

Bifurcation Behavior of a Novel Auto-thermal Circulating Fluidized Bed (CFB) Membrane Reformer

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ABSTRACT

Static Bifurcation (SB), which mostly exhibits itself as multiple steady states, is characteristic of a novel auto-thermal Circulating Fluidized Bed Membrane Steam Reformer (CFB_MSR) for hydrocarbons. The present paper focuses on the practical implications of this phenomenon on the behavior of this novel reformer with special emphasis on hydrogen yield. It is shown that SB prevails over a relatively wide range of parameters and has significant impacts on stability, start-up policy and hydrogen yield. At certain critical bifurcation points the reformer can quench to an idle state, while at other bifurcation points it may tend to run away. The SB is a result of the auto-thermicity nature of the CFB_MSR and although it adds certain degree of complexity to the design and operation of the unit; it has a very positive effect on its thermal efficiency. A parametric study is carried out in order to define the domain of the most efficient and safe operating conditions. In addition, the study **aims** to investigate the stability **at** these optimal parameters and discusses the need for a feedback control system. It is shown that an optimized and well controlled reformer of this kind is capable of superior hydrogen yields from a wide range of higher hydrocarbons including a renewable feedstock such as bio-oil from biomass.

Keywords: autothermal reforming, bifurcation, circulating fluidized bed, hydrocarbon, hydrogen, multiplicity

1 INTRODUCTION

Hydrogen is becoming a more and more promising clean energy source for the future which is mainly produced by the steam reforming of hydrocarbons [1, 2]. However, the conventional fixed bed steam reforming process is inefficient, highly polluting and suffers from catalyst deactivation [3, 4]. Recently, a novel autothermal circulating fluidized bed membrane reformer (ACFBMR) has been shown to be more efficient and more flexible for pure hydrogen production, in which a wide range of hydrocarbons such as natural gas, naphtha, gasoline, diesel and bio-oils can be used as feedstock [5]. This ACFBMR uses autothermal operation in a reaction-regeneration

process, which “breaks” not only the heat transfer limitation, but also the carbon formation/ catalyst regeneration limitation. However, autothermal operation is associated with complex static and dynamic bifurcation behavior. Deep understanding of this complex phenomenon is essential for efficient design and safe operation of this process. In this investigation the static bifurcation behavior and its practical implications are explored for two autothermal reforming configurations, as shown in Fig. 1a and Fig. 1-b. In the first configuration the catalyst regeneration is carried out before the gas–solid separation, while in the second configuration it is carried out after the gas–solid separation. Heptane is used as a model component of heavy hydrocarbons. There are a number of palladium based hydrogen permselective membranes and dense perovskite oxygen permselective membranes in the reformer. The hydrogen yield is defined as the total moles of hydrogen produced per mole of heptane fed. In the first configuration, the carbon deposited on the nickel reforming catalyst is burned off by excess air in the catalyst regenerator as well as the combustion of flammable gases such as un-reacted heptane and by-products methane and carbon monoxide. The regenerated catalyst is separated from the gases using a gas–solid separator and then recycled to the riser reformer. In the second configuration, the solid catalyst is first separated from gases and then the carbon deposited on the nickel catalyst is burned off in the regenerator. This is followed by separating the regenerated catalyst from the carbon dioxide.

2 REACTION KINETICS AND MEMBRANE REFORMER MODELING

The reactions and kinetics for the riser reformer are summarized in [6]. For the first configuration, because the gases exiting from the external hydrogen separator contains some flammable gases such as unreacted heptane, by-products methane and carbon monoxide, with the excess air feed in the catalyst regenerator, the following four reactions take place:

