



Application of heat flux as a control variable in small-scale packed-bed steam reforming

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ABSTRACT

In steam reformation, high thermal resistance and poor heat transfer of the packed catalyst bed can create time-lag between the moment when the heat is applied and the corresponding rise in temperature. Thus, problems arise from the dynamic requirements of the system, which can create a time-lag in the reactor's performance and also induce temperature oscillations resulting in a degrading catalyst. Lag compensation is necessary if one uses temperature feedback control to maintain the reactor temperature. A better solution is to recognize that heat flux is more suitable as a control variable, since available heat is what sustains the chemical reaction inside the reactor. Thus, controlling heat flux can directly influence the reaction and the resultant temperature inside the reactor. A heat flux controller is implemented for two small-scale, packed-bed, steam reformers. A standard temperature feedback controller is also implemented. The two systems are compared in their transient response. Temperature and reformate gas concentrations are measured to evaluate the performance of the two controller topologies. The heat flux based controller significantly outperforms the temperature feedback controller in both geometries tested.

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1. Introduction

Steam reforming is the method most widely used to reform hydrocarbons in large-scale hydrogen production. Steam reforming is an endothermic process that requires an external heat source, usually in the form of a burner, catalytic combustion, or electrical heating elements [1–4]. A specific catalyst is used depending upon the hydrocarbon feedstock. Energy is needed to de-volatilize the hydrocarbons and break the C–C and H–C bonds in the fuel. Thus, introducing a catalyst into the reaction creates new pathways and accelerates the reaction rate. Temperature directly influences activity, selectivity, and stability (or degradation behavior) in the catalyst [5]. Therefore, temperature control of steam reformation is critical to the reactor performance and catalyst life. The emerging small-scale reformer for distributed and mobile hydrogen production emulates its industrial-scale counterpart in many ways. However, the operating conditions required in the small-scale reactor create many implementation challenges.

In general, one temperature control strategy is to have feedback sensors located at the point of interest and to adjust the

heat source appropriately. This topic is widely discussed in process control literature [6,7]. However, with regards to an endothermic process in a chemical reactor with potentially transient operation, the literature is less developed [6–9]. Researchers have modeled the steam-reforming process [10–14] and the reformer [15–20], and also have proposed control algorithms [8,9,21]. The issue of controlling the catalyst temperature is widely recognized, although it has not been fully addressed. Typically, a high level control algorithm sends manipulated input signals to adjust the heat input to regulate temperature. While this is adequate for most current large-scale reformers operating continuously for over 12,000 h [22], the relatively large changes in demand that small-scale reformers experience requires frequent fuel feed rate transients. The thermal control of the steam reformer is critical to the reactor performance, and the control affects conversion, efficiency, effluent composition, and catalyst life [2,3,23–29]. For an integrated fuel processor in a fuel-cell power system, it is important to minimize un-wanted species and maximize fuel conversion.

A previous study, using a reactor with a discrete multiple-zone electric heater design, showed that the selection of the feedback sensor location in the reactor has significant impact on the temperature oscillation inside the catalyst bed [30]. The temperature set-points of the heating elements are changed based upon the selection of feedback location and reactor geometry. As expected, the most stable reactor temperature is achieved by placing the

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Nomenclature

m_{heater}	mass of the electric heating element
$m_{\text{reactor_housing}}$	mass of the reactor housing
m_{catalyst}	mass of the catalyst (see also m_c)
m_c	mass of the catalyst
q	heat flux
q_{in}	heat flux from the external heat source
q_{rxn}	heat required by the reaction
q_{rxnSR}	heat required by steam reforming of methanol
T_c	estimated temperature of the catalyst
ΔH_{SR}	heat consumed by the steam reformation
$\dot{m}_{\text{CH}_3\text{OH}}^*$	molar flow rate of methanol
c_h	effective heat capacity coefficient of the catalyst
c_c	effective thermal capacity of the catalyst
h_{hc}	heat-transfer rate coefficient between the catalyst housing and the catalyst
\hat{h}_{hc}	estimated heat-transfer coefficient between the housing and the catalyst
K _{isa}	controller integral gain
K _{sa}	controller proportional gain
b _a	controller derivative gain
h_a	controller heat-transfer active gain

sensor close to the heating element. However, this method effectively regulates the temperature of the heating element but requires compensation for the heat-transfer properties of the catalyst bed. This method is adequate for steady state operation but has limitations when considering transient operation when the heat-transfer properties change.

While the means and rate of heat transfer from the heat source to the catalyst are limited by the design of the reformer – including geometry, material temperature limitations, and gas flow rate [10,31,32] – the choice of using heat flux as the control variable can capture these properties and achieve better temperature control. Heat flux, as the control variable, allows more stable operation over a range of operating conditions, such as an increase of fuel flow rate as found in a transient condition. This method of using heat flux allows better utilization of the catalyst and offers insight to the trade-offs between the influencing properties in reactor performance. The selection of the control variable can also influence the overall control topology. The method presented here can be adapted to other controller topologies, such as adaptive tuning, proportional, derivative, and integral (PID) style control algorithms, without losing the general governing principles.

