OPTIMIZING A STEAM-METHANE REFORMER FOR HYDROGEN PRODUCTION USING A LUMPED PARAMETER MODEL

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1. Introduction

An efficient and reliable way to produce hydrogen gas is to reform the available natural gas fuel. A reformer is a chemical device that converts natural gas to hydrogen by chemical reaction with steam at pressures of 1.4-4.0 MPa, and temperatures in the range 750-900 (°C). The mixture is heated and led over a catalyst bed, where it converts in an endothermic way to carbon monoxide and hydrogen, while using heat. The heat necessary for this process is generated in a combustion chamber with a burner. In a next step the carbon monoxide reacts with steam to carbon dioxide and more hydrogen in the water/gas-shift reactor [1]. Downstream the water/gas-shift reactor, the product gas exists mainly of hydrogen, carbon dioxide, steam, and traces of methane and carbon monoxide. In a final step the hydrogen mixture is purified. This is done via the pressure swing adsorption process (PSA) [2]. The off-gas of the PSA is used as fuel in the above mentioned burner.

This paper will focus on an analysis and optimization of the processes in the reformer reactor. First in Section 2 the design of a tubular reforming reactor will be explained. Subsequently the modeling of the chemical reactions in, and of the heat transfer to the reactor tubes, will be discussed in Section 3. This physical modeling will be used in a lumped parameter model of the steady state operation of the reactor. In this model some design parameters are incorporated that can be used to optimize the design. The lumped parameter model and the solution procedure is described in Section 4. In Section 5 the parameter optimization will be presented. Finally in Section 6 options for the optimization of the reformer will be presented and quantified. The paper will be completed by conclusions in Section 7.

2. The Tubular Reactor Design for a Steam Reformer

In Figure 1 a schematic representation of a hydrogen production system on the basis on methane conversion is shown. It consists of a reformer with multiple additional components for pre- and post- processing. Such a system is capable of producing 99.999% pure hydrogen out of methane.

The main task of the reformer is to convert a mixture of steam and methane into a hydrogen rich mixture. This is an endothermic catalyst reaction. The reformer section consists of a set of double walled reactor tubes filled with catalyst, a burner (to deliver and distribute the required heat) and a set of heat exchangers. The reactor tubes are enveloped by a flow guide tube.

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Figure 1: Scheme of a hydrogen production system comprising a reformer

3. Chemistry and Heat Transfer in a Steam Reformer Tube

Crucial to the performance of the reformer is the design of the steam reformer tube, in which flow the reactants and the product gases. The flow guide enveloping the reformer tube has to be designed in such a way, that it forces the hot flue gases to transfer heat to the reformer tube at the location, where the endothermic processes have to take place. Inside the double walled reformer tube the chemical reactions occur, that convert the reactants natural gas and steam to hydrogen and inert product gases.

The reactants enter the reactor tube at the outside tube and flow to the tube end, reverse in direction and leave the reactor through the inner tube. The outside of the reactor tube is heated, in counter current exchange mode, by the hot flue gas passing between the flow guide and the reactor tube. Both the inner and outer tubes are filled with a porous catalyst structure. At the catalyst surface, the chemical reactions are initiated. Inside the reactor tubes two overall reactions occur: the Methane Steam Reform reaction (MSR) and the Water Gas Shift (WGS), as shown in equation (1):

$$\begin{array}{lll} \mathrm{CH}_{4} + \mathrm{H}_{2}\mathrm{O}\left(\mathrm{g}\right) & \rightleftharpoons & \mathrm{CO} + 3\mathrm{H}_{2} & \Delta H_{R}^{\circ} = 206\,\mathrm{kJmol}^{-1} \\ \mathrm{CO} + \mathrm{H}_{2}\mathrm{O}\left(\mathrm{g}\right) & \rightleftharpoons & \mathrm{CO}_{2} + \mathrm{H}_{2} & \Delta H_{R}^{\circ} = -41\,\mathrm{kJmol}^{-1} \end{array}$$
(1)

Two types of catalysts are included to support these reactions: a platinum based catalyst for the MSR reaction and another catalyst to support the WGS reaction. Since the MSR is endothermic, the platinum catalyst is located at the outside of the reactor tubes where heat is supplied. The WGS is exothermic for which reason the catalyst is placed at the inside of the reactor tube. Pieces of catalyst are clamped between the reactor tube walls to encourage good heat conduction. Flow guides are provided to prevent the mixture from reversed reforming at a lower temperature.

