Wiener Model and Extremum Seeking Control for a CO Preferential Oxidation Reactor with the CuO-CeO₂ catalyst

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Abstract: Hydrogen rich gas produced by hydrocarbon reforming contains CO up to several thousand ppm which acts as a poison for the proton exchange membrane fuel cells. Preferential oxidation (PROX) is one of the promising methods that reduce its concentration below 10ppm. The PROX reactor with the CuO-CeO₂ catalyst shows optimal reactor temperature and a control system that maintains the PROX reactor temperature at its optimal one under changing environments and catalyst deactivations. Experimental studies to obtain a dynamic model for the CO PROX reactor have been done and the Wiener-type nonlinear model is obtained. Then the extremum seeking control that can track the optimal temperature for the Wiener-type nonlinear system is applied and its performance is verified experimentally. The extremum seeking control is a non-parametric real-time optimization method and can be applied effectively to other CO PROX reactors with different operating conditions.

Keywords: PROX Reactor, CO Oxidation, PEM Fuel Cell, Wiener Model, Extremum Seeking Control.

1. INTRODUCTION

Hydrocarbon reforming can be used to produce economically hydrogen, a source for the proton exchange membrane fuel cell. The hydrogen-rich gas from hydrocarbon reforming reactors can have CO up to several thousand ppm which poisons the anode catalyst of the fuel cell. The CO concentration need be removed below 10ppm. The preferential oxidation (PROX) is one of the simplest ways for this purpose. It uses the following oxidations:

$$CO + 0.5O_2 \rightarrow CO_2 \quad (\Delta H_{298}^o = -282.984 [kJ / mol]) H_2 + 0.5O_2 \rightarrow H_2O \quad (\Delta H_{298}^o = -241.828 [kJ / mol])$$
(1)

In reactions of Eq. (1), the CO oxidation should occur preferentially over the H_2 oxidation. The copper-cerium oxide catalyst of CuO-CeO₂ has been reported to have high activity and selectivity for CO oxidation (Dudfield et al. 2001; Kim and Cha, 2003).The CO PROX reactors with CuO-CeO₂ catalyst can remove CO from 1% to less than 10ppm.

In the PROX reactors, the H_2 oxidation also occurs, degrading the overall efficiency of fuel cell system with hydrocarbon reforming. To design the CO PROX reactor, kinetics data for the CO and H_2 oxidations under various mixture conditions are necessary. Recently, Lee and Kim (2008) proposed such kinetics for CO and H_2 oxidations over the CuO-CeO₂catalyst as

$$-r_{CO}[mol /(kg \cdot s)] = 3.4 \times 10^{10} \exp\left(-\frac{94.4[kJ / mol]}{RT}\right)$$
$$P_{CO}^{0.91} P_{CO_2}^{-0.37} P_{H_2O}^{-0.62}$$

$$r_{H_2}[mol / (kg \cdot s)] = 6.1 \times 10^{13} \exp\left(-\frac{142[kJ / mol]}{RT}\right)$$

$$P_{H_2} P_{CO_2}^{-0.48} P_{H_2O}^{-0.69}$$
(2)

Here the partial pressures are in the unit of kPa. Both oxidation rates are independent of the oxygen partial pressure, i.e., zero-order reactions for the oxygen concentration, and CO and H₂ reaction rates are near first-order for CO and H₂ partial pressures, respectively. Rigorous simulations that use the above kinetics with diffusion of the reactants into the catalyst pore structure have been done (Kim et al., 2013), showing effects on the reactor performances for various process conditions such as the feed composition of oxygen and the reactor temperature. One of the results to be noted especially is that, under limited oxygen feed flow rate, there is the reactor temperature window where the CO concentration is below 10ppm. There is the optimal reactor temperature interval.

The optimal reactor temperature will change as reactor conditions and environments change. To maintain the reactor temperature at its optimal one under changing environments, a control system is required for optimal and longer operations of the reactor. For this, a dynamic model of the CO PROX reactor is studied first. The mathematical model is constructed and, for high thermally conductive reactor, the dynamics between the heater input and the CO conversion is shown to be well approximated by a Wiener-type nonlinear model. Experimental step responses support this Wiener-type nonlinear model.

