

Novel Autothermal Reforming Process for Pure Hydrogen Production

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ABSTRACT

Steam reforming of heptane for hydrogen production is investigated in a novel Circulating Fluidized Bed Membrane Reformer-Regenerator system (**CFBMRR**) utilizing a number of hydrogen and oxygen selective membranes. It is shown that although the amount of carbon deposition is significant, the effect on catalyst deactivation is negligible due to the large solid to gas mass feed ratio and the continuous catalyst regeneration in the system. The combustion of the deposited carbon in the catalyst regenerator supplies the heat needed for the endothermic steam reforming as well as the combustion of flammable gases from the riser reformer. Autothermal operation is achievable for the entire adiabatic reformer-regenerator system when the exothermic heat generated from the regenerator is sufficient to compensate the endothermic heat consumed in the reformer. Multiplicity of the steady states exists in the range of steam to carbon feed ratio of 1.444-2.251 mol/mol. The novel configuration has the potential advantages not only with respect to hydrogen production but also energy minimization.

KEYWORDS: autothermal system, bifurcation, carbon formation, catalyst deactivation, catalyst regeneration, circulating fluidized bed, heptane, hydrogen, membrane reformer, multiplicity, steam reforming.

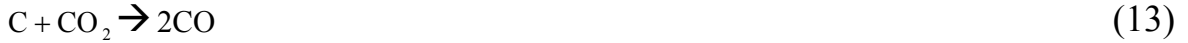
INTRODUCTION

Hydrogen is forecast to become one of two principal energy carriers with electricity in the 21st century ^[1], which is mainly produced by steam reforming of hydrocarbons in classical fixed-bed steam reformers ^[2-6]. The hydrogen produced can be used by fuel cells to produce electricity efficiently with efficiency of 45-55% and with zero emissions ^[7,8]. Recently, President Bush announced in his State of the Union Address \$1.2 billion in research funding for developing clean, hydrogen-powered automobiles and fuel cells. However, fixed-bed steam reformers are usually inefficient, polluting and suffers from carbon formation ^[2,5,9]. This fixed bed configuration also limits the range of hydrocarbons to be used as feedstocks. In order to produce pure hydrogen for fuel cells more efficiently and from a wide range of higher hydrocarbons including gasoline, diesel and bio-oils, a novel process consisting of a circulating fluidized bed membrane reformer and a catalyst regenerator has been proposed ^[6]. In this paper, we investigate the carbon deposition and hydrogen production in the circulating fluidized reformer-regenerator system.

REACTIONS AND MODEL EQUATIONS

For the circulating reformer-regenerator system, the following reactions have been considered in the reformer:





The reaction kinetics for these 13 reactions is obtained from the published literatures [3-6,10-15].

The riser reformer is modeled as a plug flow reactor with co-current flow in the reformer and membranes. The material and energy balance equations are as follows:

$$\frac{dF_i}{dl} = \rho_c(1-\varepsilon)A_f \sum_{j=1}^{13} \sigma_{ij} r_j - aJ_{\text{H}_2} \pi N_{\text{H}_2} d_{\text{H}_2} + bJ_{\text{O}_2} \pi N_{\text{O}_2} d_{\text{O}_2} \quad (14)$$

$$\frac{dT}{dl} = \frac{\sum_{j=1}^{13} r_j (-\Delta H_j) \rho_c (1-\varepsilon) A_f + \dot{Q}}{\sum F_i C_{p_i}} \quad (15)$$

where, a and b are the control indices for the membrane permeation fluxes. For hydrogen, a=1, b=0; for oxygen, a=0, b=1; and for any other components, a=0, b=0.

Due to the carbon formation, the catalyst deactivates in the riser reformer. Accordingly, the reaction rate equations are reformulated as follows:

$$r_j = r_{j0} \cdot \phi_j \quad (16)$$

$$\phi_j = \begin{cases} \exp(-\alpha_c C_k) \\ 1.0 \end{cases} \quad (17)$$

The value of ϕ_j for reaction j is calculated by Eq.17 [16] or equal to 1.0 depending on whether the jth reaction is affected by the catalyst deactivation or not.