The reactions MSR and WSG are both equilibrium reactions and a global reaction can be expressed with a forward and a backward reaction. The rate at which the reactions occur depends on the distance to the equilibrium position (thermodynamics) and the speed at which the reactions occur (kinetics). The thermodynamic part of the chemistry is the difference in the forward and backward reaction speed. This difference can be calculated by the distance to the equilibrium at which both reactions are equal in speed. The equilibrium constant for partial pressures is used (Kp). The current value is calculated for the MSR and WGS with equation (2):

$$K_{pr} = \frac{[CO] [H_2]^3}{[CH_4] [H_2O]} \qquad K_{ps} = \frac{[CO_2] [H_2]}{[CO] [H_2O]}$$
(2)

For a specific temperature the value for Kp is calculated with the equations (3):

$$K_{p} = e^{\frac{\Delta G(T)}{RT}} \quad \text{with} \quad \Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$
$$\Delta G^{\circ}(T) = \sum_{i=1}^{n} [v_{i}g_{i}^{*}] - \sum_{j=1}^{n} [v_{j}g_{j}^{*}] \quad (3)$$

In which R is the gas constant in $\begin{bmatrix} J \\ molK \end{bmatrix}$ and $\Delta G(T)$ the Gibbs free energy of formation. At a constant temperature ΔG° can be written as enthalpy change of formation (ΔH_R°) . The Gibbs free energy can be calculated with equation (3) in which the subscript i are all the produced species and the subscript j are all the reacted species. To prevent calculating and minimizing the Gibbs free energy for each species and at each iteration the Kp is calculated with the `Van't Hoff equation (4):

$$ln\left(\frac{K_p}{K_{p,298}}\right) = \frac{\Delta H_R^\circ(T)}{R} \left[\frac{1}{298} - \frac{1}{T}\right] \quad K_p = K_{p,298}e^{\wedge} \left[\frac{\Delta H_R^\circ(T)}{R} \left[\frac{1}{298} - \frac{1}{T}\right]\right]$$
(4)

The term proportional to the reciproce of T determines the speed of the reaction, and is the kinetic part. The specific reaction rate of reaction i depends on temperature and is calculated with the Arrhenius equation (5):

$$k_i(T) = A_i e^{-\frac{Ea_i}{RT}}$$
⁽⁵⁾

In which A_i is the pre-exponential factor and Ea_i is the activation energy $\left[\frac{J}{mol}\right]$. The activation energy is determined empirically. It must be noticed that practical values may differ slightly, due to uncertainties in the catalyst characteristics. See also references [3] and [4] and [5]

4. A Lumped Parameter Thermodynamic Model

The lumped parameter thermodynamic model presented here, describes the heat transfer from the flue gas to the reactant gas in the reformer tubes and the chemical reactions taking place inside the reformer tubes. Important element in the model is the interaction between heat transfer and chemical reaction. The physical domain of the model is limited to the volume between the flow guide tubes and the reformer tubes, and the reformer tubes themselves. This numerical model is

implemented in the computational computer program Matlab and is used to evaluate quantitatively modifications in the design. To obtain a model of the reactor space and the reactor tubes the physical situation is simplified. In figure 2 a layout of the simplified model is shown.



Figure 2. Physical domain of the model

The heat transport in the reformer is simulated in one dimension for three different domains: the reactor space (volume between the flow guide tube and the reactor tube), the inside of the reactor tube and the reactor wall between the tube and reactor space. At the top the hot flue gas enters the domain. It leaves at x=0 after transferring heat to the reactor wall.

$$\frac{dT_f}{dx} = \frac{h_f \pi D \Delta T_f}{F_g C_{p,g}} \tag{6}$$

The gradient in temperature of the hot flue gas with axial distance is given by the differential equation (6) above. Here ΔT_f is the difference between flue gas and wall temperature.

At the other side of the wall in counter flow the reaction mixture enters the domain in the reformer tube at x=0 and leaves at a high x value. This mixture is heated by the reactor wall and reactions occur.