In this paper, we present a controller design approach for a tubular methanol steam reformation reactor heated by external electrical nozzle band heaters using a copper-based catalyst. To illustrate the flexibility and generality of this approach, two tubular geometries are used to demonstrate the effectiveness of the controllers by measuring the reformat stream composition. The experimental results of each reactor geometry is reported in ml min^{-1} fuel feed rate rather than liquid hourly space velocity-methanol (LHSV-M) since hydrogen demand is related to reactant feed rate. LHSV-M is reported only as a reference for comparison to other systems.

2. Steam reformation and temperature control issues

Steam reformation takes place at elevated temperature using a catalyst. The steam reformation is normally limited by mass and heat transfer [33,34]. In a typical packed-bed catalyst reactor, the primary mode of heat transfer is via convection [34]. The high thermal resistance within the catalyst bed makes it difficult to maintain

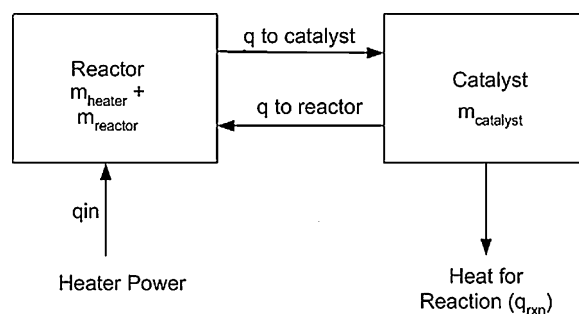


Fig. 1. The simplified energy plant block diagram of the steam reforming reactor.

uniform bed temperature in a large-radius reactor. Resistance to heat transfer also creates a significant time-lag from the time when heat is applied to the corresponding rise in the bed temperature. Thus, it is typical to use a high aspect ratio (small radius relative to length) reactor in steam reformation. However, as the reactor radius decreases, the volume of the reactor (thus the catalyst) decreases rapidly, rendering a high volume of construction material per volume of the catalyst. This can result a lower energy density and reforming capacity for the overall system. A balance must be struck between the energy density and the physical sizing of the reactor.

Temperature has a strong influence on stability and degradation of the catalyst [2,24]. Copper-based catalysts have high selectivity and become active at a relatively low temperature. However, the low melting point of copper makes these catalysts prone to degradation by sintering. In addition, premature degradation of the catalyst from contaminants and operating conditions, such as start-up and shutdown, can impact the long-term performance of the reformer [35]. The high thermal resistance of the catalyst bed makes it difficult to transfer heat from the heater to the catalyst. This also causes large temperature gradients and local high temperature near the heat input locations [10,20,22,31,32,36]. Clearly, an important link to the overall performance, stability, and robustness of the reformer, is the issue of controlling reactor temperature.

In a large-radius reactor, the heat-transfer limitation creates a cold zone in the center of the reactor. It is important to maintain the temperature in the center region to minimize un-reacted hydrocarbons from passing through the less active catalyst, which can cause coking and fouling by direct deposition or condensation. The temperature gradient during transients, however, is unavoidable due to high thermal resistance in the catalyst bed as the rate of heat consumed by the endothermic reaction is locally faster than the rate of local heat input. It is therefore difficult to maintain axial temperature during a transient operation. For example, when the reactant feed rate increases, a cold zone is developed in the center of the catalyst bed and will propagate down the length of the reactor. The controller will then increase heater power to compensate. However, due to the heat-transfer limitation, the propagation of the cold zone will effectively push the reaction zone beyond the end of the catalyst bed, resulting un-reacted hydrocarbons and undesired chemical species will leave the reactor. When more heat becomes available, the reaction zone will retract into the catalyst bed, signified by an increase of centerline temperature and a decrease of the emitted hydrocarbon species. Several cycles of axial temperature oscillation may occur before the reactor reaches steady state.

Temperature oscillation can change the catalyst structure over time by deactivating the catalyst. While Pt-based catalysts exhibit high stability, the lower cost Cu/ZnO/Al₂O₃ based catalyst can be deactivated by sintering through thermal cycling [35]. When designing a steam-reforming reactor, there will be a trade-off between maximum heater temperature, reactor radius, and fuel flow rate.

3. Selection of control variables and reactor modeling

Relying solely on temperature feedback can cause significant performance and control issues. However, it is possible to select a more appropriate control variable to achieve the same goal. In an endothermic reactor, the catalyst temperature is determined by the amount of heat input by the heating element and heat consumed by the chemical reaction. Thus, regulating heat rather than temperature will give one direct control over the temperature of the catalyst bed. To regulate the heat input, depending on the mode of heat transfer and efficiency between the catalyst and the heating source, appropriate power is adjusted. To regulate the heat consumed, regulating the reactant feed rate is sufficient.