For the catalyst regenerator, we assume that the burning of carbon and the combustion of flammable gases are highly efficient or the catalyst regenerator is over designed that we can consider these reactions to be complete. We also assume that the heat generated in the regenerator is used for pre-heating the clod feed water (to steam), heptane and the recycle catalyst. Therefore the energy balance equation in the regenerator is as follows:

$$\sum F_i(-\Delta H_c) = \sum F_k[(T_{k,b} - T_{room})Cp_{k(l)} + \Delta H_{vap} + (T_0 - T_{k,b})Cp_{k,b(g)}] + G_{cat} Cp_{cat} (T_0 - T_{exit}) \quad (18)$$

where, subscript k stands for feed water and heptane. The hydrogen or oxygen permeation flux in hydrogen or oxygen permselective membranes can be calculated using the equation reported by Shu et al. or Tsai et al. [17,18], respectively. Thus based on these equations, the complete reformer-regenerator system is simulated. The standard simulation conditions are similar to the data reported by Chen et al. [6].

CARBON DEPOSITION AND CATALYST DEACTIVATION

First we investigate the carbon deposition and catalyst deactivation in the isothermal riser reformer. Fig.1 shows the carbon deposition rate at 823K for the case without any hydrogen or oxygen membranes. The carbon deposition rate can be as high as 2.56 kg/h. It increases firstly along the reactor length and also increases when the solid catalyst fraction increases in the bed. However, after a certain reactor length or above a certain solid catalyst fraction, the carbon deposition rate decreases. This phenomenon is due to the fact that carbon formation is a catalytic process related to the amount of catalyst. The less the amount of solid catalyst, the slower the carbon formation rate by heptane cracking. At the same time with the proceeding of steam reforming of heptane, the by-products carbon monoxide and methane will also contribute to the formation of carbon on the nickel catalyst. Similarly, the less the solid catalyst in the bed, the slower the steam reforming

of heptane and the formation of carbon monoxide and methane. As a result the less the solid catalyst, the lower the carbon formation rate from carbon monoxide and methane. Summation of the above factors results in the fact that the carbon deposition rate decreases when the solid catalyst fraction decreases and vice versa. However, when the solid catalyst fraction is high, the steam reforming rate of heptane is high, which makes the reactor length for full heptane conversion short. After the full conversion of heptane at a certain reactor length, the major source of carbon formation from heptane stops, as a result the overall carbon deposition rate decreases along the rest of the reactor length as shown in Fig.1. For example, at solid catalyst fraction of 0.2, the maximum carbon deposition rate is at the reactor length of 0.3 m. This position is the place where heptane is fully converted to hydrogen and carbon monoxide in the steam reformer. Fig.1 shows that a maximum carbon deposition rate (2.56 kg/h) is developed at a solid catalyst fraction close to 0.05 v/v. The carbon deposition rate increases when the solid catalyst fraction increases from 0 to 0.05 v/v, then the carbon deposition rate decreases above 0.05 v/v. Fig.2 shows the catalyst activity as a function of the solid catalyst fraction in the bed. Although the carbon deposition rate can be as high as 2.56 kg/h in Fig.1, the catalyst activity is almost constant (0.984-1.0). Why is the change of the catalyst activity very small although so large amount of carbon deposit on the catalyst? This is due to the high mass flow ratio of the solid catalyst to the gas stream in the circulating fluidized bed and also the continuous catalyst regeneration in the regenerator in this novel process. Obviously this is a potential advantage of the circulating fluidized bed over conventional fixed-bed steam reformers.

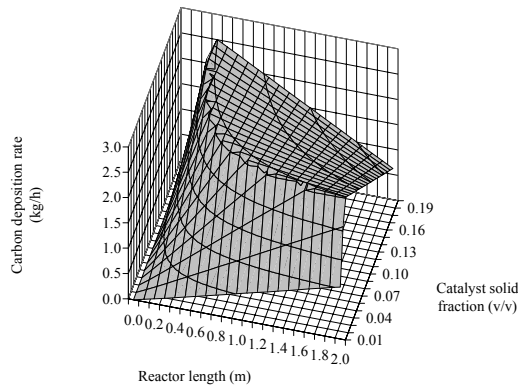


Fig.1. Carbon deposition rate at 823K for isothermal operation without any membranes (reaction pressure =1013 kPa, steam to carbon ratio=2 mol/mol)

