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Optimal design and operation of a natural gas tri-reforming reactor for DME synthesis

Wonjun Cho [a], Taekyong Song [a], Alexander Mitsos [b], J. Thomas McKinnon [b,c], Glen H. Ko [b], John E. Tolsma [b], Douglas Denholm [b], Taeshin Park [b,*]

[a] DME Project, KOGAS R&D Division, Incheon, Republic of Korea
[b] RES Group, Inc., 11 Cambridge Center, Cambridge, MA 02142, USA
[c] Department of Chemical Engineering, Colorado School of Mines, Golden, CO, USA

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ABSTRACT

Korea Gas Corporation (KOGAS) is developing a new di-methyl-ether (DME) plant. Syngas is provided by natural gas tri-reforming, in a reactor consisting of a homogenous part where oxidation leads to a temperature increase required for the reforming reactions and a catalytic part where the reforming reactions take place. A first principle model for the tri-reforming reactor is developed. A kinetic mechanism is proposed combining homogeneous gas-phase reactions and heterogeneous catalytic reactions. The proposed model is systematically calibrated and validated with global sensitivity analysis followed by global parameter estimation against concentration measurements of a lab-scale prototype reactor and comparisons of the sensitivity of the outlet as a function of inlet composition and design parameters with experimental results. The validated model is finally used for the optimization of design variables such as length ratio of homogeneous and heterogeneous section and operational variables such as the feed composition.

1. Introduction

Korea Gas Corporation (KOGAS) is planning a plant for di-methyl-ether (DME) production. DME, the simplest ether, is a colorless, non-toxic, environmentally benign compound. It is currently used as a solvent and propellant in various aerosol products. DME is considered as a substitute for diesel fuel. Compared with diesel fuel combustion, DME produces much less pollutants such as carbon monoxide, nitrogen oxides and particulates. DME can be prepared from various energy sources including natural gas or coal, as well as biomass or spent plastics. In addition to the environmental friendly property, DME has the advantage of a high cetane number and properties similar to those of LPG. Therefore, DME can be used for various purposes including diesel motors and fuel cells. DME is expected to be used after 2010 for these applications.

Thus, KOGAS has pushed forward the preliminary feasibility study on the development and commercialization of the direct synthetic technology of DME as a new energy form which is expected to form a new market in East-Asian territory (Korea, Japan, China, India, etc.) in the near future.

One of the key unit operations is the production of syngas, i.e., a mixture of hydrogen and carbon monoxide. Syngas is manufactured industrially from hydrocarbon fuels, typically natural gas, either by steam reforming (SRM) or gasification. In steam reforming the fuel reacts with steam toward synthesis gas over a Ni-based heterogeneous catalyst. Since steam reforming is endothermic, heat must be supplied to the reactor through the reactor tube walls. Gasification is an autothermal process in which the fuel is mixed with pure oxygen and noncatalytically converted to synthesis gas. Various technologies developed for producing syngas from natural gas including steam reforming and gasification processes all depend upon various combinations of the three main reactions in Table 1.

The two main operational issues in producing syngas from natural gas are obtaining the desired H_2/CO ratio and avoiding coke deposition. The desired H_2/CO ratio depends upon the intended use for the syngas. For the DME production, a ratio of 1.2:1.5 is desired [1]. The SRM produces syngas too rich in hydrogen while the syngas from carbon dioxide reforming (CDR) is too lean. The syngas from catalytic partial oxidation (CPO) is close to the desired output ratio. In principle, the H_2/CO blend can be adjusted using the water

* Corresponding author. Tel.: +1 617 306 0214; fax: +1 617 812 8042.
E-mail address: tspark@resgroupinc.com (T. Park).

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Table 1
Main reactions in syngas production

Reaction	Stoichiometry	Enthalpy of reaction (kJ/mol)
Steam reforming (SRM)	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	+206.3
Carbon dioxide reforming (CDR)	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	+247.3
Catalytic partial oxidation (CPO)	$CH_4 + 1/2O_2 \leftrightarrow CO + 2H_2$	−35.6

gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$), however this step requires additional processing and cost.

The tri-reforming is a synergetic combination of three main reactions in a single reactor, and its potential for the production of syngas from natural gas has been described recently [2–4]. Main advantages of tri-reforming are that the H_2/CO ratio in the product can be better controlled, and that the coke formation can be reduced by shifting the relative amount of oxidants (H_2O and O_2) to CO_2.