There are several implications in this heat flux approach which uses a combination of both feedback and feedforward approaches. First, the controller is adjusting heat input before there is a temperature change in the catalyst bed during a change of reactant feed rate. This can be accomplished by a feedforward command based on the reactant feed rate. It shortens the time it takes for the controller to adjust for this disturbance. Furthermore, by appropriately sizing the reactor, the controller can maintain the catalyst temperature, while subjected to large-magnitude but short-time transient loads, without the reaction zone extending beyond the reformer. Second, the controller will not feed reactant at a rate that the reactor cannot reform. This helps maintain high fuel conversion when the reactor is not up to temperature. As heat input increases, the reactant feed rate will also increase. In steam reforming of methanol, the required heat for the reaction, q_{rxn} , is given by Eq. (1)

$$q_{\text{rxn}} = \Delta H_{\text{SR}} m_{\text{CH}_3\text{OH}}^* \quad (1)$$

where $m_{\text{CH}_3\text{OH}}^*$ is the methanol mole flow rate, mol s^{-1} , and ΔH_{SR} is the heat consumed by steam reformation, or 50 kJ mol^{-1} considering 25 C inputs.

In order to bring the steam reformation to completion, sufficient heat must be provided before the fuel reaches the end of the reactor. From observing the temperature profile of a steam reformer reactor, one notes that at maximum flow rate the cold temperature extends axially from top down along the length of the reactor until the fuel is completely reacted [37]. This indicates that heat in the top region of the reactor is consumed, and the un-reacted fuel will

travel down the reactor until it is consumed. In steam reformation, heat transfer is the dominating limiting mechanism [34]; therefore, a model which captures this, will simplify the controller implementation. Considering energy alone, Fig. 1 shows a simplified plant model of a steam reformer

The goal of this model is to produce a qualitative output for a given condition. This formulation assumes uniform temperature distribution, uniform concentration of reactant, uniform reaction rate, and uniform heat exchange rate. By assuming the heating element as the primary heat source – the reactant and thus the heat required by the endothermic reaction – as the primary heat sink, one can describe the temperature of the catalyst by Eq. (2)

$$m_c c_c \frac{dT_c}{dt} = q_{\text{input}} - q_{\text{rxnSR}} \quad (2)$$

where T_c is the estimated catalyst temperature, m_c is the mass of the catalyst, c_c is the effective thermal capacity of the catalyst, q_{input} is the heat from the external heat source, and q_{rxn} is the heat required by the steam reformation. The estimated temperature will be a representative average temperature of the catalyst. This allows a reasonable estimation of the centerline temperature by using “effective” parameters to reflect the geometry factor of the reactor. For example, the effective heat-transfer constant will be used to estimate the heat transfer between the reactor wall and the catalyst.

The plant model captures the interaction between the various components necessary to model the steam reformer. Equilibrium is reached when all is balanced. The mass of the reactant is not directly included in this model because this simplification allows only heat consumed by the reaction to be the limiting factor in achieving full fuel conversion. This emulates the heat-transfer limitation in the actual catalyst bed. In other words, unless the catalyst has received sufficient heat energy, the reaction cannot go to completion.

4. Reformer controller implementation

Two reformer geometries are used in the experiment, as shown in Fig. 1. Electric nozzle band heating elements are used to provide heat for the reaction with thermocouples located between each heating element to measure the centerline and interior wall temperature. The Sud-Chemie FCRM-2 catalyst, a $\text{Cu/ZnO/Al}_2\text{O}_3$

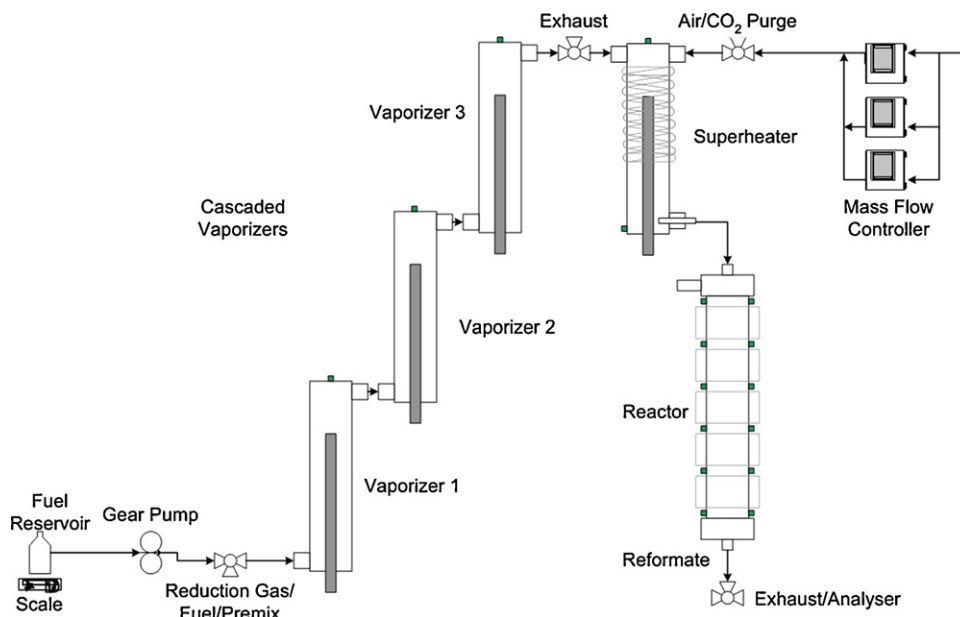


Fig. 2. Schematic of the experimental set-up.