To maintain the exit CO concentration at its minimum is a task different from the traditional control one to regulate the output at a given set point. There have been several approaches to attack this real-time optimization problem such as dynamic and static nonlinear programming with perturbation and waiting (Fu and Ozguner, 2011). Recently, Krstic and Wang (2000) have presented a simple scheme named extremum seeking control. It uses external excitation to perturb the system continuously and find the gradient. It has been extended to multivariable problems (Ghaffari et al. 2012). For processes where such excitation is allowable, it can be used effectively to track the optimal operating point. For Wiener or Hammerstein-type nonlinear processes, it has additional advantages as shown in Dochain et al. (2011). Here, the basic extremum seeking control is applied to track the optimal operating point for this CO PROX reactor.



Fig. 1. Experimental system for the CO PROX reactor.

2. CO PROX REACTOR SYSTEM

Experimental PROX Reactor System: Experimental CO PROX system is shown in Fig. 1. Gas phase reactants of CO (0.5mL/min), O₂ (0.5mL/min), H₂ (90mL/min), CO₂ (10mL/min) and N₂ (400mL/min) are fed to the tubular reactor. Their flow rates are regulated by the mass flow controllers (Brooks MFC5850E).

The tubular reactor is made of the aluminum tube of 0.25 inch diameter, which has high thermal conductivity and shows near zero temperature gradient along the axial axis. CuO-CeO₂ catalyst whose size is between 80 and 100 meshes are used and 1 gram of this catalyst is packed to the tubular reactor. Heating band is attached to the aluminum tube and its power is regulated by the SCR unit which has the control input between 0 and 5 volt. This signal is used as the manipulated variable to control the reactor temperature and consequently the exit CO concentration (or the CO conversion). The K-type thermocouple is inserted to the tubular reactor to measure the reactor temperature. Cooling is done by the natural convection by air. In the practical methanol reforming system, feed reactants for the reformer can be used to cool the PROX reactor without the overall loss of thermal energies.

The exit CO concentration is measured by the infrared gas analyzer (Teledyne Model 7500). It can measure the exit CO concentration between 0 and 200ppm.

Catalyst Preparation: The CuO-CeO₂ catalyst is made via the co-precipitation of Cu(NO₃)₂ \cdot 3H₂O and Ce(NO₃)₃ \cdot 6H₂O solution. Its fabrication steps are (Kim, 2014)

Step 1: Resolve 2.5166g Cu(NO₃)₂ \cdot 3H₂O and 18.0923g Ce(NO₃)₃ \cdot 6H₂O in the 250mL distilled water. Agitate for 5 minutes at 55°C.

Step 2: By adding 1N NaOH at 55°C, maintain the solution pH at 10 for 1 hour.

Step 3: Obtain the precipitation by filtering the solution with 1 μ m pore size filter paper (Adventec No. 5C) and wash the precipitation with the distilled water at 60°C to remove Na⁺. Repeat the filtering and washing procedure until the precipitation solution is pH=7.

Step 4: Pelletize the precipitation with a syringe and dry it at 80°C for 12 hours.

Step 5: Calcinate the dried precipitation at 500°C for 3 hours in the electric furnace.

Dynamic Model: To design a control system, a simple model for the reactor temperature and exit CO concentration dynamics is obtained. For this, following conditions are assumed.

Assumption 1: The reactor tube and catalyst are at the same temperature. Hence the reactions occur in isothermal and isobaric conditions. This assumption will be effective due to that the tubular reactor is made of aluminum tube having the high thermal conductivity and its diameter is small (0.25in.).

Assumption 2: The time derivatives about concentrations are ignored because they are small compared to that of temperature. This is a usual assumption for fast reactions in the gas phase reactor.