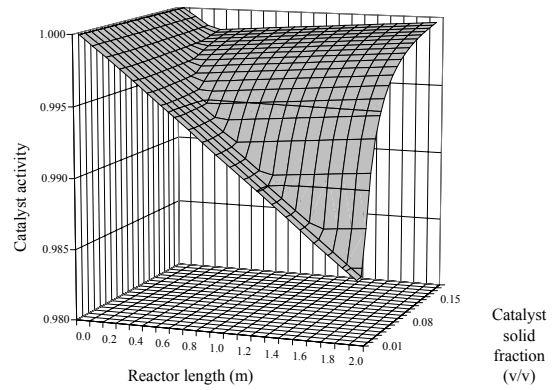


Fig.2. Catalyst activity at 823K for isothermal operation without any membranes (reaction pressure=1013 kPa, steam to carbon ratio=2 mol/mol).

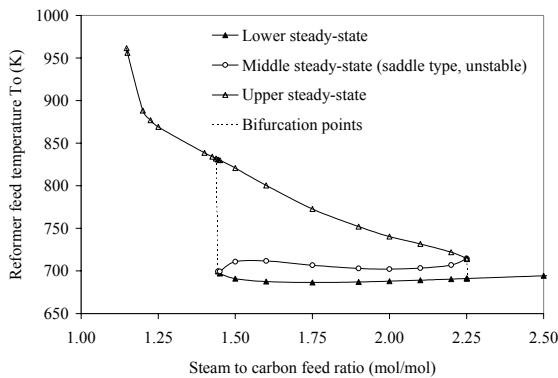


Fig.3. Circulating feed temperature to the reformer and its bifurcation behavior at different steam to carbon feed ratio when the circulating reformer-regenerator system is operated under autothermal condition.

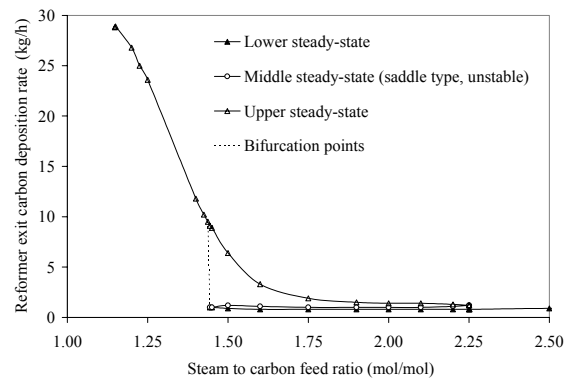


Fig.4. Carbon deposition rate at the reformer exit and its bifurcation behavior at different steam to carbon feed ratio when the circulating reformer-regenerator system is operated under autothermal condition.

AUTOTHERMAL REFORMING AND BIFURCATION BEHAVIOR

Because of the continuous catalyst regeneration, there is exothermic burning of carbon and flammable gases (such as unreacted heptane, by-products methane and carbon monoxide, and remaining product hydrogen) in the regenerator, the heat generated can be used for the endothermic steam reforming in the riser reformer. In order to investigate the thermal effect as well as the efficient production of hydrogen, the whole circulating fluidized bed membrane reformer-regenerator system is investigated under adiabatic

conditions and we assume any remaining hydrogen in the exit gas stream is further separated before entering the catalyst regenerator. If heat balance is well controlled, then the whole reformer-regenerator system can be operated under autothermal condition. That is, at steady state, the heat generated in the catalyst regenerator is equal to the heat consumption in the riser reformer. In this section, hydrogen and oxygen permselective membranes are used. Chen and coworkers have discussed the effects of these membranes ^[6]. The numbers of hydrogen and oxygen membranes are 20 and 80, respectively. The reaction pressure in the reformer is 1013 kPa. Figs. 3-6 show the performance of the reformer-regenerator system when the entire adiabatic process achieves autothermal condition. Figs. 3-6 also show that there are multiplicities (three steady states) in the range of steam to carbon feed ratio of 1.444-2.251 mol/mol. In this paper we present a preliminary static bifurcation analysis of the autothermal reformer-regenerator system.