Exploiting these advantages, the KOGAS tri-reforming process has been developed to manufacture syngas from natural gas source. This process provides a lower operating temperature, a desirable H_2/CO in the range of 1.2 and 1.5, and lower coke formation. Fig. 1 shows the schematic diagram of KOGAS tri-reforming process. It consists of a pre-reformer where C_2 and C_3 components are converted into methane and hydrocarbon at 350 °C and 30 bar, and a tri-reformer. The tri-reformer consists of a homogeneous and a heterogeneous region. The homogeneous region is catalyst-free while the heterogeneous region is packed with 10–15 mm catalyst pellets of NiO–Mg/Ce–ZrO_2/Al_2O_3. In the homogeneous region methane combustion occurs, which leads to the necessary temperature increase for the reforming reactions that take place in the heterogeneous region.

In the tri-reforming unit, natural gas and CO_2 are combined with a recycle CO_2 stream and heated in a heater to 500 °C. The recycled CO_2 comes from two locations: the first point is after the clean-up of the syngas and the second point is after the DME synthesis reaction. The natural gas and recycled CO_2 stream combines with the steam and flows to the burner of the tri-reformer. Pressurized oxygen is heated in a separate convection coil of the same heater and goes into the same tri-reformer burner. The temperatures are maintained such that reaction occurs instantaneously and a significant flame front is established.

The syngas exits the tri-reformer at temperatures of around 1000 °C and pressures of about 20 bar. This hot gas is cooled down and high pressure is reduced in the waste heat boiler. This dewatered syngas stream is then compressed to 60 bar and is routed through the CO_2 absorber which is designed to extract the CO_2 out of this stream.

The tri-reforming of CH_4 by NiO–Mg/Ce–ZrO_2/Al_2O_3 catalyst displays an excellent performance for the coke on the reactor wall and the surface of catalyst and more improvement for the water resistance. The additives of Ce–ZrO_2 and Mg play an important role in the tri-reforming of methane which provides the weak acidic site, basic site and redox ability.

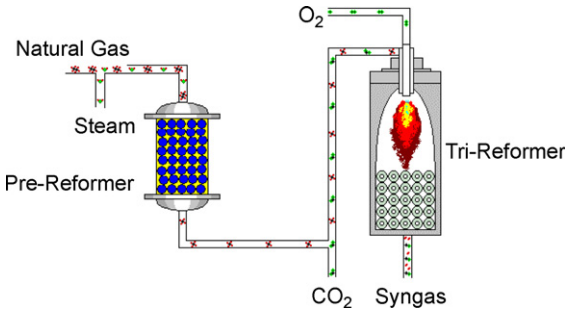

Fig. 1. Schematic diagram of KOGAS tri-reforming process.

Scale-up of the KOGAS tri-reformer is performed in three stages, namely a burner tester, a pilot unit and a demonstration unit with the sizes given in Table 2. KOGAS developed the DME direct synthesis process with a 50-kg/day pilot plant in 2001. KOGAS has launched the 10 ton/day DME demonstration plant project in 2004 at the Incheon KOGAS LNG terminal. Simultaneously, KOGAS has established the burner tester to investigate the characteristics (catalyst, operation condition and combustion) of the tri-reformer. The overall strategy for the scale-up of KOGAS tri-reformer is to study the tri-reforming process and collect data using the burner tester, to build and calibrate the KOGAS tri-reformer model at the scale of the burner tester, and to use the model to design the tri-reformers at the scale of pilot and demonstration units.

In the remainder of this article, the development and systematic validation of a space-distributed model of the KOGAS tri-reforming reactor is described. Subsequently, equilibrium analysis is performed as a benchmark for reactor operation. Finally, the developed model is used to study the optimal design and operation of the tri-reforming reactor.

2. Mechanism and model development

The homogeneous and heterogeneous regions are modeled separately and combined in series to build a complete two-zone reformer model. For each region, a reactor model and a reaction mechanism are developed. A steady state one-dimensional plug flow reactor model is employed for each region. Steady state model is employed since the primary purpose of the model is to design reactors for scale-up. The high temperature and adiabatic operation ensures that radial temperature and concentration gradients are insignificant, and that a one-dimensional model with axial gradient is sufficient [5–7]. Negligible axial dispersion is expected due to high flow rate. In the following, the reaction mechanism for each region is described.