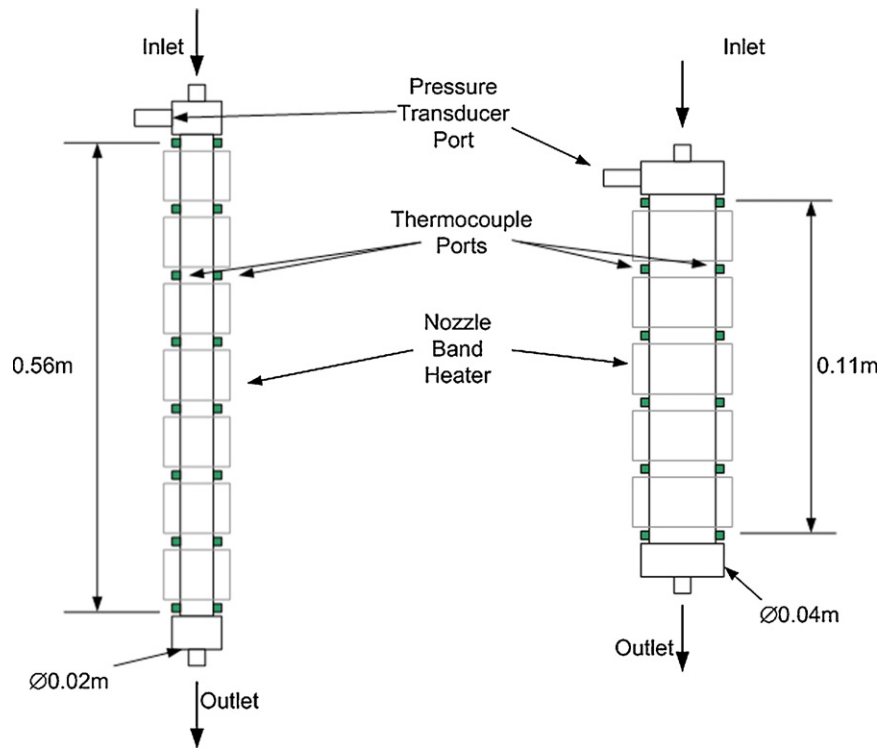


Fig. 3. Schematics of the reactors used in the experiment. Reactor A is a small radius fully packed catalyst bed depicted on the left while Reactor B is the large radius reactor shown on the right.

pelletized catalyst, is crushed, screened with a wire mesh, and loaded into the reactors. The larger of the two reactors (Housing B) is 25.4 cm (10 in) long, 3.81 cm (1.25 in) nominal diameter schedule 40 stainless-steel pipe, which can hold 450 g of crushed catalyst. Five nozzle band heaters are installed. The small-radius reactor (Housing A) is 55.9 cm (22 in) length, 1.9 cm (0.75 in) nominal diameter schedule 40 stainless-steel pipe, which can hold 250 g of crushed catalyst. Seven nozzle band heaters are installed. A pre-mix of water and methanol at 1.6 steam-to-carbon ratio was used

in order to avoid coke formation. This general experimental set-up, shown in Fig. 2, is the same used by Davieau and Erickson [20], Yoon and Erickson [38], and Liao [32].

A NOVA Analytical Systems Inc. 79404 CM gas analyzer is used to measure the reformat composition. The reformat is cooled and the condensate is collected. The fuel conversion is measured by the density of the condensate. The reactor can be changed for use with a different catalysts and reactor geometries. Fig. 3 shows the schematic of the two reactors used in the experiments.

