

219 OPERABILITY ANALYSIS OF ADIABATIC WATER SHIFT REACTOR SYSTEMS FOR HYDROGEN GENERATION FOR FUEL CELLS

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In this work, steady-state mathematical models were developed to describe water gas shift (WGS) reactors. Gas cleaning unit includes WGS reactor and preferential reactor which converted carbon monoxide into hydrogen for fuel cell systems in order to prevent ppm level of carbon monoxide poisoning Pt catalyst in the anode side of PEMFCs. WGS reactor systems consisted of WGS reactors and intercoolers. Based on the WGS reactors model, optimization problems were formulated to minimize the reactor volume while maintaining the hydrogen flow rate (3 kW PEMFC used) and CO concentration constraint 0.953 mol%. The WGS reactor structures, single and multiple, were investigated. The optimization procedure was carried out by using SQP method and the optimal variables studied include: reactor inlet temperatures and water feed flowrate. The results show that two WGS reactors in series with an intercooler can reduce the volume of a single reactor by 30.75%. Then, design heuristic was built to provide a quick determination of WGS reactor system flowsheet. From sensitivity analysis, control structures are explored here. The result shows a single WGS reactor system has larger operability range than two WGS reactors in series.

1. INTRODUCTION

Hydrogen can be produced from diverse sources. The main source of hydrogen production is from fossil fuel steam reforming (SR). Syn-gas is used to produce chemicals (eg., Methanol, DME..etc.) by adjusting the H₂/CO ratio with a water shift gas (WGS) reactor. High purity hydrogen, which was used in hydrodesulfurization and hydrogenation, can be obtained with an additional pressure swing adsorption (PSA). It also became a popular energy carrier due to high energy efficiency and zero carbon emission with PEMFC use. The feed of steam reforming can be cataloged into: 1. Alkane (Methane, ethane, nature gas..), 2. Alcohol (MeOH, EtOH...), 3. Hydrocarbons (LPG, diesel...) [1-14]. In order to reduce CO to acceptable levels from syn-gas, gas cleaning units which included WGS and ProX reactors were installed and followed by SR reactors. The no. of WGS reactors in series which are used in fuel processes depends on fuel types, CO removal levels and operating conditions. Few papers discussed the systematic method to determine the no. of WGS reactors in series. In this work, determining the minimum size of WGS was our objective by searching different operating conditions and feed compositions. Control structures were proposed to handle effluent of WGS reactor at

specified CO concentration. Finally, the design heuristic was generated and the operability was studied to find the interaction between design and control.

2. STEAM REFORMING FEEDS

Steam reforming (SR) from fossil fuels can be cataloged into Alkanes, Alcohols and Hydrocarbons. In this section, effluent compositions of steam reformers from fossil fuels were discussed. In order to understand the syn-gas composition distribution, dimensionless groups of WGS feed were defined. Moreover, the equilibrium conversion of WGS can be derived as a function of dimensionless groups and equilibrium constant.

2.1 Sources of Hydrogen Carbons

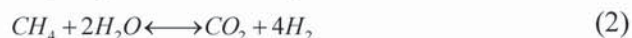
Steam reforming reaction took place with water gas shift reaction in the reactor. Sources of hydrogen carbons were investigated one by one in this section.

2.1.1 Alkane

Alkane steam reforming reaction took place at temperatures over 700 °C in order to completely convert the reactant [1]. The equilibrium conversion of the WGS side reaction decreased due to high temperature operation. Thus, syn-gas of SR reactors has moderate ratios of H₂/CO and CO₂/CO.

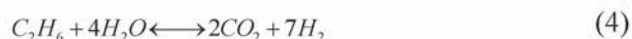
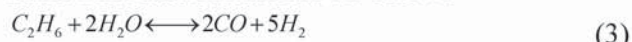
Methane steam reforming(MSR)

MSR is a highly endothermic reaction and can generate syn-gas with high H/C ratio. The reactions are shown as follows:



Ethane steam reforming

Ethane steam reforming has high H₂/C ratio and CO/C ratio. The reactions are shown below:

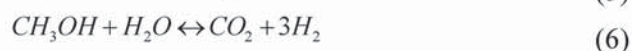


2.1.2 Alcohol

Compared to Alkane, alcohol steam reforming takes place at 200 to 400 °C [1]. High operating temperature reduces the equilibrium conversion of WGS. Syn-gas produced from alcohol steam reforming has higher H₂/C and CO/C ratio.