Usually, high steam to carbon feed ratio increases the hydrogen yield and hydrogen production. On the other hand, the higher the steam feed, the higher the energy consumption for preheating the cold water to generate steam. Thus in order to produce hydrogen efficiently and economically, the steam to carbon feed ratio is an important parameter for energy consumption in industrial applications. Under autothermal conditions the adiabatic riser reformer and catalyst regenerator system produces hydrogen with “zero” external heat input. That is, when the circulating reformer-regenerator system is operated under autothermal conditions, the heat consumed for preheating the cold feed water (to generate steam), heptane and hot catalyst is just supplied by the heat of reactions from the catalyst regenerator, in which it supplies the necessary heat for endothermic steam reforming in the adiabatic riser reformer.

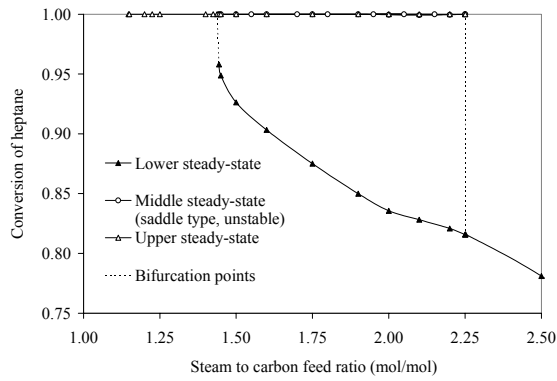


Fig.5. Conversion of heptane and its bifurcation behavior at different steam to carbon feed ratio when the circulating reformer-regenerator system is operated under autothermal condition.

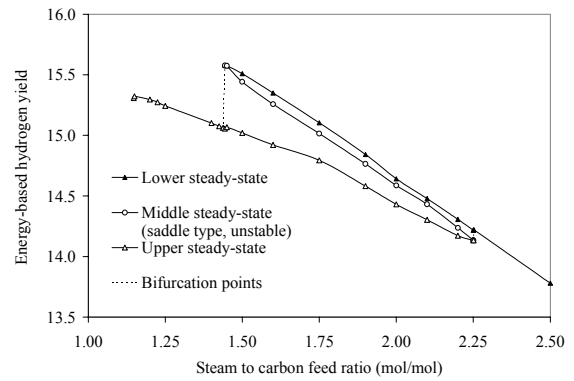


Fig.6. Energy-based hydrogen yield and its bifurcation behavior at different steam to carbon feed ratio when the circulating reformer-regenerator system is operated under autothermal condition.

Figs. 3 and 4 show the circulating feed temperature to the reformer and reformer exit carbon deposition rate at different steam to carbon feed ratio when the entire adiabatic reformer-regenerator system is operated under autothermal conditions. Note, in the autothermal process the reformer feed temperature is a result from the heat supply in the regenerator by preheating the cold water and heptane, and recycled catalyst. It is a system variable instead of feed parameter. According to the value of reformer feed temperature to the reformer, the multiple steady states are classified with regard to temperature as lower, middle and upper steady state, respectively. When steam to carbon feed ratio is higher than 2.251 mol/mol, the autothermal circulating feed temperatures are almost constant with the change of steam to carbon feed ratio. This is due to the fact that the higher the steam feed, the higher the reaction extents of endothermic steam reforming (of heptane and methane) and water gas shift reaction, and the lower the carbon formation. In order to maintain the reformer-regenerator system operate autothermally under these conditions, the conversion of heptane has to be low to provide enough “fuel” for combustion in the regenerator to supply the necessary heat for the endothermic steam reforming. Therefore under

