

**Modeling the Transient Response
of Heat Exchange Reformers**

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Abstract

One method of producing hydrogen for fuel cells is the steam reforming of conventional hydrocarbons, an established refinery process. It has been proposed to carry out this process in a heat exchange reformer – a reformer that has a flow configuration analogous to a heat exchanger. The catalyst, in the form of a conventional pellet, is usually placed in the tubes of the reformer and a hot gas (i.e. from a combustor) or effluent from another process is circulated in the shell side. Key design objectives of the Heat Exchange Reformer are a high, steady state, thermal efficiency and a compact unit both in volume and mass.

It is well known that many applications of fuel cells require transient operation which requires that the production of hydrogen rich feed also varies. Otherwise excess hydrogen is generated and not consumed, leading to a significant loss in overall energy efficiency. The implication is that the transient response of the heat exchange reformer also needs to be considered in its design.

In this work, the transient response of a simplified heat exchange reformer is modeled. The geometry of the reformer is two concentric cylinders, filled with conventional pellet catalyst, a common design element in many heat exchange reformers. The model can be characterized as one-dimensional, homogenous packed bed reactor with thermal coupling between different parts of the reactor. The model incorporates the kinetics of methanol steam reforming.

Typical transients considered are step changes (both positive and negative) in the feed flowrate or the composition of the feed (i.e. steam to carbon ratio). Other investigations are changes in heat transfer coefficients and feed composition.

1 Introduction

The widespread adoption of fuel cells will require an economic technology for producing a hydrogen rich feed. The reforming of liquid fuels, especially conventional hydrocarbons, is one attractive means of generating a feed of the correct quality and quantity for a given fuel cell type and application. The reforming of hydrocarbons, conducted in conventional packed-bed reactors, is an established technology that has been extensively developed for refinery operations. The key characteristics of tubular steamed fired reformers, the least expensive means of generating hydrogen, are large production of hydrogen (100,000 Nm³/hr or even larger), high thermal efficiency (~80%) and an export of steam for refinery consumption [1].

Reforming technology has been developed for plants that require lesser amounts of hydrogen and no steam production. These reformers maintain the high thermal efficiency found in large tubular steam reformers by virtue of their geometry which is similar to heat exchangers. These 'Heat Exchange Reformers' (HER) are a commercial technology and manufactured by a variety of companies: Haldor Topsoe (Haldor Topsoe Convection Reformer - HCTR) [2], Syntex (Advance Gas Heated Reformer - AGHR) [3], Kellogg, Brown & Root (Kellogg Reformer Exchange System - KRES) [4].

The detailed design of a Heat Exchange Reformer varies with company but the similarity to conventional heat exchangers is unmistakable. The shell side of the vessel contains a hot gas, generated by combustion, which is the source of heat for the endothermic reforming reaction. The tubes of the Heat Exchange Reformer are filled with the reforming catalysts and there is appropriate piping to supply a steam/hydrocarbon feed to the reformer and to remove products. Other designs assume that hot gas is generated external to the reformer. The reformer contains multiple tubes so that a significant surface area is presented to the hot gas to enhance heat transfer.

In some designs (Syntex AGHR), there is only one pass of feed through each tube. In other designs, the tube is in the form of a bayonet – that is the tube is two concentric cylinders capped with a hemisphere at one end. The two sections of the bayonet, the inner cylinder and the annulus between the inner & outer cylinder, form one continuous flow path albeit of different cross-sectional area. Feed can enter the bayonet at the inner cylinder and products leave via the annulus. The reverse path is also possible: feed enters the annulus and leaves via the inner cylinder. In either configuration, the feed effectively makes two passes through the reformer. The tube design in Haldor Topsoe HCTR is similar to the bayonet style although there are important differences.

The advantages of Heat Exchange Reformers, compact and high efficiency, invites efforts to extend the technology to the production of hydrogen for fuel cells. Indeed, the original impetus for the development of the technology in the mid 1980's was the need to produce smaller quantities of hydrogen for molten carbonate and phosphoric acid fuel cells [5].