Dynamic model used is

$$mC_{p} \frac{dT}{dt} = -Q_{E} - Q_{C} + Q_{R} + P_{H}u$$

$$0 = -\frac{dF_{CO}}{\zeta dz} + \eta_{CO}r_{CO}$$

$$0 = -\frac{dF_{O2}}{\zeta dz} + \eta_{O2}\frac{1}{2}(r_{CO} + r_{H2})$$
(3)



Fig. 2. Schematic diagram for the PROX reactor modelling.

Here notations are

- T: reactor temperature [°C]
- mC_p: heat capacity of the reactor [J/°C]
- Q_E: convective heat flux to the environment [J/s]
- Q_C : conductive heat flux through reactor connection [J/s]
- Q_R: heat generated by reactions [J/s]
- P_Hu: heat added by the heater [J/s] (u is the manipulated variable)
- F_{CO}, F_{O2}: Flow rates of CO and O₂ [mol/s]
- η_{CO} , η_{O2} : effectiveness factors for CO and O_2
- r_{CO} , r_{H2} : reaction rates for CO and H_2
- z, L: axial variable and total length of the reactor [m]
- ζ: loading factor of catalyst (ζ=Wt/L, Wt: total mass of catalyst loaded) [kg/m]

Boundary conditions at z=0 are given as the feed compositions.

The convective heat loss can be described as

$$Q_E = h_E A_E (T - T_{env})$$
⁽⁴⁾

Here $h_E A_E$ is the overall heat transfer coefficient.

The inlet and outlet parts of the aluminum tube are heated. In this case, the convective heat loss to the feed gas and the conductive heat loss Q_C can be negligible.

The reaction heat Q_R is sum of heat generated due to the reactions along the reactor

$$Q_{R} = \int_{0}^{L} (\Delta H_{CO} r_{CO} + \Delta H_{H2} r_{H2}) \zeta dz$$
 (5)

For fixed feed conditions, last two static equations in Eq. (3) can be solved and concentrations and heat generation Q_R can be described in terms of the reactor temperature. Dynamic model of Eq. (3) becomes

mC
$$_{p} \frac{dT}{dt} = -h_{E}A_{E}(T - T_{env}) - k_{C}A_{C}(T - T_{env}) + Q_{R}(T) + P_{H}u, \quad y = c_{CO}|_{z=L} = q(T)$$
 (6)

Here c_{CO} at z=L is the exit concentration of CO which is a nonlinear function of reactor temperature q(T). Detailed computations including the effectiveness factors are given in Kim et al. (2013).

3. WIENER MODEL

In Eq. (6), the term $Q_R(T)$ is nonlinear and difficult to obtain. Here we approximate it to be constant. This approximation is based on that

(1) Amounts of active reactants are small and their conversions are over 90% throughout operating temperatures.

(2) The activation energy for the hydrogen oxidation is greater than that for the CO oxidation (Eq. (2)). Hence, for lower reactor temperature, CO becomes more reactive under limited oxygen amount and heat generation decrement due to low reaction rate can be reduced because the heat of reaction for the CO oxidation is greater than that of hydrogen oxidation (Eq. (1)). Reverses are valid for higher reactor temperature. Temperature dependence of $Q_R(T)$ will be weak.

With a constant Q_R , the dynamic model becomes

$$\tau_{T} \frac{dT}{dt} = -T + T_{bias} + k_{T}u, \ y = q(T)$$
 (7)

The model of Eq. (7) consists of a linear dynamic subsystem for the reactor temperature and a nonlinear static subsystem for the exit CO concentration. They are connected in series as shown in Fig. 3. The model is called Wiener model.



Fig. 3. Wiener model for a PROX reactor.

4. EXPERIMENTAL RESULTS AND DISCUSSIONS

To verify the accuracy of approximate model of Eq. (7), experimental open-loop tests have been done. Figure 4 is one of several tests. The heater signal u is set to 3.5V, 2.5V and 3V successively. The reactor temperature and exit CO concentration have been recorded.



Fig. 4. Experimental open-loop step responses.



Fig. 5. Reactor temperature responses for four step changes of the heater input.



Fig. 6. Plots of the CO concentration versus the reactor temperature.