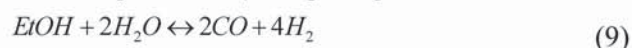
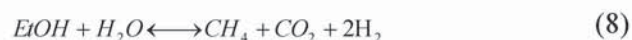
Methanol steam reforming

Methanol is an important industrial solvent. The reactions of methanol steam reforming are shown as follows:



Ethanol steam reforming

Considering the carbon cycle, ethanol which can be produced from bio-mass has a potential to become an energy carrier. Ethanol steam reforming reactions are complex and the main reactions are shown in Eqs. (7-9).



2.1.3 Hydrocarbons

High carbon content hydrocarbons steam reforming generated large CO in the reformer outlet. Its operating temperature is over 900 °C [2]. Equilibrium conversion of WGS decreases due to high temperature operation. Syn-gas composition includes lower H₂/CO and CO₂/CO ratio than Alkane and alcohol.

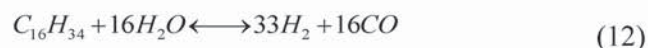
LPG steam reforming

The primary components of LPG are propane and butane. The steam reforming of the two components are listed below:



Diesel Steam Reforming

Diesel is a high carbon content hydrocarbon. The main component of diesel is C₁₆H₃₄ and the reaction is shown below:



2.2 Water Gas Shift Reaction

The purpose of WGS reaction is to increase the H₂/CO ratio of syn-gas. The outlet CO concentration of WGS reactor is normally around 0.5 to 1 %. The number of reactors in series can be varied. The reaction is exothermic and listed below:



2.2.1 Dimensionless Feed Compositions

Syn-gas composition from steam reforming outlet depends on the hydrocarbon type. In order to understand the WGS feed composition effect on reactor design, dimensionless groups were used to represent each feed composition and are shown as follows:

$$\theta_{i,0} = y_{i,0} / y_{CO,0} \quad \text{where } i = H_2O, H_2, CO_2 \quad (14)$$

Where

$\theta_{i,0}$: *i* species to CO mole fraction ratio of WGS feed.

$y_{i,0}$: *i* species mole fraction of WGS feed.

$y_{CO,0}$: CO mole fraction of WGS feed.

2.2.2 Equilibrium Constant

Equilibrium constant (K_{eq}) of WGS reaction can be calculated from Gibbs free energy under standard condition. The equation is shown below:

$$K_{eq} = \exp\left(\frac{-\Delta G_r^0}{RT}\right) \quad (15)$$

Where ΔG_r^0 stands for Gibbs free energy under standard condition. For WGS reaction, its value is 141.86 (kJ/mol). *R* denotes gas constant (kJ/mol-K). *T* is operating temperature (K).

2.2.3 Equilibrium Conversion ($X_{CO,e}$)

When WGS reaction reaches equilibrium, the equilibrium constant can be represented as a function of reactant and product concentrations. Substituting equilibrium conversion ($X_{CO,e}$) and feed dimensionless groups (θ_{H_2O} , θ_{H_2} , θ_{CO_2}), we have:

$$K_{eq} = \frac{(\theta_{CO_2} + X_{CO,e})(\theta_{H_2} + X_{CO,e})}{(1 - X_{CO,e})(\theta_{H_2O} - X_{CO,e})} \quad (16)$$

From the above equation, the relationship between X_{CO} and θ_{H_2O} , θ_{H_2} , θ_{CO_2} can be evaluated.

Figure 1 shows WGS equilibrium conversion with different steam reforming outlet compositions. For Alkane, the moderate levels of θ_{H_2O} , θ_{H_2} and θ_{CO_2} caused the equilibrium conversion of WGS reaction within a range of 70 to 90 %. Alcohol has highest θ_{H_2O} , θ_{H_2} and θ_{CO_2} , and caused equilibrium conversion within a narrow range of 75 to 85 %. Hydrocarbons have smaller θ_{H_2O} , θ_{H_2} and θ_{CO_2} due to higher operating temperature and greater water requirement. The

equilibrium conversion has a wider range of 55 to 90 %.