The mechanism in the heterogeneous region is built in JACOBIAN® dynamic modeling and optimization software [8]. The mechanism for the homogeneous region is exported from OpenChem Pro® and imported into JACOBIAN®, and the complete reformer model is then assembled by including a steady state plug flow reactor model. The complete model is mathematically formulated as a set of differential-algebraic equations, and the simulation problem is formulated as an initial value problem

Table 2
Sizes of burner tester, pilot and demonstration units

Reactor	Catalytic section volume (L)	Capacity (Nm^3/h)	Homogeneous section		Heterogeneous section	
			L (m)	D (m)	L (m)	D (m)
Burner tester	2.5	25	0.500	0.107	0.370	0.107
Pilot unit	13.3	33	0.748	0.214	0.470	0.214
Demonstration unit	349	2503	1.137	0.718	1.091	0.718

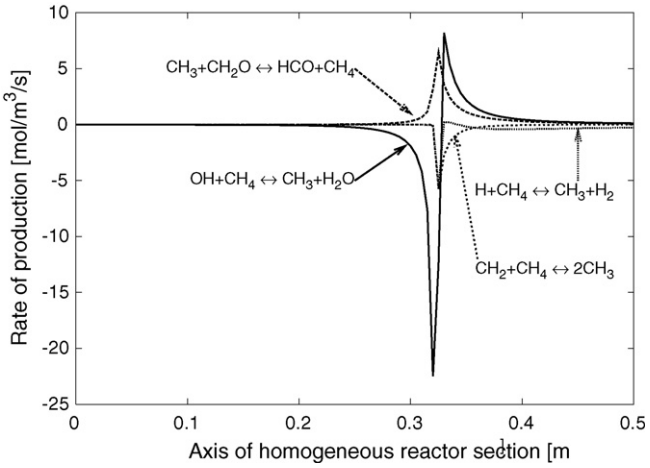

Fig. 2. GRI 3.0 mechanism in Mechanism Viewer in OpenChem Pro® Software. Dominant reactions for the production/consumption of CH_4.

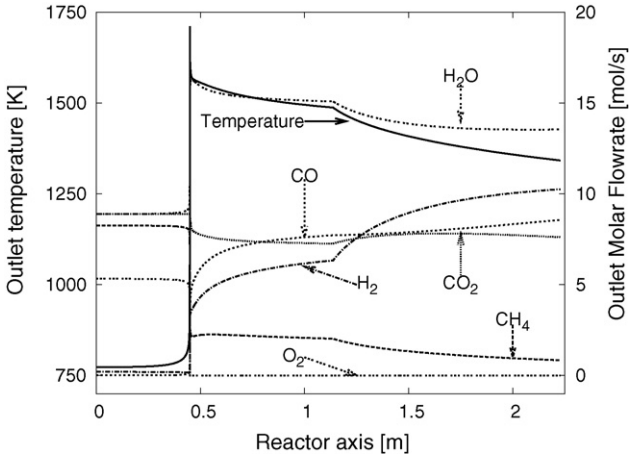

Fig. 3. Typical temperature and concentration profile along the reformer length.

where the independent variable is the axial length of the reformer. The modeling equations account for the change in velocity due to density variation (change of moles by reaction and change of temperature).

2.1. Homogeneous region

Methane combustion reactions occur in the gas-phase homogeneous region without any catalyst. The well-established GRI mechanism version 3.0 by the Gas Technology Institute (formerly Gas Research Institute) [9] is employed. This mechanism includes 53 species and 325 gas-phase reversible and irreversible reactions. The mechanism is built and analyzed in OpenChem Pro® Reaction Kinetic Analysis and Development Software [8]. Fig. 2 shows the CH_4 rate of production of the four main reactions; these reactions are automatically selected by OpenChem Pro® Reaction Kinetic Analysis and Development Software based on the highest absolute rate of CH_4 production.

2.2. Heterogeneous region

Four global surface reactions as proposed by de Smet et al. [6] and shown in Table 3 are used to describe the heterogeneous part. The effective rate equations for the four global reactions are also given in Table 3. It is interesting to note that from the point of view of stoichiometry, these four reactions are not linearly independent. The species participating in the reactions are six and they contain three elements. Therefore linear combinations of three independent reactions are sufficient to describe any reaction among these species [10]. Reactions (1)–(3) are a possible set of independent reactions. For instance, CDR reaction in Table 1 can be described as reaction (2) minus reaction (3). It is however advantageous to use all four reactions since the kinetic rate expressions have been validated in the literature.