Figure 5 shows temperature responses for step changes of the heater input *u* at various operating points. All dynamic responses are almost the same and tell that the temperature dynamics is linear and independent of reaction changes due to the reactor temperature changes. Our assumptions will be effective and the model Eq. (7) can be used. Model constants estimated graphically are τ_T =600sec, k_T =37.9°C/Volt and T_{bias}=50.4°C.

Figure 6 shows plots between the reactor temperature and the exit CO concentration. Run 1 curve is the responses of static operations. Run 2 and run 3 are plots between the reactor temperatures and the exit CO concentrations for the step responses. Fitting result for the run 1 is

$$y = q(T) = 2.4892 + 0.13534 (T - 160) + 0.15272 (T - 160)^{2}$$
(8)

Here y is the exit CO concentration in ppm and T is the reactor temperature in $^{\circ}C$.

5. EXTREMUM SEEKING CONTROL

To maintain the exit CO concentration at its minimum is a task different from the traditional control one to regulate the output at a given set point. There have been several approaches to attack this real-time optimization problem such as dynamic and static nonlinear programming with perturbation and waiting (Fu and Ozguner, 2011) and the extremum seeking (ES) control (Krstic and Wang, 2000; Tan et al., 2010; Scheinker and Krstic, 2014). Here, the ES control is applied to this system.

For a static nonlinear system showing the maximum point,

$$\mathbf{y} = f(\mathbf{u}) \tag{9}$$

the ES control of

$$u(t) = \overline{u}(t) + a \sin(\omega t)$$

$$\xi(t) = y(t) \sin(\omega t)$$
(10)

$$\overline{u}(t) = k_{1} \int_{0}^{t} \xi(\hat{t}) d\hat{t}$$

can find the optimum point $\overline{u} = \overline{u}_{opt}$ such that

$$f'(\overline{u}_{ont}) = 0 \tag{11}$$

Under several assumptions such as differentiable f(u), the feedback system of Eqs. (9) and (10) will converge to the optimum point.

For an analytic f(u) and a constant \overline{u} ,

$$f(\mathbf{u}) = f(\overline{\mathbf{u}}) + f'(\overline{\mathbf{u}})a\sin(\omega t) + f''(\overline{\mathbf{u}})a^{2}\sin^{2}(\omega t)/2 + \cdots$$
(12)

and the average value of $\xi(t)$ becomes

$$\overline{\xi} = \frac{1}{p} \int_{t-p}^{t} y(\hat{t}) \sin(\omega \hat{t}) d\hat{t}$$

$$= \frac{af'(\overline{u})}{p} \int_{t-p}^{t} \sin^{2}(\omega \hat{t}) d\hat{t} + O(a^{3})$$

$$= \frac{af'(\overline{u})}{2} + O(a^{3}), \quad p = 2\pi / \omega$$
(13)

When the integral controller gain k_I is small, \overline{u} is slowly varying and Eq. (13) is effective. Consequently, the integral control of Eq. (10) will steer \overline{u} to the point such that $f'(\overline{u}) = 0$, the optimum point.

Although the ES control is derived for the static process, it can be applied to nonlinear dynamic processes. For the closed-loop stability, the frequency ω of continuous perturbation signal should be low enough to ensure the timescale separation between the real-time optimization and the process dynamics. Formal convergence proof can be found in Krstic and Wang (2000) and Tan et al. (2009).

Figure 7 shows the ES control system applied to our PROX reactor system. Because the ES control system finds the maximum, we use the CO conversion:

$$y_{conv} = 1 - y / 1000$$
 (14)

The high pass filter (HPF(s)= $\tau_H s/(\tau_H s+1)$) is used to remove static bias term in $y_{conv}(t)$. The low pass filter (LPF(s)=1/($\tau_L s+1$)) produces the average, removing perturbation due to the excitation of sine wave. The delay block for sin(ωt - ϕ) is used to compensate the phase shift due to the process dynamics.