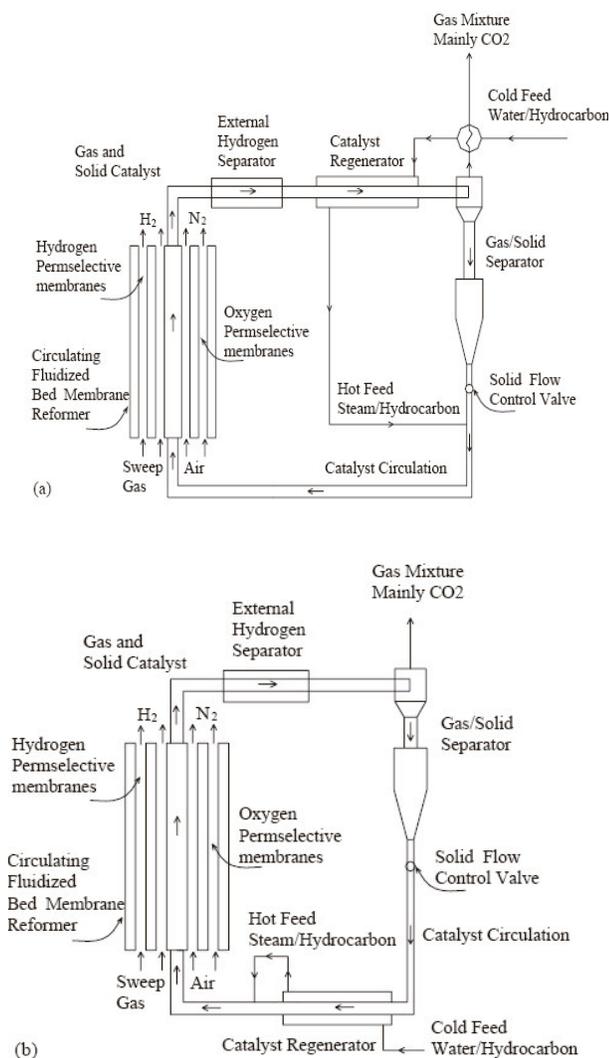
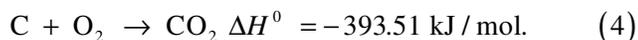
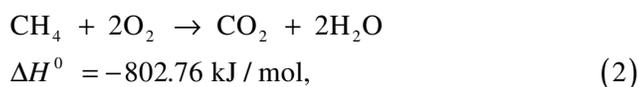
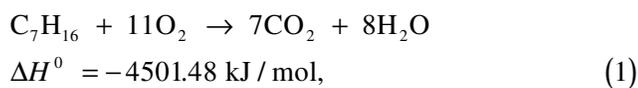


Figure 1: ACFBMR with continuous catalyst regeneration (a) before, and (b) after the gas–solid separation.



While for the second configuration, only the burning of carbon (Eq. (4)) takes place. Unless otherwise specified, it is assumed that the reactions in the catalyst regenerator are highly efficient or the catalyst regenerator is over designed so that we can consider these reactions to be complete. Thus for the ACFBMR modeling, only the heat produced in the catalyst regenerator and its thermal effects on the entire

system are considered. The main assumptions are as follows [6]:

- (1) Steady-state adiabatic process.
- (2) There is no oxidation of hydrogen or carbon monoxide over nickel reforming catalyst.
- (3) Membranes are 100% selective for the permeation of hydrogen and oxygen, respectively and their performance is not affected by carbon deposition.
- (4) Constant heat capacitance.
- (5) Constant pressures in the riser reformer, hydrogen and oxygen membrane tubes.

3 RESULTS AND DISCUSSION

Figure 2 shows the bifurcation behavior for Configuration I (see Fig. 1-a) when steam to carbon (S/C) feed ratio is used as the bifurcation parameter. For S/C feed ratio lower than 1.44 mol/mol, only one steady state exists. In this region the extent of steam reforming is small. On the other hand, the carbon formation competes for the reactant heptane. The higher the reformer exit carbon flow rate, the more the amount of carbon deposited on the catalyst and the higher the heat generation in the catalyst regenerator. As a result, the autothermal circulating feed temperature to the reformer is high. For S/C feed ratios just below 1.50 mol/mol, the autothermal circulating feed temperature increases sharply, leading to thermal “run away” shown in Fig. 2a. When S/C feed ratio is between 1.44 and 2.25 mol/mol, multiplicity with three steady states occur, which are usually classified into lower, middle and upper steady states according to the feed temperature to the reformer, respectively (Fig. 2-a). Figure 2-c shows that at the middle and upper steady states the conversion of heptane is 100%, while at the lower steady state the conversion of heptane is between 81.6% and 95.8%. In the multiplicity region, the higher the reformer exit carbon flow rate (net carbon deposition on the catalyst), the higher the autothermal feed temperature to the reformer. But the trend of net hydrogen yield is totally reversed. As shown in Fig. 2-d, the higher the autothermal feed temperature to the reformer, the lower the net hydrogen yield. For example, at S/C feed ratio of 2 mol/mol, the net hydrogen yield is 14.4 at upper feed temperature 740 K, while it is 14.6 at middle feed temperature of 702K and 14.6 at lower feed temperature of 688 K. This reverse relationship between the net hydrogen yield and the autothermal circulating feed temperature is due to the carbon formation-burning process in the autothermal system. Steam reforming does not only extract hydrogen from hydrocarbons but also extract hydrogen from steam, while carbon formation only extracts hydrogen from hydrocarbons. Therefore the larger the part of heptane cracking for carbon formation, the more the carbon generation, the higher the autothermal circulating feed temperature and the lower the net hydrogen yield.