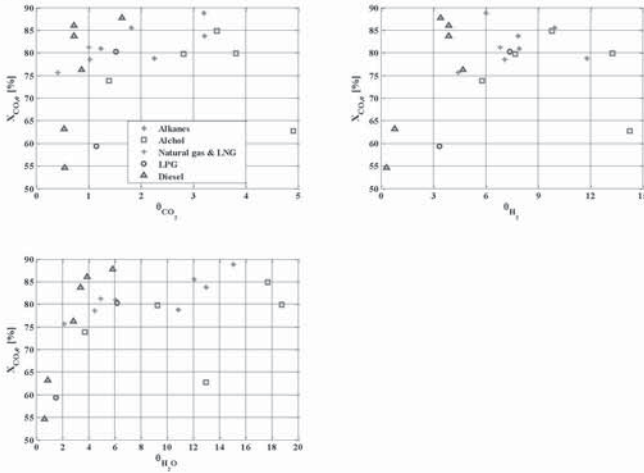


Fig. 1 The dimensionless feed composition of water gas shift reactions[3-14]

3. WGS REACTOR SYSTEMS DESIGN

In this section, we discussed adiabatic WGS reactor design. WGS reactor systems were built to validate MSR experiment data [3]. Considering fuel processors efficiency, the most compact WGS reactor systems were designed. Moreover, syn-gas compositions varied with different hydrocarbons sources steam reforming. WGS reactor systems design was affected by feed dimensionless groups. The general WGS reactor systems design rule was generated as a future design guide.

3.1 Modeling

Aspen Plus Tech. Software was used in this research. Peng- Robinson equation of state was chosen as our thermodynamic model. WGS reactor model used Rplug. The pressure drop along the WGS reactor was set at 0.1 psig, therefore a honeycomb support coated Pt catalyst was used.

The rate law of WGS reaction with Pt catalyst is shown as follows [3]:

$$r_{WGS} = k_w (P_{CO} P_{H_2O} - \frac{P_{CO_2} P_{H_2}}{K_{eq}}) \quad (17)$$

where r_{WGS} is reaction rate (mol/min/kg-cat). k_w is rate constant (mol/min/kg-cat/Pa²). The frequency factor and activation energy are 9.886×10^5 (mol/min/kg-cat/Pa²) and 47.4 (kJ/mol), respectively. P_{CO} , P_{CO_2} , P_{H_2} and P_{H_2O} are partial pressures of each component. Maximum operating temperature of Pt catalyst is 402 °C.

3.2 Simulation Result and Model Validation

The feed condition and reactor size followed Lin's work [3]. The WGS reactor simulation was divided into 40 sections to maintain the simulation accuracy. The simulation result fit the experiment data well and

is shown in Fig. 2.

3.3 Optimization

The objective function of the WGS reactor design was to minimize the size of the WGS reactor system. The size of WGS reactor systems included reactor and heat exchanger volume. Single and two WGS reactors in series systems were investigated. The optimization equations are shown below:

Single WGS reactor:

Minimize (V_I)

$$\Omega = \{T_1\}$$

$$\text{Subject to } \left\{ \begin{array}{l} y_{CO} = 0.953 \text{ mol\%} \\ T_{1,out} \leq 402^\circ \text{C} \\ L_I / D_I = 0.7639 \end{array} \right\}$$

WGS reactors in series:

Minimize ($V_I + V_{II} + V_{HX}$)

$$\Omega = \{T_1, T_2\}$$

$$\text{Subject to } \left\{ \begin{array}{l} y_{CO} = 0.953 \text{ mol\%} \\ T_{1,out} - T_2 \geq 10^\circ \text{C} \\ T_{1,out} \leq 402^\circ \text{C} \\ T_{2,out} \leq 402^\circ \text{C} \\ L_I / D_I = 0.7639 \\ D_{II} / D_I = 1 \end{array} \right\}$$

(18)

(19)

The optimization of Eq. (18) and Eq. (19) was performed by using Aspen Plus Sequential quadratic programming (SQP) toolbox. The result shows the size of two WGS reactors in series system is smaller than a single reactor by a factor of 30.75% (shown in table 1).