autothermal condition, the circulating feed temperature in this case is the lowest to ensure that the conversion of heptane is low. For example, at steam to carbon feed ratio of 2.5 mol/mol, the conversion of heptane is 78.11%, the net carbon deposition rate is 0.9 kg/h in the riser reformer and the autothermal circulating feed temperature is 694.31 K. If the energy-based hydrogen yield is defined as the amount of hydrogen produced per mole of heptane fed under autothermal conditions. The more the feed heptane is consumed for generating the necessary heat in the regenerator for the endothermic process, the smaller the energy-based hydrogen yield. Fig. 6 shows the energy-based hydrogen yield in the autothermal reformer-regenerator system. At higher steam to carbon feed ratio, the energy-based hydrogen yield is shown to be the lowest. For example, at 2.5 mol/mol steam to carbon feed ratio, the yield of hydrogen is 13.78 mole of hydrogen per mole of heptane feed. While when steam to carbon feed ratio is between 1.444-2.251 mol/mol, multiple steady states occur with lower, middle and upper autothermal feed temperatures. For example, at steam to carbon feed ratio of 2.0 mol/mol, three steady states exist at reformer feed temperatures of 687.99, 702.15 and 740.34 K. Fig. 5 shows that at middle and upper steady state, the conversion of heptane is 100%. While at lower steady state, the conversion of heptane is between 81.60-95.80%. The conversion of heptane decreases when steam to carbon feed ratio increases. This is the opposite of the usual operation where the performance improves as the steam to carbon feed ratio increases. However, in this autothermal operation, we have to notice that high steam to carbon feed ratio prevents carbon formation causing the heat supply by burning carbon to decrease, forcing the system to lower conversion. Fortunately, due to the large mass flow ratio of catalyst in this configuration and the continuous catalyst regeneration, the catalyst activity is always kept high (>0.985), even at low steam to carbon feed ratio of 1.1475 mol/mol. The controlling factor in this novel autothermal process is the heat supply associated with the burning of

carbon in the regenerator. In the multiplicity range of steam to carbon feed ratio, the higher the carbon deposition rate, the higher the autothermal feed temperature to the reformer. But the trend of hydrogen yield is totally reversed. As shown in Fig.6, the higher the autothermal feed temperature to the reformer, the lower the energy-based hydrogen yield. That is, at the upper temperature steady state, the energy-based hydrogen yield is the lowest. At the lower temperature steady state, the energy-based hydrogen yield is the highest. For example, for steam to carbon feed ratio of 2 mol/mol, at the upper feed temperature of 740.34 K, the energy-based hydrogen yield is 14.43. At the middle feed temperature of 702.15 K, the energy-based hydrogen yield is 14.59. While at the lower feed temperature of 687.99 K, the energy-based hydrogen yield is 14.64. This reverse relationship between the hydrogen yield and the autothermal feed temperature can be explained by the carbon formation-burning process during the steam reforming of hydrocarbons and regeneration of the catalyst. Since steam reforming not only extracts hydrogen from hydrocarbons but also extracts hydrogen from the reactant steam. While carbon formation only extracts hydrogen from hydrocarbons. Therefore, the larger the part of the hydrocarbon which cracks for carbon formation, the more the carbon generation, the higher the autothermal feed temperature and the lower the hydrogen production. According to the bifurcation theory^[19], only the lower and upper steady states are stable and the middle steady state is an unstable saddle type state. If the start-up is above the middle steady state, the system will finally settle at the upper steady state. If the start-up is below the middle steady state, the system will settle at the lower steady state. When steam to carbon feed ratio is below 1.444 mol/mol, only one stable steady state exists in the reformer-regenerator system. Since in this region (<1.444 mol/mol) low steam to carbon feed ratio is fed, the extent of steam reforming becomes small. On the other hand, the carbon formation and deposition competes for the reactant heptane. Since