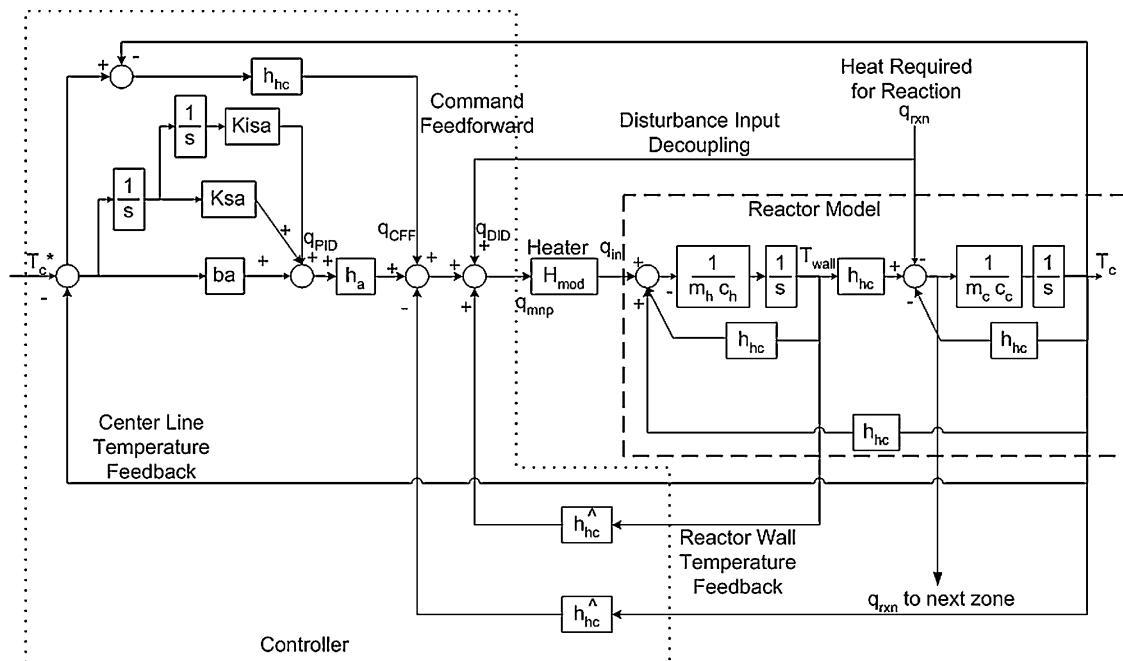


Fig. 4. Block diagram of the steam reformer controllers for both reactors.

With the reactor naturally divided into sections by the nozzle band heaters, the reactor controller is constructed to individually control each section. At high fuel flow rates, the top section centerline is relatively cold. As long as the total heat in the reactor is sufficient, the low temperature zone will not extend beyond the lowest section of the reactor. A cascaded controller topology is used to emulate this phenomenon. Fig. 4 shows the control block diagram of each individual section of the reactor. Eqs. (3) and (4) show the governing equations of the reactor model, and Eq. (5) is one possible formulation of the controller. The heat required by the reaction is modeled as a disturbance input to the catalyst model. Heat is consumed by the reactant. If insufficient heat is available in the section, the remaining reactant will travel down and consume the available heat in the next section. This is represented by the heat required to reform the remaining reactant flowing into the next section. Note that from this topology, the total heat currently available in the reactor can be estimated and used to regulate the reactant flow rate input. Thus, in order to maintain the reactor temperature and high fuel conversion rate, this regulating action of fuel flow rate controls heat consumed by the reaction.

$$m_h c_h \frac{dT_{\text{wall}}}{dt} = q_{\text{in}} + (T_c - T_{\text{wall}})h_{\text{hc}} \quad (3)$$

$$m_c c_c \frac{dT_c}{dt} = (T_{\text{wall}} - T_c)h_{\text{hc}} - q_{\text{rxn}} \quad (4)$$

$$q_{\text{in}} = H_{\text{mod}}[q_{\text{PID}} + q_{\text{CFF}} + q_{\text{DID}} + (T_{\text{wall}} - T_c)\hat{h}_{\text{hc}} + (T_c^* - T_c)\hat{h}_{\text{hc}}] \quad (5)$$

The presented controller is one possible implementation. The important key is that it is regulating heat as the control variable. This controller has several features. It uses the temperature feedback to produce heat command as a manipulated input, q_{mnp} , to the heat modulator, H_{mod} . It also commands a heat input based on the heat required by the reaction, q_{rxn} , as a decoupled disturbance input. The command feedforward using T_c , and decoupled state feedback for the reactor wall, T_{wall} , and catalyst temperature, T_c , are additional enhancements to improve the overall dynamics of the reactor.

The temperature feedback loop is essential for driving a temperature to convergence. The feedforward path can shorten the system's response time by changing the heat input before the temperature changes. Since these steps complement each other, the feedback loop and the feedforward path should be used in tandem, while a distinction should be made between the feedback variable and control variable. In many thermal management controllers, temperature is a directly accessible variable while heat is not. Thus, in order to indirectly assess the heat stored in and transferred from a control volume, it is necessary to use temperature. A similar concept is applied to a motion controller. Controlling motor torque will give one control over velocity and position, but the only accessible feedback variable is motor current.

Additional details are not explicitly shown in the block diagram. First, the non-linearity and discontinuity of catalyst activity is included in the controller. Since the catalyst shows very low activity at around 180 °C, the catalyst will remain at this temperature when insufficient input heat is available. This property has been included in the actual implementation. Next, the heat modulator has finite power and limited heat-transfer rate. This detail is hidden from the presented block diagram. This heat modulator can be modified based on the specific design of the heating element or method, and the block diagram will remain valid. Also, a maximum temperature set-point is used to avoid sintering the catalyst near the reactor wall.

Since the dynamics of the reactor are relatively slow, the controller characteristic polynomial is tuned for roots or eigen-frequencies at 0.06 Hz, 0.01 Hz, and 0.001 Hz. These frequencies were selected based on the reactor characteristic time described

Table 1

Constants used by the steam reformer controllers.