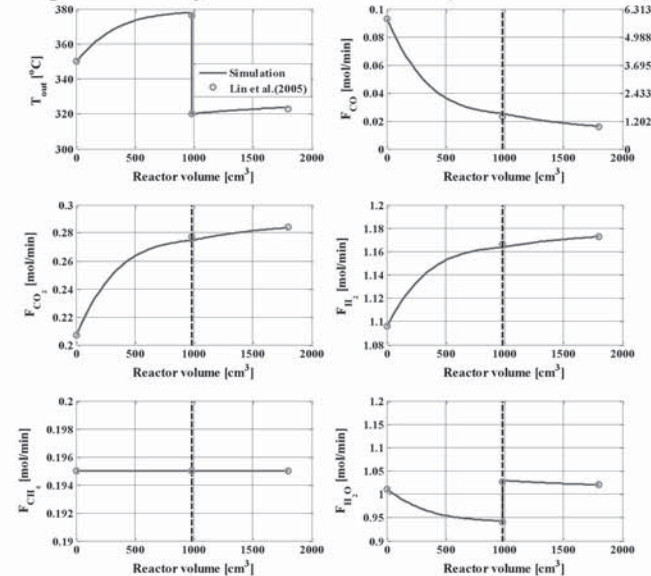


Fig. 2. Temperature and concentration profiles in the WGS reactors

Table 1 Optimization design of WGS reactors

Reactor type	Single	In series	Lin et al. (2005)
$V_{Total} [\text{cm}^3]$	2023.29	1547.44	1801
$T_1 [^\circ \text{C}]$	305.14	375.81	350
$T_2 [^\circ \text{C}]$	336.69	318.82	320
$\Delta V / V_{Total} [\%]$	30.75	-	16.39

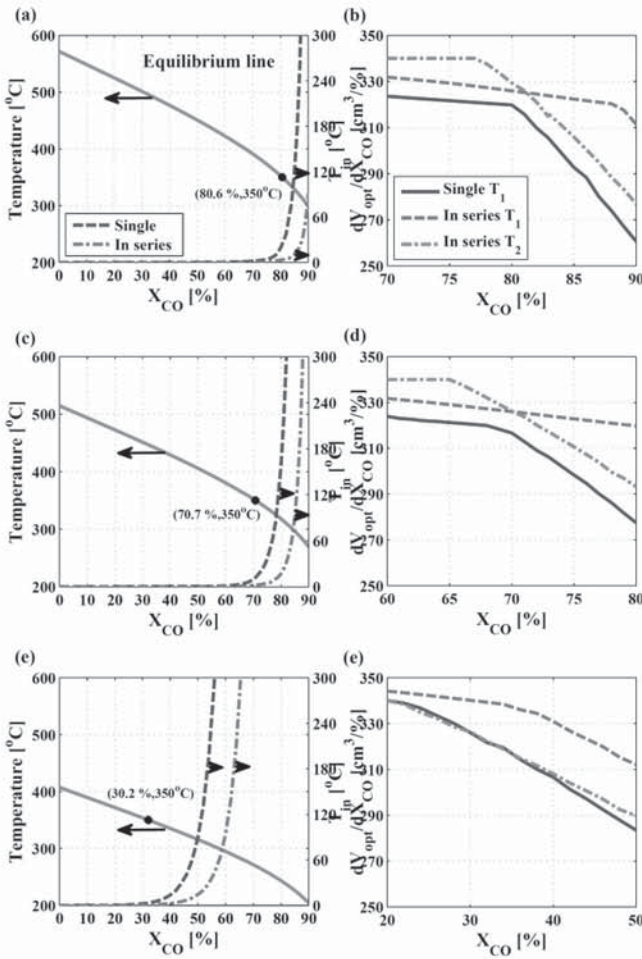


Fig. 3 Volume difference between single and two WGS reactors in series by varying (a),(b) $\theta_{H_2O}=11.8$, (c),(d) $\theta_{H_2O}=7.7$, (e)&(f) $\theta_{H_2O}=2.9$

3.4 Reactor Structure Selection

For further study, syn-gas compositions were varied by using different types of hydrocarbons as steam reforming feed which meant feed dimensionless groups also changed. The proper conversion of WGS reactions is not mentioned in literature. Most WGS reactor designs set the outlet concentration at a range of 0.5 to 1 mol%. Here, conversion (X_{CO}) and feed dimensionless groups (θ_{H_2} , θ_{H_2O} and θ_{CO_2}) are referred to as our unknown variables. Our target is to determine the minimum reactor sizes of single and two WGS reactors in series systems by varying conversion and feed dimensionless groups.