However, it is not certain that the advantages of Heat Exchange Reformers can be maintained as the physical size of the reformer and the process flows are reduced to the scale required by fuel cells. Presently, Heat Exchange Reformers are industrial size units. For example, the Haldor Topsoe HCTR uses bayonet tubes 10m long and has a typical production rate of 2000 – 5000 Nm³/hour of hydrogen [5]. If this flow of hydrogen is feed to a bank of PEM fuel cells [typically 1kWe = 10 SLPM], they would generate 3.3 MW – 8.3 MW of electricity. In contrast, many commercial applications for fuel cells are sized at 1 – 50 kWe.

In this article, we report on a preliminary modeling study of the bayonet tube which is a common design element in some Heat Exchange Reformers. It offers compact design and mechanical simplicity. However heat transfer is clearly an issue due to the limited external surface area. In particular, we focus upon the transient response of the bayonet tube to changes in the feed flow. In many applications of fuel cells (e.g. transportation), it is rare for the demand for power to be steady between startup to shutdown. The fuel cell, and subsequently the reformer, must be able to respond to changing demands in a time span appropriate for the application. Fuel cells can respond within seconds or shorter if needed to changes in demand. The response of the reformer will usually be much longer, depending on the specific design, but it is usually much longer than that of the fuel cell. Thus, the reformer dominates the overall response of the fuel cell/reformer combination and it is important that the transition of the reformer from one steady state to another be speedy.

The basis of the reformer is a semi-commercial methanol reformer that has been reported in previous work [6]. It had a maximum capacity of 4.4 kWe (1kWe = 10 SLPM of hydrogen) at a liquid feed rate of 70 cm³/min of a 54% by weight methanol-water feed. The reactor was constructed from standard 2" diameter Schedule 5 stainless steel pipe and the catalyst bed occupied the central portion of the pipe. The bed was about 1.2L in volume (5.715 cm ID by about 47 cm long) and held about 1.5 kg of a commercial Cu/ZnO/Al₂O₃ catalyst. The reactor was electrically (tape) heated. Further details are available in [6].

The exterior dimensions and standard inlet flows (35 cm³/min of a 54% by weight methanol-water feed) are maintained but the interior is divided into inner and outer annuli to form a bayonet tube. To reduce model complexity, the exterior wall is held at constant temperature equal to the inlet temperature of the feed (300°C). The cross-sectional areas of the inner and outer annuli are equal so that the mass of catalyst contacting the gas is the same in both annuli.

2 Model Description

The model of the reformer can be categorized as one-dimensional, homogenous and transient. The model is a balance between being computationally tractable and providing insight into the dynamics of heat transfer within the reactor. Accounting for additional important phenomena such as radial temperature gradients or interphase mass transfer would improve the predictive power of the model but would also require lengthy compute times to converge.

The endothermic steam reforming of hydrocarbons is modeled by methanol steam reforming. The advantages of doing so are two-fold. First, there are validated rate expressions for methanol steam reforming that, as a result, reliably compute the heat of reaction at local conditions (temperature, composition). The temperature profile, obtained from the energy equation, accurately reflects the effect of reaction upon its development during a transient. The second reason for using steam reforming is that there is still significant interest in using methanol as a convenient means of transporting hydrogen

The model is implemented in Multiphysics 3.2b (COMSOL) with calls to MATLAB® subroutines to compute molecular properties (viscosity, thermal conductivity, etc). A typical run is about 40 minutes on a PC powered by a Xeon CPU operating at 3.4 GHZ.

