintained. Then, the heat transfer rate is explained as follows:

$$q_w = \frac{2\pi Lk(T_s - T_i)}{\ln\left(\frac{r_o}{r_i}\right)} = \bar{h}A_s \,\vartriangle\, T_{lm} \left(T_\infty = \text{constant}\right) \tag{23}$$

$$\Delta T_{lm} = \frac{\Delta T_o - \Delta T_i}{\ln\left(\frac{\Delta T_o}{\Delta T_i}\right)} \tag{24}$$

$$\frac{\Delta T_o}{\Delta T_i} = \frac{T_{steam} - T_{s,o}}{T_{steam} - T_{s,i}} = \exp\left(-\frac{PL}{mc_p}\overline{h}\right) (T_{steam} = \text{constant}).$$
(25)

The convection heat transfer coefficient on the wall of a circular tube is calculated by the following Equation [19].

$$\overline{h} = \frac{Re_{\delta}\mu_l h_{fg}}{4L(T_{sat} - T_s)} \tag{26}$$

where,

$$Re_{\delta} = \left[\frac{3.70k_{l}L(T_{sat} - T_{s})}{\mu_{l}h_{fg}\left(\frac{v_{l}^{2}}{g}\right)^{\frac{1}{3}}} + 4.8\right]^{0.82} (30 \le Re_{\delta} \le 1800).$$

All liquid property should be obtained from the film temperature $T_f = (T_{sat} + T_s)/2$, and h_{fg} should be obtained from T_{sat} . T_s in Equation (25) is calculated by the arithmetic average of T_s in between the inlet and outlet. Since the average heat transfer coefficient \overline{h}_L is calculated by Equations (22) and (25), a new temperature T_s is updated by iteration.

The temperatures in Table 3 were used to determine the frequency factors of each heat flux case. Then, the frequency factor was fixed, and the phase change phenomena were analyzed.

Table 3. Inner wall temperature and inter-wall temperature in terms of constant heat flux conditions.

Heat Rate [kW]	<i>T_s</i> [K]	<i>T_i</i> [K]
1	545.17	542.54
2.5	534.79	527.96
5	514.39	500.73

3. Simulation Results and Discussion

3.1. Phase Change Trends with Surface Heat Absorption

As the heat fluxes were increased, the steam temperature decreased in the radial direction. Condensation was also observed on the surface. Figure 3 shows the steam temperature profile and liquid volume fraction profile in the outer tube. As expected, the near-wall temperature is about 7 K lower for the 1 kW heat absorption. Then, the wall temperature further decreased with a higher heat absorption rate. Near the inter-wall, the steam temperature slope was dramatically decreased due to heat absorption. Then, the steam temperature in the phase change zone rose rapidly to 280 °C, which is the inlet temperature of the steam. Another aspect was the temperature profile in the radial direction. As shown in Figure 3, the near-wall temperature gradient was quite large, and a very thin boundary layer was observed regardless of the absorbed heat. This is because the condensed liquid increases the thermal resistance of the heat transfer. Accordingly, the outer zone from the temperature boundary layer maintained its temperature at the phase change condition.



Figure 3. Vapor temperature and water volume fraction along flow direction (three different heat fluxes as well boundary conditions).

As the heat absorption increased, the liquid volume fraction near the wall is almost 1.0, which implies that the surface is covered with a thin liquid film. The gravity force made the liquid volume fraction boundary layer become thicker along the channel. As steam flows into the outer tube, the liquid volume fraction steeply increased. The more heat is absorbed, the earlier the saturated water is observed through the tube. Then, the liquid volume fraction grew near the inter-wall along the longitudinal direction. It was also shown that most of the area in the outer tube was occupied by saturated steam.

The thermal boundary layer thickness was defined as 0.999 of the free stream temperature, and the liquid volume fraction was defined as 0.999 of the saturated vapor. The results are shown in Figure 4. The thickness of the temperature boundary layer was thinner than the thickness of the liquid volume fraction boundary layer. It shows that the mixture of steam and liquid water stayed on the liquid boundary layer. As observed, the concentration boundary layer is thicker for all the heat absorption rates, and the thickness increased linearly. The thickness difference between the boundary layer is large for the 1 kW heat absorption condition. As the heat absorption rate was increased, the thickness difference between the two boundary layers changed little.

The radial temperature profile is shown in Figure 5. The linear increase zone is the solid inter-wall, and a steep temperature increase was observed from the surface of the inter-wall to the steam zone. The overall steam temperature in the radial direction was mainly constant at the saturated condition. Another observation was the gradual temperature down along the longitudinal direction. Even though the temperature of the steam was maintained, the wall temperature decreased with a higher heat flux. One interesting feature is the steam temperature. The steam temperature was maintained over

the various heat flux conditions, while the wall temperature dramatically changed with the higher heat flux.



Figure 4. Temperature and liquid volume fraction boundary layer thickness at the exit of the outer tube for the three different heat absorption rates.



Figure 5. Evolution of radial temperature profile in terms of the heat fluxes.

The water volume fraction of the outer tube rapidly increased right after inducing the steam, and the water volume fraction was then 1 at the exit. Figure 6 shows the water volume fraction at the inlet and exit. As observed, the water volume fraction at the inlet is steeper with a higher heat absorption rate, and the water volume fraction at the exit is thicker with a higher amount of heat flux.



Figure 6. Water volume fraction near the wall in terms of the heat flux.