3. Mechanism and model calibration

Fig. 3 shows typical temperature and concentration profiles along the reformer length. Close to the reactor inlet the temperature is approximately constant until ignition occurs at which point in the reactor the temperature rises nearly instantaneously. The oxygen concentration decreases to practically zero immediately after ignition. After the ignition, the remaining methane is slowly converted via reforming reactions. At the transition between the homogeneous and heterogeneous regions, there is a kink in temperature and molar flowrate profile because the catalyst accelerates the reforming reactions.

3.1. Systematic model calibration strategy

The experimental data available for model calibration are several measurements of temperature and composition for the burner tester while the reformer model contains at least several hundred parameters that can be adjusted to match the experimental data. The ratio of the number of parameters to the number of measurements is quite high, and this is typical in calibration of kinetic models. Furthermore, parameter estimation problem formulated as an optimization problem suffers from multiple local optimal solutions. Fig. 4 shows our strategy for model calibration addressing these difficulties. As a first step, the

Table 3
Four global reactions and reaction rates in heterogeneous region (rate expressions without efficiency factor)

Reactions	Effective rate equations
$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$	$r_1 = \frac{k_{1a}\, p_{CH_4}\, p_{O_2}}{(1+K^{ox}_{CH_4}\, p_{CH_4}+K^{ox}_{O_2}\, p_{O_2})^2} + \frac{k_{1b}\, p_{CH_4}\, p_{O_2}}{(1+K^{ox}_{CH_4}\, p_{CH_4}+K^{ox}_{O_2}\, p_{O_2})}$
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	$r_2 = \frac{k_2^{Xu}/p_{H_2}^{2.5}\,(p_{CH_4}\, p_{H_2O} - p_{H_2}^3\, p_{CO}/K_{eq.2})}{(1+K_{CO}p_{CO}+K_{H_2}\, p_{H_2}+K_{CH_4}\, p_{CH_4}+K_{H_2O}\, p_{H_2O}/p_{H_2})^2}$
$CO + H_2O \leftrightarrow CO_2 + H_2$	$r_3 = \frac{k_2^{Xu}/p_{H_2}\,(p_{CO}\, p_{H_2O} - p_{H_2}\, p_{CO_2}/K_{eq.3})}{(1+K_{CO}\, p_{CO}+K_{H_2}\, p_{H_2}+K_{CH_4}\, p_{CH_4}+K_{H_2O}\, p_{H_2O}/p_{H_2})^2}$
$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$	$r_4 = \frac{k_2^{Xu}/p_{H_2}^{3.5}\,(p_{CH_4}\, p_{H_2O}^2 - p_{H_2}\, p_{CO_2}/K_{eq.4})}{(1+K_{CO}\, p_{CO}+K_{H_2}\, p_{H_2}+K_{CH_4}\, p_{CH_4}+K_{H_2O}\, p_{H_2O}/p_{H_2})^2}$

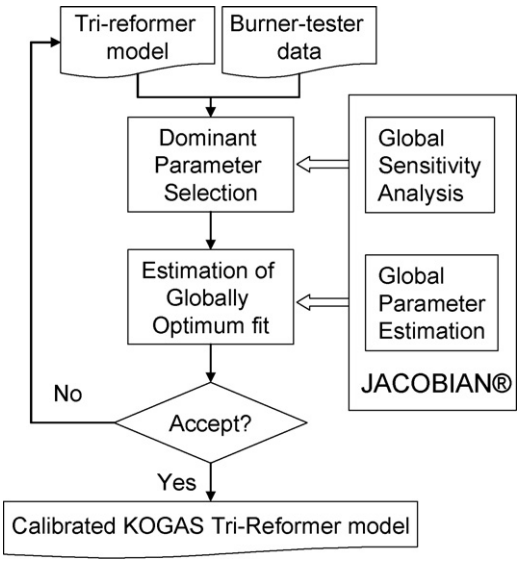

Fig. 4. Systematic model calibration strategy.