carbon is burned-off by excess air in the catalyst regenerator, the more the carbon deposition, the higher the heat supply. As a result, the autothermal feed temperature to the reformer is higher. Since the feed temperature and carbon formation affects each other, at low steam to carbon feed ratio, the autothermal feed temperature and carbon deposition rate are high as shown in Figs. 3 and 4. Fig. 3 shows that if the steam to carbon feed ratio is smaller than 1.1475 mol/mol, the autothermal circulating feed temperature is very high, leading to thermal “run away”. Figs. 3-6 show that if the steam to carbon feed ratio is higher than 2.251 mol/mol or lower than 1.444 mol/mol, the reformer-regenerator system will have only one steady state. In the region of 1.444-2.251 mol/mol, the upper (or lower) steady state will shift to the lower (or upper) steady state suddenly at the bifurcation points. In this investigation the maximum energy-based hydrogen yield is about 15.58 moles of hydrogen produced per mole heptane fed at the lower steady state when steam to carbon feed ratio is very close to the bifurcation point of 1.444 mol/mol. It is about 70.82 % of the maximum theoretical hydrogen yield of 22 when the final steam reforming products are carbon dioxide and hydrogen. Since the sweep gas in hydrogen permselective membranes is steam, if the exit mixture gas is cooled to 300K at down stream, most of steam is condensed and the hydrogen concentration can be high. For example, when the above maximum energy-based hydrogen yield of 15.58 is obtained in the autothermal process, the hydrogen concentration in hydrogen permselective membranes is about 56.95mol%. After condense the most steam, the hydrogen concentration is about 98.14mol%. If any remaining steam is further removed using some de-humidification agents, the hydrogen purity can be almost 100%, which is ideal for fuel cells.

CONCLUSION

This investigation highlights the great advantages associated with the novel circulating fluidized bed membrane reformer and catalyst regenerator system for the efficient production of pure hydrogen with minimum energy consumption. Due to the high mass flow ratio of solid catalyst to gas stream and continuous catalyst regeneration, the steady-state catalyst activity is high despite the large carbon deposition rate. When the heat generated from the burning of carbon and other exit flammable gases from the riser reformer is equal to the heat consumed for preheating the cold water (to generate steam), heptane and hot recycle catalyst to the feed temperature (in which it supplies the heat necessary for the endothermic steam reforming reactions in the reformer), the riser reformer and catalyst regenerator system can be operated under autothermal conditions. Under autothermal conditions, the reformer-regenerator system shows a bifurcation behavior in the range of steam to carbon feed ratio of 1.444-2.251 mol/mol. It is interesting to notice that the energy-based hydrogen yield decreases when steam to carbon feed ratio increases. In the multiplicity region, the energy-based hydrogen yield at the upper steady state (or high autothermal feed temperature to the reformer) is the lowest one and at the lower steady state is the highest one. This is due to the high carbon formation rate associated with the high feed temperature. The maximum energy-based hydrogen yield is about 15.58 moles of hydrogen per mole of heptane fed at the lower steady state when steam to carbon feed ratio is close to the bifurcation point of 1.444 mol/mol.

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NOMENCLATURE

A_f	free cross-section area of the reactor (m^2)
C_k	concentration of deposited carbon (g/gcatalyst)
$C_{p_{cat}}$	specific heat of solid catalyst (J/g catalyst/K)
C_{p_i}	specific heat of component i (J/mol/K)
d_{H_2}	outside diameter of hydrogen membrane tubes (m)
d_{O_2}	outside diameter of oxygen membrane tubes (m)
F_i	molar flow rate of component i (mol/s)
G_{cat}	mass flow rate of catalyst (g/s)
ΔH_C	heat of combustion (J/mol)
ΔH_j	heat of reaction for the j^{th} reaction (J/mol)
ΔH_{vap}	heat of vaporization (J/mol)
J_{H_2}	permeation fluxes of hydrogen ($mol/m^2/s$)
J_{O_2}	permeation fluxes of oxygen ($mol/m^2/s$)
l	length of reactor (m)
N_{H_2}	number of hydrogen permselective membrane tubes
N_{O_2}	number of oxygen permselective membrane tubes
\dot{Q}	rate of heating along the reactor length (J/s/m)
r_j	reaction rates (mol/gcatalyst/s)
r_{j0}	reaction rates with fresh catalyst (mol/gcatalyst/s)
T	temperature (K)
T_{exit}	riser reformer exit temperature (K)
T_0	autothermal feed temperature to reformer (K)
T_{room}	room temperature (K)

Greek letters

α_c	deactivation constant (gcatalyst/gcoke)
ε	void fraction
π	3.1415926
ρ_c	density of catalyst (kg/m ³)
$\sigma_{i,j}$	stoichiometric coefficient of component i for the j th reaction
ϕ	catalyst activity function

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