The MSR is an endothermic reaction, this reaction consumes heat. The WGS is exothermic, which results in a heat production. The speed at which the reactions occur, rr for the MSR and rs for the WGS, is calculated at each location. This is done by taking the difference in speed of the forward and backward reaction (thermodynamics) times the reaction speed (kinetics). The thermodynamic part is determined by the pressure equilibrium constant (Kp) times the partial pressures of the reactants. The Kp is calculated at a fixed temperature with the reaction heat. Next the `Van't Hoff'-equation is used to include the Kp temperature dependency. The kinetic part is calculated with the `Arrhenius'-equation. The total amount of heat production is calculated with the rj over flow area A times the reaction heat of reaction j. When all parts are joined together this leads to the differential equations for the gradient of the temperature of the reformer gas, the gradient of the CO concentration and the gradient of the wall temperature respectively:

$$\frac{dT_g}{dx} = \frac{h_g \pi D \Delta T_g + A \Delta H_{R,j}^\circ r_j}{F_i C_{p,i}}$$
(7)

Here ΔT_g is the difference between reformer gas and wall temperature.

$$r_{CO} = \frac{d[CO]}{dx}$$
(8)

$$T_{wall} = \frac{h_f}{h_f + h_g} T_{flue} + \frac{h_g}{h_f + h_g} T_{tube}$$
(9)

The temperature of the wall is taken as the average temperature of both flue gas and reactor mixture times each heat transfer coefficient fraction. See for these equations also references [5] and [6].

This set of ordinary differential equations is solved with boundary conditions at x=0 for the reformer gas temperature and concentration, and for the hot flue gas temperature at large x. The set of ordinary differential equations was integrated with a Runge-Kutta method. As boundary conditions were imposed at both ends, a shooting method had to be applied. An estimated value was picked for the temperature at x=0, at x=large the calculated value for the temperature is compared with the calculated estimate and the initial value is corrected. Then the value of the temperature at x=0 is recalculated and again compared. This iteration is repeated till the difference is acceptable. This process is depicted in figure 3.



Figure 3. Shooting method for the calculation.

5. Simulation Results and Comparison with Measurement Data

An efficient lumped parameter thermodynamic model has been presented in Section 4. The qualitative behavior and accuracy will be discussed in this section. To this end a reference case was simulated and the results compared with measured data. In the measurements performed by HyGear on a reformer tube of their design, temperatures in the reformer were recorded during a period of 78 minutes after startup. The transient effects have already disappeared approximately 50 minutes after turning the system on. During this operation the methane flow was 60% of maximum capacity and the burner was fed with methane and regulated on a maximum wall temperature of 900 °C³.

The heat transfer coefficients h_f and h_g as used in the model are hard to estimate by conventional Nusselt correlations, as the presence of the catalyst material has an important effect also on heat transfer. Therefore these parameters were used to fit measurements to modeled temperatures. It was found that the best fit for h_g is 700 W/(K.m²) and h_f ranges from 500 to 950 W/(K.m²) depending on geometry.



Figure 4: Comparison of measured and simulated temperatures in the reformer

The predicted and measured temperatures of the flue gas, reformer tube wall and the reformer gas are presented in Figure 4 as a function of axial distance. The flue gas enters at 1300 K at x=0.9 m and exits at x=0 at 1000 K. The steam and natural gas mixture enter at x=0 the reformer tubes and is reformed to CO and hydrogen when passing to the end of the reformer tube, where it exits the MSR process at 1000 K, after which it reverses to the WSG path in the inner tube. It can be

 $^{^{3}}$ Not applicable in this model but nevertheless important information following from the measurement results is that temperature differences between the tubes are significant, approximately 100 K. This effect is observed between the tubes. Because the model only simulates one tube, this fact is not included in the model.

observed that the measured wall temperatures fall well in between the predicted flue gas and reformer gas temperatures.

The predicted reactant and product concentrations are depicted in Figure 5, as a function of axial distance. The methane concentration can be observed to decrease to 50% of its initial value, while Hydrogen and CO is produced, consuming steam in the process. About as much CO as CO_2 is produced. This can be explained by the WSG reactions which already participate in the process. Hence the CO_2 produced is not necessarily a loss. Unfortunately measured concentration data are not available for validation of these results.



Figure 5. Predicted concentrations of reactants and products as a function of distance.

6. Evaluation of the Effect of Design Modifications

Next, the model has been used to evaluate the effect of design modifications on the performance of the reformer.

Nine design modifications were proposed:

- 1. an increase of the length of the reactor tubes;
- 2. an increase of the air factor in the burner fuel;
- 3. a change of the geometry of the holes in the outer reactor tube;
- 4. a change of the location of the holes in the outer reactor tube;
- 5. an increase of the steam factor in the reaction mixture;
- 6. a change of the reactor tube material;
- 7. modification of the design to create a variable reactor mixture speed;
- 8. a change of the size of the holes in the insulating shield
- 9. a change of the thickness of the insulating shield.