dominant set of parameters is described that can be effectively determined from available data employing global sensitivity analysis. Local parametric sensitivities $\partial X_i/\partial P_j$ of a variable X_i with respect to a parameter P_j are defined at specific parameter values, and are not suitable in determining the dominant parameters. Global sensitivities are defined as averages of local sensitivities over parameter bounds to overcome this limitation of local sensitivities. It is relatively easy to obtain physically meaningful bounds on parameters. Based on global sensitivities, rankings of parameters with respect to their influence on measured variables can be determined. Once the dominant parameters are determined, the next step is to estimate these parameter values. Parameter estimation problems are notoriously multi-modal, i.e., they have multiple local optimum solutions. In order to calibrate the model with respect to experiments, it is essential to locate a globally optimum parameter solution. Approaches from practical multi-start parameter estimation performing local optimization from multiple initial guesses to global dynamic optimization [11] can be applied for this purpose. This methodology has been successfully applied to several kinetic model calibration problems [12].

3.2. Calibration results

Rate constants in the GRI 3.0 mechanism for homogeneous region are not adjusted since this mechanism is based on elementary reactions and already validated with respect to extensive data. However, rate constants in the heterogeneous region are highly uncertain and need to be estimated using experimental data. Among the kinetic parameters in the heterogeneous region, the pre-exponential constants for global reactions (2)–(4) in Table 3 are determined to be dominant parameters based on global sensitivity analysis, whereas the influence of the parameters in reaction rate (1) was relatively insignificant. This result can be explained intuitively since most oxygen has reacted in the heterogeneous section. Then multi-start parameter estimation is applied to fit the model globally against the experimental data. The entire procedure of model development, simulation, global sensitivity analysis, and multi-start parameter estimation has been performed on JACOBIAN® Dynamic Modeling and Optimization Software [8].

Fig. 5 shows the result of model calibration indicating a good agreement between model calculation and experimental data. The

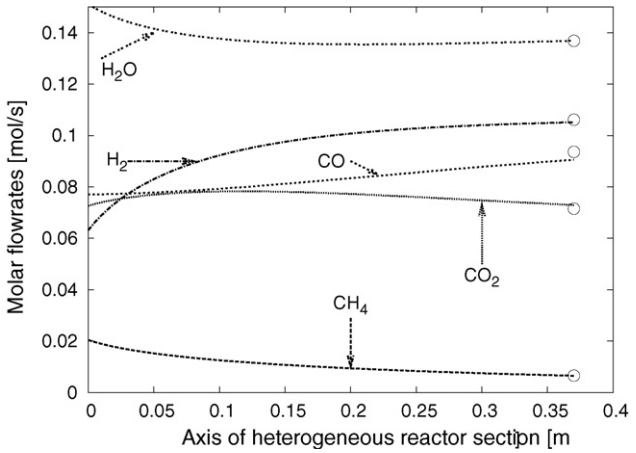

Fig. 5. Comparison of measurements from burner tester (circles) and model predictions (lines).

good agreement shows that the multi-start parameter estimation was successful. However, the following additional studies are required to ensure that the model correctly describes the reactor. Within our methodology-independent validation studies are performed for that purpose without any further adjustment of the modeling parameters. As an independent test of the calibrated model, the syngas ratio at the reformer outlet is calculated at different values of feed composition and compared with burner tester data as shown in Fig. 6. For increasing water content, the hydrogen fraction in the outlet increases as expected. The effect is nonlinear due to the kinetic rate dependence. The model describes the qualitative trend and the quantitative comparison of model and measurement is in the order of the measurement errors. Fig. 6 also shows that the prior to calibration the model did not correctly predict the trend (curve-labeled "non-calibrated model").

4. Application study

The validated model is used for the optimization of design variables, such as the length of homogeneous and heterogeneous section, and operational variables, such as the feed composition.

4.1. Equilibrium analysis

An ideal catalyst could in principle be more selective towards syngas generation than thermodynamic equilibrium, but in

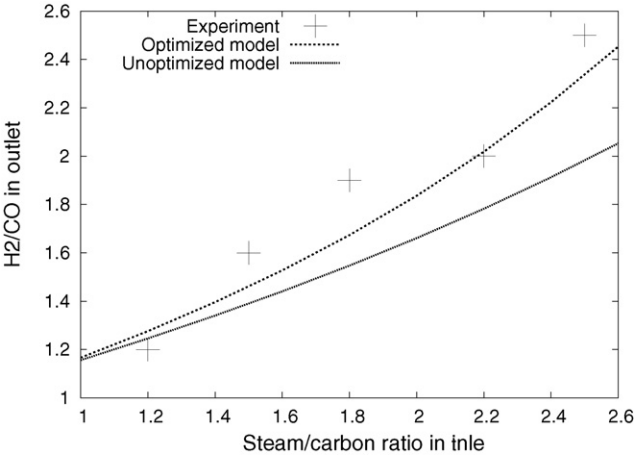

Fig. 6. Prediction of syngas ratio as a function of steam/carbon ratio in feed.