Figure 3 shows WGS reactor volumes comparison between single and in series WGS reactor systems by varying θ_{H_2O} and X_{CO} for a fixed θ_{H_2} and θ_{CO_2} . When θ_{H_2O} equaled 11.8, the optimal volumes of single and in series WGS reactor systems can be evaluated from Eqs. (18,19) by scanning X_{CO} . The result is shown in Fig. 3(a). At lower conversion, volumes of single and in

series WGS reactor systems are very similar. This is because two WGS reactors in series need an additional intercooler. When conversion is higher than $X_{CO,e}$ (80.6 %), a single reactor system is much larger than two reactors in series. The same situation was found for $\theta_{H_2O}=7.7$ (shown in Fig. 3(b)) and $\theta_{H_2O}=2.9$ (shown in Fig. 3(c)) where the equilibrium conversion are 70.7 and 32.1 %, respectively. The result is also proven by varying θ_{H_2} and θ_{CO_2} .

3.5 Result and Discussion

From the last section, the general design rule was found regardless of feed dimensionless group changes and listed below:

- (1) $X_{CO} < X_{CO,e}$: In this case, volumes of single and in series WGS reactor systems are very similar. However, from capital cost view points, two WGS reactors in series is more expensive than a single reactor. The single WGS reactor system is preferred in this design area.
- (2) $X_{CO} > X_{CO,e}$: In this case, the volume of single reactor systems is much larger than two reactors in series. The two WGS reactor in series system is preferred in this design area.

From this agreement, the design heuristic was generated and the procedure was listed below:

- (1) T (temperature)- X_{CO} (conversion) diagram can be plotted from Eq.(15).
- (2) For a given syn-gas composition which is generated from hydrocarbons steam reforming, feed dimensionless groups (θ_{CO_2} , θ_{H_2} and θ_{H_2O}) can be calculated.
- (3) For a specified catalyst, the maximum operating temperature is known and used to calculate equilibrium conversion from Eq.(15).
- (4) For a given feed dimensionless group and equilibrium constant, the equilibrium conversion of WGS reaction can be evaluated from Eq. (16).
- (5) For a specified CO purity of WGS effluent steam, the conversion of WGS reaction can be calculated.
- (6) If the conversion is located on the lower value side of the equilibrium conversion graph (shown in Fig. 4), single WGS reactor systems are chosen; otherwise, two WGS reactors systems are preferred (shown in Fig. 4).

This methodology provides a rapid determination of WGS reactor system flowsheets.

4. CONTROL STRUCTURE DESIGN

The effluent flowrate from fuel processes is changed in order to satisfy the electricity demand from PEMFC. The feed conditions of WGS reactors are affected by the electricity set-point change. The purpose of this work is to build a control structure to

maintain the outlet CO concentration of WGS reactor systems.

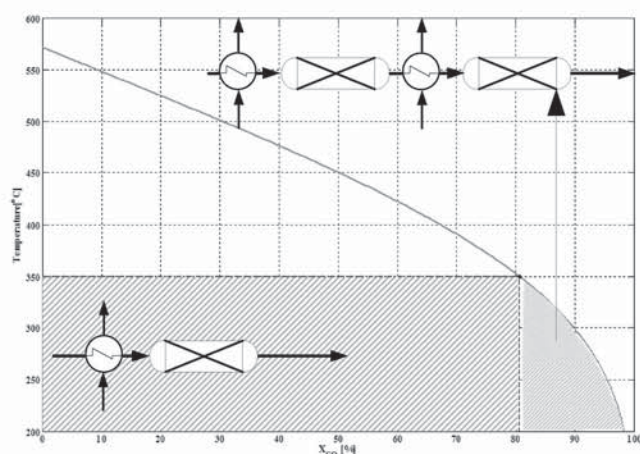


Fig. 4 Design flowsheet selection for WGS reactor systems

4.1 Sensitivity Analysis

Figure 5 shows the sensitivity analysis of single and in series WGS reactor systems. The result shows inlet water flowrate is sensitive to the CO concentration. When the feed flowrate or composition load changed, the water injection flowrate was adjusted to maintain the CO concentration at the same level.

4.2 Control Structure Design

From sensitivity analysis, the control structure was built and is shown in Fig. 6. The control loops are listed below:

- (1) Syn-gas inlet flowrate was used as our throughput manipulated variable.
- (2) The water injection flowrate was used to control the CO concentration below 0.953 mol% (dry based).
- (3) The cooling water flowrate was adjusted to maintain the reactor inlet temperature.
- (4) WGS reactor outlet flowrate controlled the reactor pressure.