3 Model Formulation

3.1 Energy

The reformer consists of two concentric cylinders. The diameter of the outer cylinder is D_o while the diameter of the inner cylinder is D_i . Using the pseudo-homogenous methodology, the energy equation for computing the temperature (T_i) of the inner cylinder is:

$$\rho_{cat} C_{p,cat} \frac{\partial T_i}{\partial t} + FC_{p,gas} \frac{\partial T_i}{\partial z} = \eta \rho_{cat} \sum_j (-\Delta H_{rxn})_j r_j + \frac{4}{D_i} U_{total} (T_o - T_i) \quad \text{Eq. 1}$$

where ρ_{cat} is the bulk density of the catalyst, (kg m⁻³), $C_{p,cat}$ is the heat capacity of the catalyst pellets (J-K⁻¹-kg⁻¹ of catalyst), $F (=u_s c)$ is the molar flux, is the product of the superficial velocity (m-sec⁻¹) and total concentration c (moles m⁻³), $C_{p,gas}$ is the heat capacity of the reaction mix (J-K⁻¹-kg⁻¹), ε is the fraction of the reactor volume occupied by gas (void fraction), η is the effectiveness factor, r_i is the rate of i^{th} reaction (moles-sec⁻¹-kg of catalyst⁻¹, see below), $(\Delta H_{rxn})_i$ is the heat of the reaction for the i^{th} reaction (W-kg of catalyst⁻¹) at the given reaction conditions (temperature, pressure and composition), U_{total} is the overall heat transfer coefficient for the heat transfer between the inner and outer cylinders.

A similar equation is written to compute the temperature for the bed in the annulus between the inner and outer cylinder (T_o). It has an additional term to account for the heat transfer from the wall of the outer cylinder:

$$\rho_{cat} C_{p,cat} \frac{\partial T_o}{\partial t} + FC_{p,gas} \frac{\partial T_o}{\partial z} = \eta \rho_{cat} \sum_j (-\Delta H_{rxn})_j r_j + \frac{4D_o}{(D_o^2 - D_i^2)} U_{wall} (T_{wall} - T_o) - \frac{4D_i}{(D_o^2 - D_i^2)} U_{total} (T_o - T_i) \quad \text{Eq. 2}$$

where U_{wall} is the heat transfer coefficient (W-m⁻²-K⁻¹) that accounts for heat transfer between the outer cylinder and hot gas.

3.2 Species

The following equation for species mole fractions (x_i), applies in both packed bed in the inner cylinder and the annulus:

$$\varepsilon c \frac{\partial x_i}{\partial t} + F \frac{\partial x_i}{\partial z} = \rho_{cat} R_i - x_i \rho_{cat} \sum_i R_i \quad \text{Eq. 3}$$

where R_i is the rate of production of the i^{th} species (moles-sec⁻¹-kg of catalyst⁻¹, see below),

The overall molar balance also applies in both the inner and outer tubes and allows computation of the respective molar flux (F , moles-m²-s⁻¹) in each tube:

$$\varepsilon \frac{\partial c}{\partial t} + \frac{\partial F}{\partial z} = \rho_{cat} \sum_i R_i \quad \text{Eq. 4}$$

3.3 Reactions & Rate Expressions of Methanol-Steam Reforming

There are three overall reactions and five species involved in the steam reforming of methanol [7]



We have proposed a mechanistically based reaction scheme for methanol steam reforming based upon the Langmuir-Hinshelwood approach and developed corresponding (complex) rate expressions [8]. There are three rates, one for each reaction, denoted by r_i (moles-sec⁻¹-kg of catalyst⁻¹),

$$r_R = \frac{k_R K_{\text{CH}_3\text{O}'}^* \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{H}_2}^{1/2}} \left(1 - \frac{P_{\text{H}_2}^3 P_{\text{CO}_2}}{K_R P_{\text{CH}_3\text{OH}} P_{\text{H}_2\text{O}}} \right) C_{S_1}^T C_{S_{1a}}^T S_A}{\left(1 + K_{\text{CH}_3\text{O}'}^* \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{H}_2}^{1/2}} + K_{\text{HCOO}'}^* P_{\text{CO}_2} P_{\text{H}_2}^{1/2} + K_{\text{OH}'}^* \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}^{1/2}} \right) \left(1 + K_{\text{H}^{1a}}^{1/2} P_{\text{H}_2}^{1/2} \right)} \quad \text{Eq. 5}$$