Table 4
Comparison of nominal operation with equilibrium

	Inlet	Outlet from homogeneous section	Reactor outlet	Equilibrium	Ratio outlet/equilibrium
Molar flowrate CH_4	8.25 mol/s	2.20 mol/s	0.83 mol/s	0.14 mol/s	5.9
CH_4 conversion	0	73%	90%	98%	0.92
Molar flowrate H_2	0	6.3 mol/s	10.3 mol/s	12.1 mol/s	0.85
Molar flowrate CO	0	7.7 mol/s	8.6 mol/s	9.9 mol/s	0.86
Molar flowrate ratio H_2/CO	0	0.82	1.2	1.2	1

practice this is not observed, because hydrogen and oxygen are much more reactive than methane [7]. As a consequence equilibrium analysis is very informative and the reactor performance can be measured against thermodynamic equilibrium. Equilibrium calculations are performed via OpenChem Pro® Reaction Kinetic Analysis and Development Software [8].

The basic inputs to an equilibrium analysis are the inlet state (the flowrate, temperature, pressure, and composition at the reactor inlet), and the set of chemical species to be considered in the calculation. The result from the equilibrium calculation is the outlet state. To obtain this equilibrium state, one of many operating conditions must be specified. The simplest such condition is isothermal–isobaric operation for which thermodynamic equilibrium is achieved by minimizing the Gibbs free energy subject to elemental balance (using the non-stoichiometric formulation). Because of the high temperature and relatively low pressures, the gas-phase is assumed ideal and the resulting optimization problem is convex [13], and can be easily solved with general-purpose solvers for nonlinear programs or with specialized algorithms, see Ref. [13] for examples. A more suitable approximation for the tri-reforming reactor is adiabatic–isobaric operation, resulting in constant enthalpy. The corresponding thermodynamic principle is maximization of entropy; alternatively the outlet temperature can be used as a guess variable in an outer loop to converge the enthalpy balance, while in the inner loop the Gibbs free energy is minimized. Here the former, computationally superior, approach is used.

4.1.1. Comparison of nominal operation with equilibrium

Equilibrium analysis can be used as a benchmark of the operation. As Table 4 shows, the performance of the reactor at nominal operation is quite close to the equilibrium limit. Not shown in Table 4 are the inlet flows of steam (8.89 mol/s), oxygen (5.32 mol/s) and CO_2 (8.89 mol/s). The methane conversion is approximately 0.9 of the equilibrium conversion, while the production of hydrogen and carbon monoxide are around 0.85 of the equilibrium production. The ratio of hydrogen and carbon monoxide is essentially the same as at equilibrium.

4.1.2. Dependence of equilibrium on operation

In this subsection the effect of the inlet conditions on the equilibrium conversion is discussed. Fig. 7 shows the effect of inlet temperature with the inlet composition fixed at the nominal value. Since the overall reactor is exothermic, mostly due to the exothermic methane oxidation, an inlet temperature of around 800 K gives an outlet temperature of approximately 1250 K. As expected the outlet temperature increases with increasing inlet temperature; this effect however is not linear as the equilibrium shifts with changing temperature. The residual oxygen is essentially zero and therefore not plotted in Fig. 7. For the temperature range of interest the equilibrium conversion of methane is sufficiently high. It is interesting to observe that the residual equilibrium methane is decreasing with increasing temperature. This effect seemingly contradicts the exothermic overall reaction, but can be explained by the Le Châtelier's principle, since the equilibrium-limited reforming reactions are endothermic, while the exothermic oxidation reactions are essentially complete. The hydrogen production goes through a maximum while the carbon monoxide production increases monotonically for the temperature range of interest.

Fig. 8 shows the effect of varying the water content in the inlet on equilibrium. The water flowrate is varied relative to the nominal value, while the inlet temperature and the flowrates of the other species are kept constant. For a 20% increase or decrease the conversion of methane and oxygen are not significantly affected. As suggested by the Le Châtelier's principle, increased water in the inlet results in a slight increase of the hydrogen production and therefore a slight decrease of carbon monoxide production from the water gas shift. Moreover, the outlet temperature is decreased, due to the increased overall heat capacity of the gas. Both effects are nearly linear. Analogous results are observed for variable carbon dioxide inlet.