4.3 Operability Analysis

The purpose of the control structure is to maintain CO concentration from WGS reactor effluent below 0.953 mol% (dry based). For a given fixed water amount, single WGS reactor systems can deal with a larger inlet flowrate or CO concentration disturbance load change than two WGS reactors in series. This is because a larger WGS reactor volume results in a longer residence time than two WGS reactors in series. Single WGS reactor systems have wider operability ranges than two WGS reactors in series.

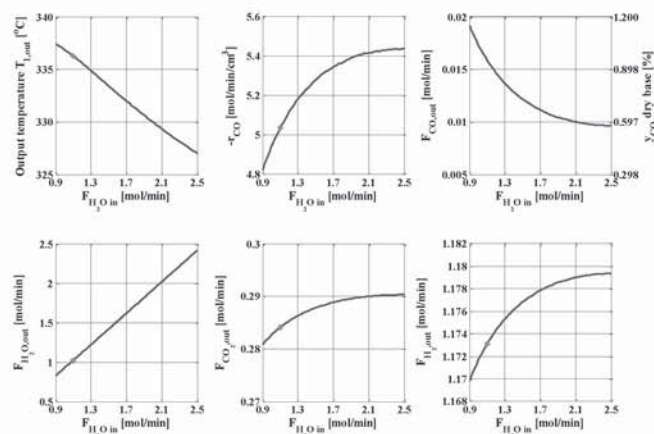
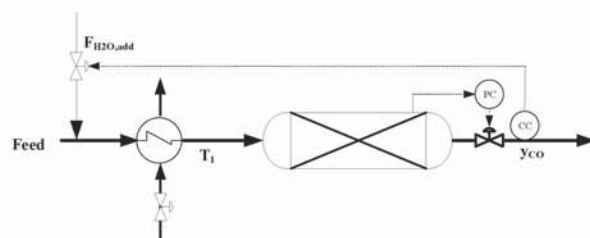


Fig. 5 Sensitivity analysis of single and in series WGS reactor systems

(a)



(b)

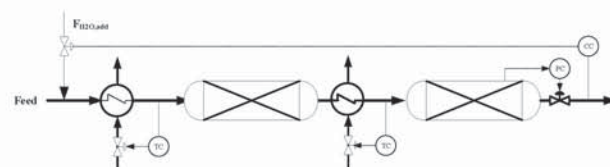


Fig. 6 Control structures of (a) Single, (b) in series WGS reactor systems.

5. CONCLUSION

In this work, the Aspen Plus Tech. software was used to build model WGS reactor systems which validated experiment data [3]. The objective of this research is to minimize the volume of WGS reactor systems. The optimal volumes comparison between single and in series WGS reactor systems were found by scanning feed dimensionless groups and CO conversion. The result shows if X_{CO} is smaller than $X_{CO,e}$, single WGS reactor systems are preferred in this design area. If X_{CO} is larger than $X_{CO,e}$, two WGS reactor in series systems are preferred. Then, design heuristic was built to provide a rapid determination of WGS reactor system flowsheets. After the sensitivity analysis was performed, control structures were built for single and in series WGS reactor systems. The result shows single WGS reactor systems have wider operability ranges

than two WGS reactors in series.

NOMENCLATURE

D_I	= diameter of first WGS reactor	[cm]
D_{II}	= diameter of second WGS reactor	[cm]
k_w	= rate constant	[mol / min / kg-cat]
K_{eq}	= equilibrium constant	[-]
L_I	= length of first WGS reactor	[cm]
L_{II}	= length of second WGS reactor	[cm]
P_{CO}	= CO partial pressures	[Pa]
P_{CO_2}	= CO ₂ partial pressures	[Pa]
P_{H_2}	= H ₂ partial pressures	[Pa]
P_{H_2O}	= H ₂ O partial pressures	[Pa]
R	= gas constant	[kJ / mol-K]
r_{WGS}	= reaction rate	[mol / min / kg-cat]
T	= operating temperature	[K]
T_I	= first WGS reactor inlet temp.	[K]
$T_{I,out}$	= first WGS reactor outlet temp.	[K]
T_2	= second WGS reactor inlet temp.	[K]
$T_{2,out}$	= second WGS reactor outlet temp.	[K]
V_I	= first WGS reactor volume	[cm ³]
V_{II}	= second WGS reactor volume	[cm ³]
V_{HX}	= intercooler volume	[cm ³]
X_{CO}	= CO conversion	[-]
$X_{CO,e}$	= equilibrium conversion	[-]
$y_{i,0}$	= i species mole fraction of WGS feed	[-]
$y_{CO,0}$	= CO mole fraction of WGS feed	[-]
$\theta_{i,0}$	= i species to CO mole fraction ratio of WGS feed	[-]
ΔG_r^0	= gibbs free energy at standard condition of WGS reaction	[kJ / mol]