$$r_W = \frac{k_W K_{\text{OH}'}^* \frac{P_{\text{CO}} P_{\text{H}_2\text{O}}}{P_{\text{H}_2}^{1/2}} \left(1 - \frac{P_{\text{H}_2} P_{\text{CO}_2}}{K_W P_{\text{CO}} P_{\text{H}_2\text{O}}} \right) C_{S_1}^{T^2} S_A}{\left(1 + K_{\text{CH}_3\text{O}'}^* \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{H}_2}^{1/2}} + K_{\text{HCOO}'}^* P_{\text{CO}_2} P_{\text{H}_2}^{1/2} + K_{\text{OH}'}^* \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}^{1/2}} \right)^2} \quad \text{Eq. 6}$$

$$r_D = \frac{k_D K_{CH_3O^{(2)}}^* \frac{P_{CH_3OH}}{P_{H_2}^{1/2}} \left(1 - \frac{P_{H_2}^2 P_{CO}}{K_D P_{CH_3OH}}\right) C_{S_2}^T C_{S_{2a}}^T S_A}{\left(1 + K_{CH_3O^{(2)}}^* \frac{P_{CH_3OH}}{P_{H_2}^{1/2}} + K_{OH^{(2)}}^* \frac{P_{H_2O}}{P_{H_2}^{1/2}}\right) \left(1 + K_{H^{(2a)}}^{1/2} P_{H_2}^{1/2}\right)} \quad \text{Eq. 7}$$

In equations 5-7, S_A is the BET surface area of the catalyst, and $C_{S_1}^T$, $C_{S_{1a}}^T$, $C_{S_2}^T$ & $C_{S_{2a}}^T$ are total site concentrations (mole-m⁻²). As discussed above, the site concentrations are determined by fitting the packed-model to experimental data as described in [6].

The rates of reactions are combined to give the rate of the species formation R_i (moles-sec⁻¹-kg of catalyst⁻¹):

$$\begin{aligned} -R_{CH_3OH} &= r_R + r_D \\ -R_{H_2O} &= r_R + r_W \\ R_{H_2} &= 3r_R + 2r_D + r_W \\ R_{CO_2} &= r_R + r_W \\ R_{CO} &= r_D - r_W \end{aligned}$$

3.4 Heat Transfer Coefficients

The one dimensional heat transfer coefficients are computed from the standard correlation [9]

$$\frac{U d_t}{k} = 2.03 \text{Re}^{0.95} \exp\left(-6d_p/d_t\right) \quad \text{Eq. 8}$$

The heat transfer coefficient appearing in Eq. 2 (U_{wall}) is obtained by straight application of the above correlation using the local conditions in the annulus.

The overall heat transfer coefficient (U_{total}) appearing in Eq. 1 and Eq. 2 is computed as

$$\frac{1}{U_{total}} = \frac{1}{U_{inner}} + \frac{1}{U_{outer}} \quad \text{Eq. 9}$$

where U_{inner} is computed from Eq. 8 using conditions (velocity, density, etc) appropriate for the inner cylinder. As a simplification, U_{outer} is set equal to U_{wall} . An additional simplification is that resistance of the wall of the inner cylinder has not been considered in Eq. 9.

4 Results

It is well known that heat transfer between a packed bed and its bounding (exterior) wall is poor. The void fraction near the wall rapidly increases to 1, reducing particle contact and increasing the resistance to heat transfer in spite of the increased velocity adjacent to the wall. The heat transfer through the bed itself, away from the wall, is quite good although dependent on the speed of the fluid.

The factors operative at the exterior wall ensure that heat transfer through the wall of the inner cylinder will also be poor. This will greatly reduce the radial flow of heat in the bayonet tube compared to a conventional tube (i.e. the flow path is straight rather than U-shaped as in the bayonet).

The initial expectation is that the transient response of the bayonet tube would be slower to that of the straight tube. To test whether this expectation is correct or not, we compute the time required for the bayonet tube to move from one steady state to another. A similar computation is done for the straight tube.

The test case is chosen to represent the transient induced when the demand on the fuel cell drops from normal operation to a standby mode. The flow of methanol/water feed drops by 90% from a nominal value of 35 cm³/min to 3.5 cm³/min. The inlet temperature and wall temperature are kept constant. The feed is to the inner annuli and exits via the outer annuli.