	Small-radius fully packed reactor A	Large-radius fully packed reactor B
m_c [kg]	0.049	0.089
c_h [J (kg K) ⁻¹]	475	475
c_c [J (kg K) ⁻¹]	900	900
h_{ch} [W K ⁻¹]	0.4389	0.7219
h_{hc} [W K ⁻¹]	0.4389	0.7219
K_{isa} [W K ⁻¹ s ⁻²]	0.0000427	0.0000657
K_{sa} [W K ⁻¹ s ⁻¹]	0.14	0.1
ba [W K ⁻¹]	23.4	17.6
h_a [J]	14.88	14.86

by Yoon [39] and the liquid hourly space velocity of methanol (LHSV-M) for the specific reactor. At these eigen-frequencies, the large-radius reactor is expected to be limited by the heat-transfer at the high fuel flow rate settings used. Table 1 tabulates the parameters and the corresponding controller gains for the two reactor geometries.

5. Results

Figs. 5 and 7 shows the resultant temperature using a temperature feedback controller and the proposed heat regulator (without regulating fuel feed rate) over 20 min when the pre-mix fuel flow rate is increased from 4 ml min⁻¹ to 8 ml min⁻¹ at $t=200$ s from both the small-radius Housing A and large-radius Housing B systems. Figs. 6 and 8 show the gas concentration during the same time periods. Typically, the hydrogen, H₂ concentration at complete conversion is 72%, with less than 1% hydrocarbon, CH₄. In Figs. 5a and 7a, the temperature control responded only after the

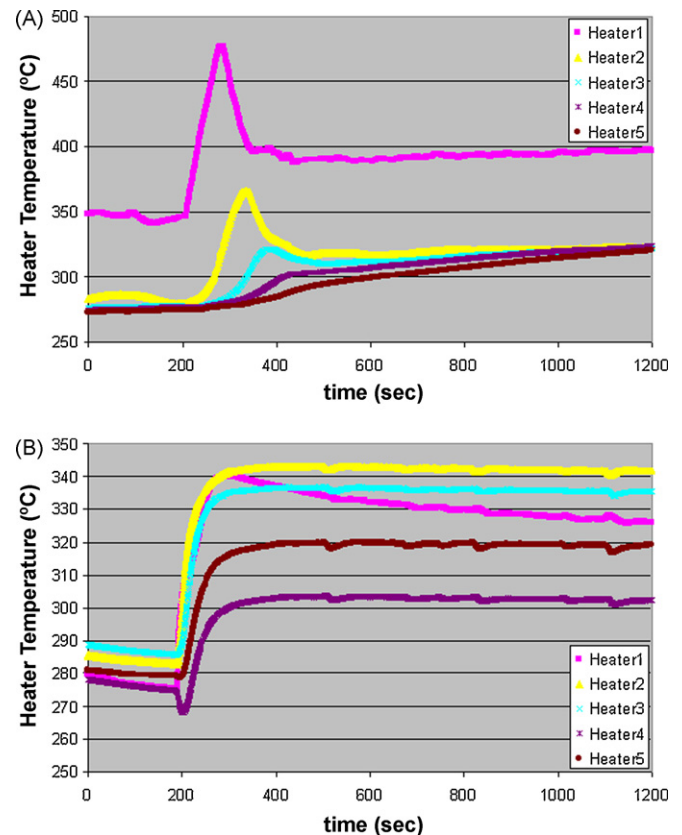


Fig. 5. Temperatures of the heaters from the temperature controller (a) and heat controller (b) in the large-radius reactor Housing B during an increase of the pre-mix fuel flow rate from 4 ml/min to 8 ml/min at $t=200$ s.

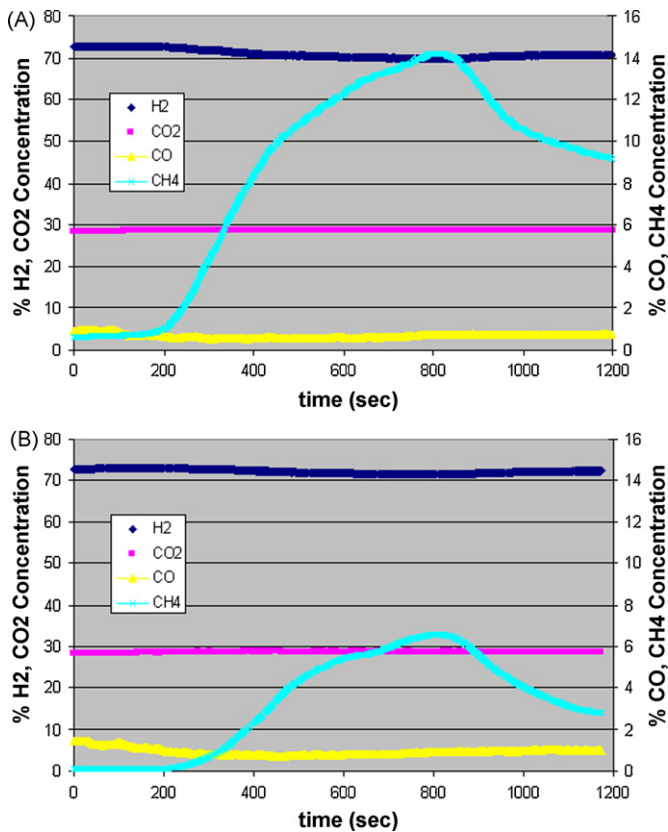


Fig. 6. Gas concentrations in the Large-radius reactor Housing B with the temperature controller (a) and the heat controller (b). At $t=200$ s, the pre-mix fuel flow rate increased from 4 ml/min to 8 ml/min, equivalent in LHSV-M increase from 0.59 (1/h) to 1.03 (1/h).

temperature in the reactor has changed. Due to high thermal resistance in the packed-bed reactor, insufficient heat is available to reform the methanol. In Figs. 5b and 7b, as soon as the command of fuel increased, the heating element responded quickly to compensate for the demand of heat required by the reaction.