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REFERENCES

- Joensen, F. and J. R. Rostrup-Nielsen: "Conversion of Hydrocarbons and Alcohols for Fuel Cells", *J. Power Sources*, **105**, 195-201 (2002)
- Schadel, B. T., M. Duisberg, and O. Deutschmann: "Steam Reforming of Methane, Ethane, Propane, Butane, and Natural Gas Over a Rhodium-Based Catalyst", *Catalysis Today*, **142**, 42-51 (2009)
- Lin, S. T., Y. H. Chen, C. C. Yu, Y. C. Liu, and C. H. Lee: "Modeling of an Experimental Fuel Processor", *J. Power Sources*, **148**, 43-53 (2005)
- Boyano, A., T. Morosuk, A. M. Blanco-Marigorta, and G. Tsatsaronis: "Conventional and Advanced Exergoenvironmental Analysis of a Steam Methane Reforming Reactor for Hydrogen Production, *J.*

- Cleaner Prod.*, **20**, 152-160 (2012)
- Huang X. W., and R. Reimert: "Kinetics of Steam Reforming of Ethane on Ni/YSZ (yttria-stabilised zirconia) Catalyst, *Fuel*, **106**, 380-387 (2013)
- Laosiripojana, N., W. Sangtongkitcharoen, and S. Assabumrungrat: "Catalytic Steam Reforming of Ethane and Propane over CeO₂-Doped Ni/Al₂O₃ at SOFC Temperature: Improvement of Resistance Toward Carbon Formation by the Redox Property of Doping CeO₂, *Fuel*, **85**, 323-332 (2006)
- Chuang, C. C., Y. H. Chen, J. D. Ward, C. C. Yu, Y. C. Liu, and C. H. Lee: "Optimal Design of an Experimental Methanol Fuel Reformer", *Int. J. Hydrogen Energy*, **33**, 7062-7073 (2008)
- Perez-Hernandez R., A. Gutierrez-Martinez, J. Palacios, M. Vega-Hernandez, and V. Rodriguez-Lugo: "Hydrogen Production by Oxidative Steam Reforming of Methanol over Ni/CeO₂eZrO₂ catalysts", *Int. J. Hydrogen Energy*, **36**, 6601-6608 (2011)
- Salemme L., L. Menna, M. Simeone: "Thermodynamic Analysis of Ethanol Processors-PEM Fuel Cell Systems", *Int. J. Hydrogen Energy*, **35**, 3480-3489 (2010)
- Lopez E., V. Gepert, A. Gritsch, U. Nieken, and G. Eigenberger: "Ethanol Steam Reforming Thermally Coupled with Fuel Combustion in a Parallel Plate Reactor", *Ind. Eng. Chem. Res.*, **51**, 4143-4151 (2012)
- Zeng, G., Y. Tian, and Y. Li: "Thermodynamic Analysis of Hydrogen Production for Fuel Cell via Oxidative Steam Reforming of Propane", *Int. J. Hydrogen Energy*, **35**, 6726-6737 (2010)
- Suzuki T., H. I. Iwanami, O. Iwamoto, and T. Kitahara: "Pre-Reforming of Liquefied Petroleum Gas on Supported Ruthenium Catalyst", *Int. J. Hydrogen Energy*, **26**, 935-940 (2001)
- Kang I., and J. Bae: "Autothermal Reforming Study of Diesel for Fuel Cell Application:, *J. Power Sources*, **159**, 1283-1290 (2006)
- Kolb G., C. Hofmann, M. O'Connell, and J. Schurer: "Microstructured Reactors for Diesel Steam Reforming, Water-Gas Shift and Preferential Oxidation in the KiloWatt Power Range", *Catalysis Today*, **147S**, S176 - S184 (2009)