This is a difficult case as the velocity of the reformate drops reducing the heat transfer coefficients and presumably retarding the re-establishment of a steady state.

It should be noted that a proper control strategy would alter the inlet and/or wall temperature to control the reformer effluent to an appropriate composition and flow.

The specific heat capacity of the catalyst ($C_{p, gas}$) is set to 775 J·kg⁻¹·K⁻¹. This agrees with values developed from heat transfer measurements on the methanol reformer [6] and from open literature sources [10].

Figure 1 shows temperature versus time plots for the conventional tube reformer at three locations. The first two are at 1/10 and 1/5 of the total length of the reformer (47 cm) while the third displays the exit temperature. As can be seen, the reformer reaches steady state after about 5500 seconds or an hour and half.

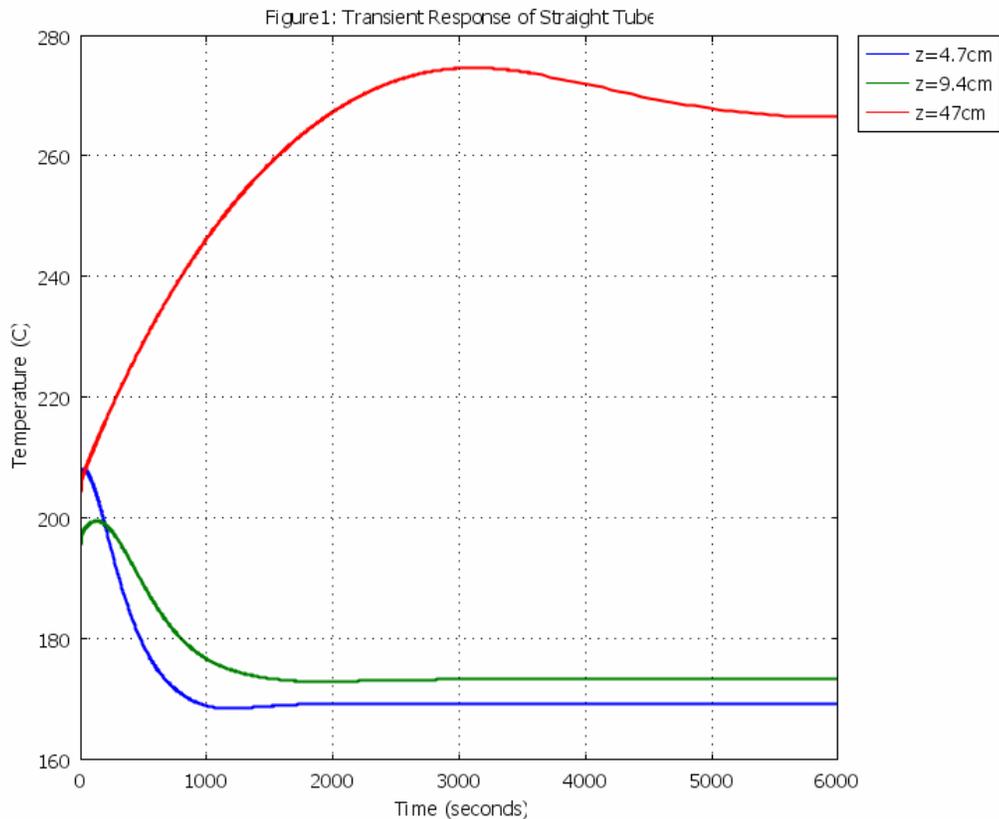


Figure 2 shows a similar time versus temperature plot for the bayonet tube reformer. A number of locations are sampled to yield an indication of the temperature-time variation in both the inner and outer annuli. The first two plots ($z=9.4\text{cm}$ and $z=47\text{cm}$) are the temperature in the inner cylinder. In particular the point $z = 47\text{cm}$ is the juncture where the flow reverses direction from the inner cylinder to the annulus.