In Figs. 6 and 8 Figs. 6a and 8a, with temperature control of the large-radius reactor Housing B, the CH_4 concentration increases as the pre-mix fuel flow rate increases at $t=200$ s. In Figs. 6b and 8b, using the proposed heat regulator the CH_4 concentration increases at a lower rate and at peaks at lower concentration. With the large-radius reactor Housing B, which is limited to 8 ml min^{-1} maximum pre-mix flow rate at which the reaction zone will extend beyond the catalyst bed, the presented controller improves the overall conversion indicated by a smaller peak in the CH_4 concentration. At the same time, the output H_2 concentration quickly recovers.

Improvement is noticed with the small-radius reactor Housing A in Fig. 8 because the smaller radius helps to improve heat transfer from the reactor wall to the catalyst. Despite the use of the temperature feedback controller, the changes in H_2 and CH_4 concentration (see Fig. 8a) are less severe than they are with the large-radius reactor during the increase of pre-mix fuel flow rate. In Fig. 8b, by applying the proposed heat regulator, there is no change in H_2 and CH_4 concentration during the increase of pre-mix flow rate. As shown, this heat flux controller completely eliminates the concentration changes in output gases and maintains temperature better than the temperature feedback controller.

The maximum reforming capacities of the two reactors were determined experimentally. While the small and large-radius reactors have the maximum reforming capacities of 13 ml min^{-1} and 8 ml min^{-1} pre-mix fuel feed rate, respectively, the experimental results shown above did not use the full reforming capacity

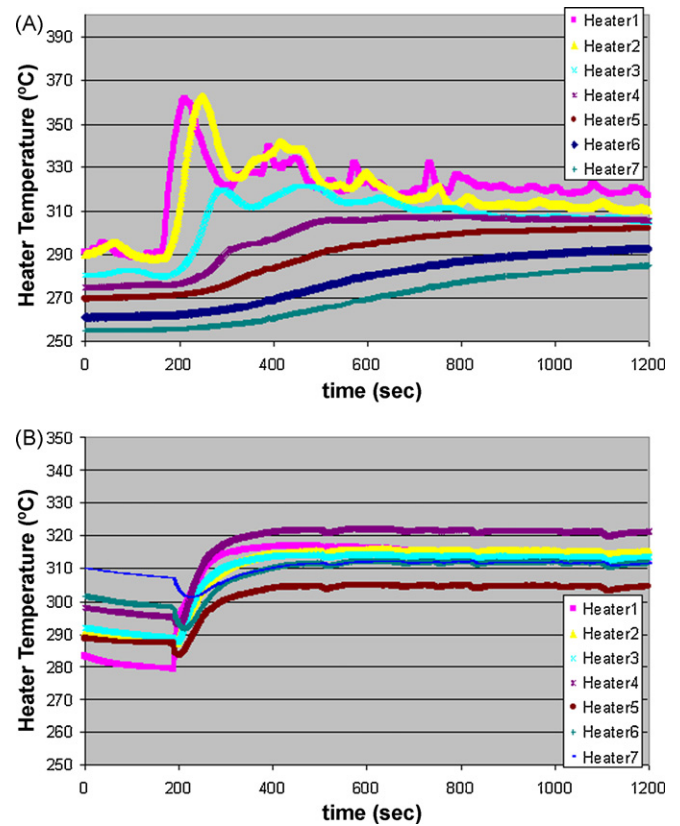


Fig. 7. Heater temperatures from the temperature controller (a) and heat controller (b) in the small-radius reactor Housing A during an increase of the pre-mix fuel flow rate from 4 ml/min to 8 ml/min at $t=200$ s.

of the small-radius reactor. While reactor geometry is critically important, the goal here is to demonstrate that using the heat flux controller also plays an important role in reformat gas concentration and fuel conversion, as shown in Fig. 9. It also shows that the choice of the proper control variable can simplify the controller design. The temperature controller only responds to the change in temperature, while the heat flux controller provides heat as required by the energy balance. This energy balance is based on the fuel flow rate. With an endothermic reaction consuming heat rapidly, the temperature controller will inherently be lagging in response. The faster and more stable response occurs for the heat flux controller through essentially bypassing the plant's response time.

It is obvious that for a heat-transfer-limited endothermic reaction, the small-radius reactor Housing A has advantage over the large-radius reactor Housing B. The overall catalyst effectiveness is higher with faster dynamic response for the small-radius reactor. With only temperature feedback control, the small-radius reactor already has reasonable performance with respect to fuel conversion, hydrogen gas, and unconverted hydrocarbon gas concentration, as shown in Fig. 9. With the application of the heat flux controller, the reformat stream gas concentration shows noticeable improvement during the transient as shown in Figs. 6 and 8.