There are 6 parameters of ω , ϕ , *a*, k_I, $\tau_{\rm H}$ and $\tau_{\rm L}$. Design guidelines can be found elsewhere (Krstic and Wang, 2000; Dochain et al. 2011). Here they are determined roughly via simulations. The purpose in this study is not to find the best extremum seeking control but to show that the extremum seeking control can find the optimal operating point and maintain it under the slow reactor changes such as catalyst deactivations.

The extremum seeking control adds a continuous excitation of $u = \overline{u} + a \sin(\omega t)$. This continuous excitation may not be a serious problem because the perturbation of exit CO concentration below 10ppm is allowed.



Fig. 7. Extremum seeking control system (HPF(s)= $\tau_{H}s/(\tau_{H}s+1)$ and LPF(s)=1/($\tau_{L}s+1$)).

6. EXPERIMENTAL CONTROL RESULTS

Figure 8 shows simulation results. Parameters for the extremum seeking control are obtained via simulations. For a=1, $\phi=1.57$, $\omega=0.1$ rad/sec, $k_I=0.5$, $\tau_H=10$ sec and $\tau_L=5$ sec. Both responses starting from T=120°C and 200°C converge to the optimum output where the CO concentration is below 10ppm.

The high pass and low pass filters can be omitted. However, without the high pass and low pass filters, responses were very sensitive on the controller parameters of ω and k_I. Such sensitivities can be reduced much by introducing filters. Filters are HPF(s)=10s/(10s+1) and LPF(s)=1/(5s+1). Filter time constants are set to be similar time scale of 1/ ω .

The phase delay ϕ compensating the process dynamics was very important. We set it to be $\pi/2$ (ϕ =1.57) because the dynamics part of our PROX reactor is first order and its time constant (τ_T =600sec) is very large compared to the angular frequency ω of perturbation. Without ϕ , the ES control system diverges when a time delay due to the CO measurement about several seconds is introduced to y(t).



Fig. 8. Simulation results for the extremum seeking control. (ω =0.1rad/sec, *a*=1, ϕ =1.57, k₁=0.5, τ _H=10sec, τ _L=5sec).

Figure 9 shows experimental results for the ES control. We can see that the ES control steers the CO concentration to its minimum. Here controller parameters are a=1, $\phi=1.57$, $\omega=0.1$ rad/sec, $k_I=0.1$, $\tau_H=10$ sec and $\tau_L=5$ sec. For this PROX system, we know that the optimum temperature is around 160°C. So the heat input is set to maximum and minimum for T below 140°C and higher than 180°C, respectively.

For the O_2 flow rate of 0.5mL/min, the minimum CO concentration is on the border of 10ppm as shown in Fig. 9. So, for a lower CO concentration, we doubled the O_2 flow rate. Figure 10 shows experimental results for initial reactor temperature higher than 200°C and the increased O_2 flow rate of 1mL/min. We can see that the ES control steers the CO concentration to near zero. Here controller parameters except for the integral gain (k_1 =0.15) are the same as in the above experiment of Fig. 9.



Fig. 9. Experimental results of the ES control for the PROX reactor.



Fig. 10. Experimental results of the ES control for the PROX reactor.

7. CONCLUSIONS

Preferential oxidation (PROX) can reduce CO concentration in the hydrogen rich gas of reformer up to 10ppm tolerable in the proton exchange membrane fuel cells. The dynamics of a CO PROX reactor with the CuO-CeO₂ catalyst is shown to be described well by a Wiener-type nonlinear system where a linear dynamic subsystem is followed by a static nonlinear subsystem. Conditions for which the Wiener model can be applied are investigated. It is verified experimentally how well the Wiener model can describe the dynamics of CO PROX reactor. Model parameters for this Wiener model are obtained experimentally. The PROX reactor with the CuO-CeO₂ catalyst shows optimal reactor temperature and a control system that maintains the PROX reactor temperature at its optimal one under changing environments and catalyst deactivations. The extremum seeking control that can track the optimum point for the Wiener-type nonlinear system is applied and its performance is verified experimentally. It is a non-parametric real-time optimization method and can be applied effectively to other CO PROX reactors without detailed models.

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