The second points ($z=9.4\text{cm}$ and $z=0$) are temperatures in the annulus. The first ($z=9.4\text{ cm}$) is the located 9.4 cm from the exit/inlet and is the counterpoint to the temperature presented at $z= 9.4\text{ cm}$ for the inner annuli. The point $z = 0\text{ cm}$ is the temperature at the reformer exit.

Inspection of the graph shows that the reformer reaches a new steady state after about 3000 seconds or about 50 minutes.

The model shows, for these specific operating conditions and geometry, the bayonet tube reaches it's a new steady state in less time than the straight tube.

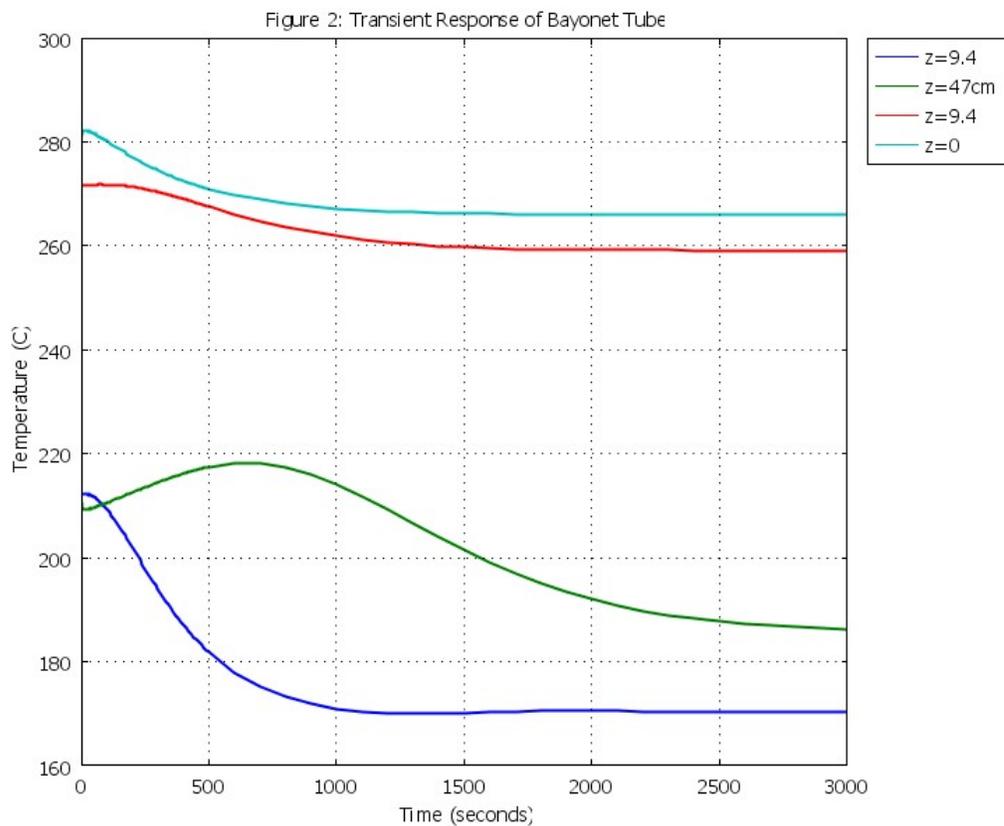
This is counter to the initial expectation based upon the increased resistance to radial heat transfer due to the interior wall.

A plausible explanation for these results is based upon the consideration that heat flows not only in the radial direction but is advected by the fluid. The bayonet tube, having a smaller cross-sectional than the straight tube, has greater fluid velocities that effectively redistributes heat at a greater rate than the straight tube.

The fluid velocities in the bayonet tube range form 0.08 – 0.14 m/s while the velocities in the straight tube are lower at 0.04 – 0.07 m/sec.

5 Summary

The computations show that the transient response of a bayonet tube can be faster than that of a straight tube in spite of the added resistance to radial heat flow due to the wall of the inner cylinder. However, in both cases the attainment of a new steady state takes a significant length of time, typically an hour. This is most likely not acceptable for most fuel cell applications.



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