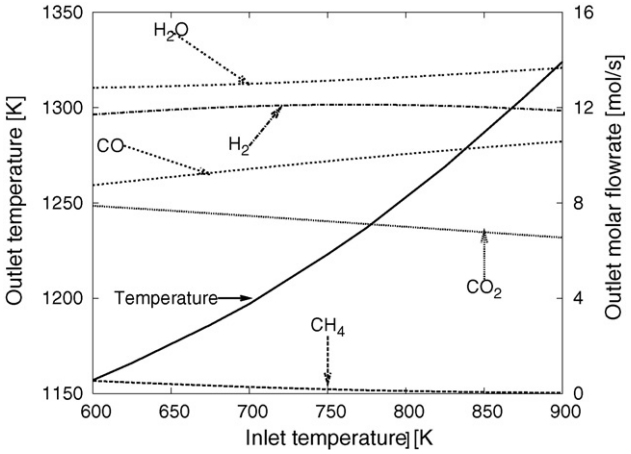

Fig. 7. Effect of inlet temperature on equilibrium.

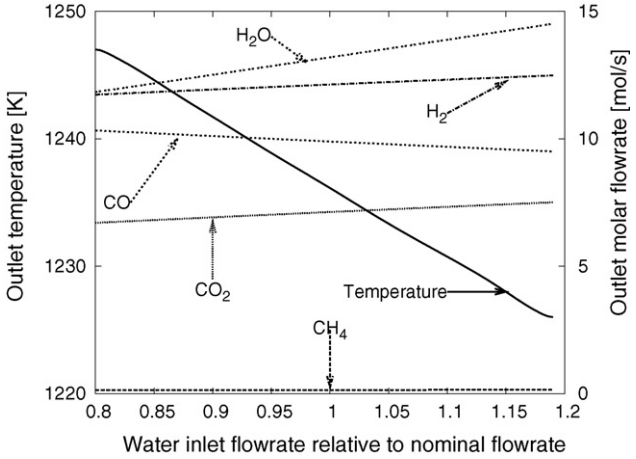

Fig. 8. Effect of inlet water concentration on equilibrium.

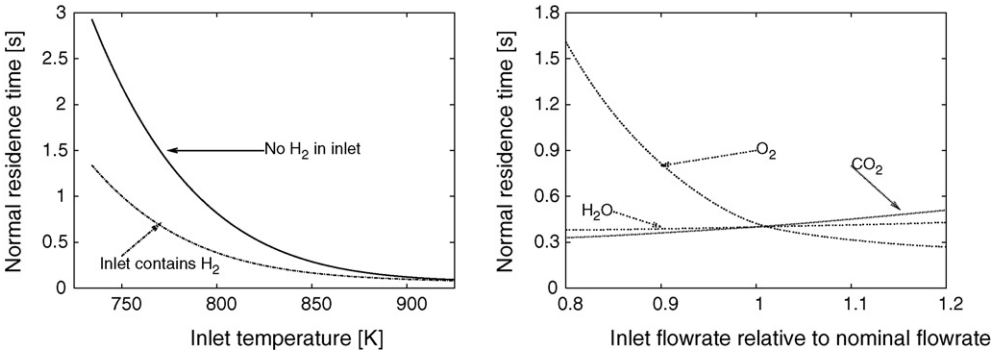

Fig. 9. Required residence time in the homogeneous section as a function of the inlet temperature and composition.

4.2. Optimal reactor length

One of the key design variables is the residence time ratio of homogeneous to heterogeneous section. Since the diameter is fixed due to prior design choices, the residence times are equivalent to the lengths. The validated model can be used to optimize these key design variables and show their relation to operational variables.

4.2.1. Required residence time in the homogeneous region

For fixed inlet temperature and composition, a basic requirement is that the homogeneous section is sufficiently long so that the residence time allows ignition to takes place. Moreover, homogeneous reactions need to take place to avoid catalyst poisoning in the heterogeneous section. On the other hand a longer than necessary homogeneous section results in an increase of fabrication cost as well as potentially to an unfavorable outlet composition, because the catalytic section is more selective. The main goal of the homogeneous section is to increase the temperature by oxidizing methane and depleting the oxygen. In order to establish what a sufficient length is as a function of the inlet temperature and composition, some quantitative criteria are needed.