The overall liquid fraction of the saturated steam along the outer tube is determined by the integration of the liquid mass over the space. Thermodynamically, the quality is the ratio of the steam mass to the total mass and is calculated as follows.

$$x = \frac{m_g}{m_g + m_f} \tag{27}$$

$$x_w = 1 - x = \frac{m_f}{m_g + m_f} \tag{28}$$

Here, *x* is the quality; x_f is the water mass ratio; m_g is the mass of them steam, and m_f is the mass of the water. Figure 7 shows the total mass ratio of condensed water in the outer tube. As shown, the ratio of condensed water is proportional to the heat flux to the steam reforming process. The ratios of the water mass to the total mass for each heat flux condition were 26.38%, 33.95%, and 40.10%. Accordingly, the volume of the liquid is relatively small, and the mass of the steam is not negligible.



Figure 7. Ratio of water mass to total mass over three different heat fluxes.

The heat absorption from the phase changing steam results in a temperature change on the inter-wall surface. The surface temperature of the inner tube (T_i) is captured in Figure 8. As shown, the surface temperature non-linearly decreased, and the initial temperature was lower than the steam methanol inlet temperature. One reason is from heat transfer through the solid wall. The solid wall is acting as thermal resistance to the heat transfer. Another reason is the condensation of the steam from the inlet. As shown in Figure 4, a significant temperature drop is observed at the near inlet of the phase change zone. The temperature drop results in a lower temperature of the solid surface (T_i) at the inlet of the methanol steam reforming zone.



Figure 8. Inner wall temperature profile along the channel with 2.5 kW heat flux.

3.2. Physical Behavior in the Methanol Steam Reforming Reaction

The temperature profile through the inner tube was determined by the boundary conditions and reaction characteristics. The temperature trends were observed at the 2.5 kW heat flux boundary conditions. Due to the presence of the porous methanol steam reforming catalyst, the temperature profile in the radial direction is almost flat. The longitudinal temperature profile is determined by the temperature profile in Figure 8 and the symmetry condition. Figure 9 shows the temperature profile of the chemical reaction zone. The gas inlet temperature was 553 K, which was a higher temperature than the wall temperature. As observed, the initial gas temperature rapidly dropped due to the temperature difference between the gas temperature and the wall temperature. After the first hill from the higher temperature to the lower temperature, the temperature profiles can be seen in Figure 8. Then, the methanol steam mixture temperature is similar to the wall temperature. The mixture temperature was 553 K at maximum and 527 K at minimum.



Figure 9. Temperature of chemical reaction zone (2.5 kW heat flux).

Methanol steam reforming reaction consists of three reaction mechanism: steam reforming reaction, water gas shift reaction, and methanol decomposition reaction. Those three reactions are traced in Figure 10. As observed, the order of the steam reforming reaction is almost 10^3 times greater than the other two reactions. Accordingly, the products of the reforming reaction will be mainly H₂, CO₂, and H₂O. Another aspect is that the reaction rates decay along the channel. Initially, the reaction rate of the steam reforming reaction was quite high and steeply decreased along the channel. It was observed that the wall temperature profile affects the decay of the methanol decomposition rate. However, the methanol steam reforming reaction rate looks less affected by the wall temperature profile. Instead, the concentration of methanol has a more significant effect on the methanol steam reforming reaction.



Figure 10. Contribution of elementary reaction kinetics along the tube. MD: methanol decomposition, SR: methanol steam reforming reaction, WGS: water gas shift.

Because the steam reforming reaction mechanism dominates the overall reaction, the products are mostly H_2 , CO_2 , and H_2O . Figure 11 shows the mole fraction evolution of the product gases and the decay of methanol. As observed, the concentrations of H_2 and CO_2 gradually increase along the pipe. The maximum mole fraction of H_2 is 0.58, and CH_3OH gradually decreases at the rear end of the reaction zone, resulting in a mole fraction of 0.09. The mole fraction of the reactants CH_3OH and H_2O decreases as the reaction proceeds in the Z direction. Another aspect is the consumption rate of H_2O . As observed, the H_2O concentration decreased over a short time in the frontal regime, and the concentration gradually decreased. Because the hydrogen production is dominated by steam reforming, it was observed that the consumption of water corresponded to the hydrogen concentration.



Figure 11. Cont.



Figure 11. Species concentration of the methanol steam reforming reaction zone. (**a**) Mole fraction of CH₃OH, (**b**) Mole fraction of CO, (**c**) Mole fraction of CO₂, (**d**) Mole fraction of H₂, (**e**) Mole fraction of H₂O.

4. Conclusions

In this study, computational analysis of high pressure methanol steam reforming reaction with the phase change of steam at saturation pressure are conducted.

- (1) High-pressure methanol reforming reaction and high-pressure steam condensation phenomena are connected by constant heat flux conditions. Therefore, two different physical phenomena is explained by transferred heat flux.
- (2) As the heat absorption of methanol steam reforming process results in vapor condensation, the inter-wall temperature between reforming zone and phase change zone is decreased.
- (3) Since the temperature boundary layer is thinner than the liquid volume fraction boundary layer, the steam liquid mixture stays on the liquid water layer.
- (4) The non-linear solid temperature of the inner wall affects the kinetics of the methanol decomposition reaction, but the kinetics of the steam reforming reaction and water gas shift reaction are rarely affected by the non-linear temperature profile of the inner wall.
- (5) Since the overall reaction takes place within narrow radius porous media, the negligible concentration difference is observed through the steam reforming zone.

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