Modification 1 to 5 and 9 appeared to be suitable to be modeled in our analytical model and were therefore fit for further evaluation. Modification 6 to 8 could not be modeled with the tool at our disposal and will not be discussed in the following sections.

Six design modifications are analyzed with our model. The effect of the modification on the performance of the reformer is expressed by the change of the efficiency of methane conversion due to the modification. This conversion efficiency of methane Φ_{CH_4} is calculated by the following equation:

$$\Phi_{CH_4} = \frac{[CH_4]_{in} - [CH_4]_{out}}{[CH_4]_{in}}$$

The results are visualized in Figure 6. From this figure it follows that the six design modifications proposed have indeed a positive effect on the methane conversion efficiency. Three modifications have a considerable effect, i.e. the extension of the reformer tubes, an increase of the air fraction in the burner and an increase of the thickness of the insulating shield. It is found that up to 12 % more hydrogen can be produced by increasing the length of the reactor tubes by 50 %, 9.5% more hydrogen can be produced by increasing the air fraction in the burner fuel by 50 %, and by increasing the thickness of the insulating shield by 50 %, 11% more hydrogen can be produced.

The results of the design modifications are comparable because the maximum tube temperature is similar for all cases, which is accomplished by decreasing the amount of fuel fed into the system. The results are explained by two mayor effects. To start with, the increase in temperature of the tube happens everywhere except for at the end of the insulating shield. The second effect is comparable; an improved insulation at the end of the tube allows the burner to use more fuel which forces a higher temperature at the other parts of the reactor tube.

7. Conclusions

A fast and accurate model of a reformer has been developed by which several design modifications can be evaluated.

It is found that up to 9.5% more hydrogen can be produced by increasing the air fraction in the burner fuel by 50 %, which requires minimal modification impact. More modification impact requires the increasing the thickness of the insulating shield by 50 %, which results in 11.2% more hydrogen production. Besides this, this modification results in a desirable increase in heat distribution between the reactor tubes.

Apart from the technical optimization of a reformer, the feasibility of the improvements proposed still have to be investigated while taking in account costs and aspects related to production of the installation. However our first results indicate that the application of analytical modeling in the design phase of a project can have beneficial effects on the final performance of an apparatus



Figure 6: Conversion efficiency of methane to hydrogen by a change of 50 % of six different design modifications (1) Tube length, (2) Air fraction, (3) Hole geometry, (4) Hole location, (5) Steam fraction, (6) Thickness Shield,. Results are normalized to a reference reformer mentioned 'Start Values'

8. References

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9.Biographies

<u>Maarten de Jong</u> has finished his graduation project at the University of Twente in the department of Design, Production and Management of Mechanical Engineering. His graduate research (described above) combines both design engineering with thermal mechanical engineering in his field of interest: Hydrogen Technology.

dr. Angèle Reinders received her MSc degree in Experimental Physics in 1993. In 1999 she completed her PhD in Photovoltaic Systems at the Faculty of Chemistry of Utrecht University in the Netherlands. Currently she is assistant professor at the Department of Design, Production and Management of the University of Twente in the Netherlands. Her research aims at implementing sustainable energy technology, i.e. hydrogen and solar technology, in innovative

products. Prior to joining University of Twente in 2002, dr. Reinders did research in the field of portable applications of fuel cells at Delft University of Technology (NL) and she worked as a scientific advisor in the Asia Alternative Energy Program of the World Bank in Washington D.C. (2001).

dr. Jim. Kok received his MSc degree in Mechanical Engineering in 1985 and his PhD degree in Applied Physics in 1989 from the University of Twente in the Netherlands. He is associate professor at the Mechanical Engineering department of this university since 1998. In 1996-1997 he spent a year as visiting associate professor at the Sibley School of Engineering at Cornell University in Ithaca, NY, USA. His research covers the fields of turbulent combustion, heat transfer, thermo acoustics and thermodynamics. Both numerical and experimental methods are used. Specific applications studied are gas turbine power generation and generation of hydrogen on basis of hydrocarbon gas and oil reforming.

<u>Gerard</u> Westerdorp is a simulation specialist at HyGear B.V. He has worked on the modeling of reactors, heat exchangers and burners for industrial applications, and on mass-produced consumer products. Prior to joining Hygear in 2003, he worked for PlugPower Inc., Nefit Fasto B.V. and Zowel B.V. He graduated in Physics in 1988 at Delft University in the Netherlands