For the nominal composition, ignition occurs at a normal residence time of around 1/4 s. Immediately after the ignition, the oxygen is depleted and approximately 3/4 of the available methane are consumed. In the following the much slower reforming reactions take place. Out of the 53 species considered in the GRI mechanism describing the homogeneous section, the only significant non-equilibrium components are C_2H_2 and C_2H_4 which are consumed after an approximately 0.4 s additional residence time. Based on these observations the homogeneous section is considered sufficiently long if (i) the oxygen conversion is higher than 99.9% and (ii) the C_2H_2 and C_2H_4 flowrates are less than 1% of the methane inlet flowrate.

In Fig. 9, the effect of key operation variables on the required residence time is shown. Increasing the inlet temperature accelerates the ignition and therefore reduces the required residence time. The temperature effect is exponential and more pronounced when there is no hydrogen in the inlet. Varying the oxygen inlet flowrate has a strong influence on the required residence time. With increasing oxygen, the ignition is faster and a smaller residence time is required. However, this leads to a decrease in the production of CO and H_2. Finally, increasing the water or carbon dioxide flowrate in the reactor inlet slightly increases the required residence time. The effect is linear and can be explained by the fact that H_2O and CO_2 do not contribute to ignition and therefore just dilute the reactants and effectively increase the heat capacity.

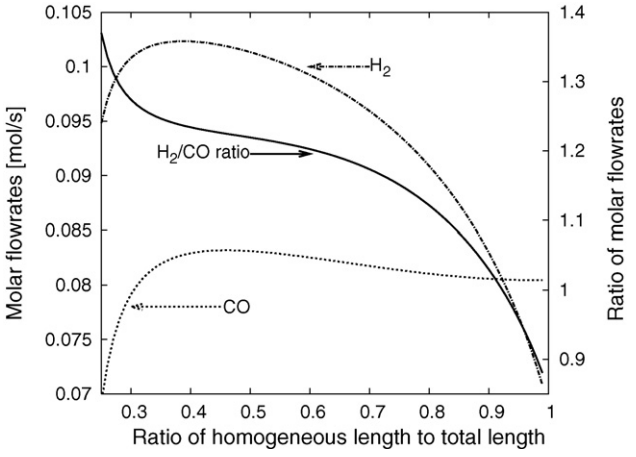

Fig. 10. Effect of homogeneous section length on CO/H_2 production at a fixed total length.

4.2.2. Optimal reactor length

In Fig. 10 a fixed inlet composition and temperature as well as overall length is considered. The ratio of homogeneous to overall length is varied in the regime for which ignition takes place and which is considered sufficient as described in the previous section. Both hydrogen and carbon monoxide production go through a maximum. The dependence of hydrogen production on the length ratio is more pronounced than the dependence of the carbon monoxide production. The optimal ratio for hydrogen production is around 0.37 while for carbon monoxide around 0.4 and the ratio of hydrogen to carbon monoxide production decreases monotonically with the length ratio. These observations allow the optimization of the reactor lengths for production and selectivity, or amount and composition of the produced syngas.

5. Conclusion

A first principle model for a tri-reforming reactor with a homogeneous and a heterogeneous section is developed. The mechanism includes a combination of homogeneous gas-phase reactions and heterogeneous catalytic reactions. The model is calibrated by adjusting kinetic parameters in the heterogeneous reactions using a set of experimental measurements with JACOBIAN® Dynamic Modeling and Optimization Software. The model is then validated with various case studies, including the comparison with another set of measurements; at this stage no further calibration is performed. The model shows a very good agreement with both sets of measurements.

An equilibrium analysis shows that the reactor performance is close to the thermodynamic limit. The validated model is used to analyze the reactor performance. It is shown that the required

residence time in the homogeneous section is strongly influenced by the reactor inlet conditions. Either the volume of the reactor or the inlet conditions can be used to maximize the production of synthesis gas and tune its composition.

The findings of this study are currently used in the design and operation of the reactor in the demonstration unit (2500 Nm^3/h). The extension of the model to consider radial effects as well as transients is of interest for future work. Moreover, it would be important to conduct further experiments using only the heterogeneous section of the reactor and a range of inlet conditions. This would further validate the kinetic rate expressions and parameters.

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