For the large-radius reactor Housing B, the heat flux controller did not achieve the same degree of improvement as with the small-radius reactor. However, the reduction of CH_4 concentration during the transient is still significant. Choosing heat flux as the control variable helps to maximize hydrogen gas yield and minimize unconverted hydrocarbons in the reformat stream, thus improving the performance and fuel conversion. Due to the high thermal resistance of the catalyst bed, the large-radius reactor is less preferable for steam reforming. However, larger reactors with higher

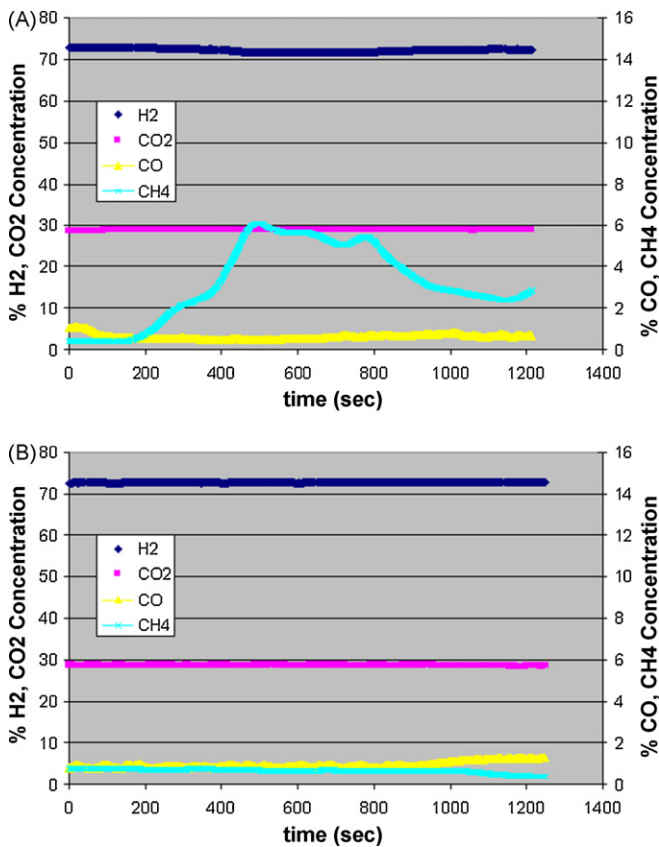


Fig. 8. Reformate Gas Concentration in the small-radius reactor Housing A with the temperature controller (a) and the heat controller (b). At $t = 200$ s, the pre-mix fuel flow rate increased from 4 ml/min to 8 ml/min, the equivalent LHSV-M increases from 0.75 (1/h) to 1.5 (1/h).

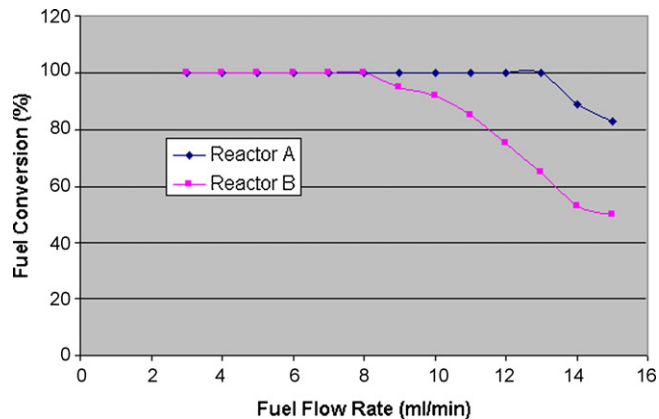


Fig. 9. Fuel conversion of the reactors at steady state for various fuel flow rates.

heat capacity at temperature are also somewhat more stable with respect to short-term transient loads. Further work in optimizing transient performance is taking place at the UC Davis Hydrogen Production and Utilization Laboratory.

6. Conclusion

For hydrogen production using small-scale reactors, it is especially challenging to control temperature and gas concentration due to the dynamic load requirements. Maintaining proper reactor temperature can improve fuel conversion and maintain proper gas concentration. The temperature controlled system has severe

limitations in terms of maintaining catalyst life and overall reactor performance. The proposed heat flux controller is a general solution for a thermal regulator and it is suitable for regulating these small-scale reactors. This controller takes advantage of the physical properties of the reactor, such as the inherent thermal storage and the geometry of the reactor. It relaxes the design constraints such as reactor geometry and catalyst volume while maintaining desirable performance.

The presented block diagram and the controller topology offer insight to where additional enhancement can be implemented, such as the heat modulator or the heating element. The use of state feedback decoupling and disturbance input decoupling can further improve the controller's response time. Furthermore, any additional disturbance can be decoupled quickly using the presented block diagram. These enhancements help the heat flux controller to significantly outperform a temperature-based controller in both the reactor geometries tested as measured by maintenance of temperature and output gas concentration.

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