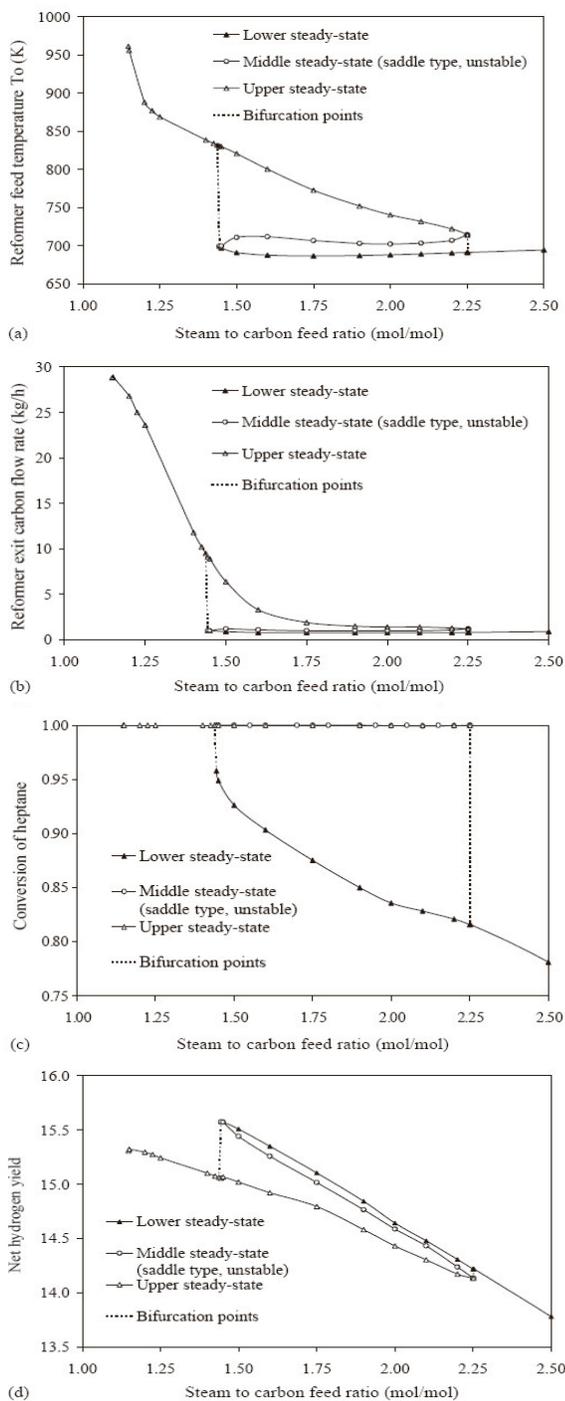


Figure 2: Bifurcation behavior with steam to carbon feed ratio as the bifurcation parameter in the ACFBMR when catalyst is regenerated before gas–solid separation.

Only the lower and upper steady states are stable and the middle steady state is an unstable saddle type. When S/C feed ratio is higher than 2.25 mol/mol, the autothermal circulating feed temperatures and the reformer exit carbon flow rates are almost constant while the conversion of heptane is decreasing. Because the net hydrogen yield is defined as the amount of hydrogen produced per mole of

heptane fed, the more the feed heptane is burned in the regenerator, the smaller the net hydrogen yield (Fig. 2-d). In this investigation the maximum net hydrogen yield is about 15.6 mol of hydrogen per mole of heptane fed at the lower steady state when steam to carbon feed ratio is close to 1.44 mol/mol, as shown at the left hand bifurcation point in Fig. 2-d.

In the second configuration (see Fig. 1-b) only the burning of carbon deposited on the nickel catalyst supplies the heat for the endothermic reforming reactions and for the vaporization of cold feed water and heptane. Because steam reforming of heptane is a highly endothermic reaction, the heat supply requirement from the burning of carbon in the catalyst regenerator is high. In order to generate enough carbon on the catalyst as energy source for autothermal operation, the steam to carbon (S/C) feed ratio is much lower than usual processes. The standard S/C feed ratio is 1 mol/mol.

Figures 3(a–d) show the bifurcation behavior when S/C feed ratio is the bifurcation parameter. There are three steady states in the autothermal CFB membrane reformer when S/C feed ratio is between 0.994 and 1.023 mol/mol. In this configuration the multiplicity is over a very narrow region from S/C feed ratio of 0.994 to 1.023 mol/mol. The conversion of heptane is always 100%. Fig. 39-c shows that the yield of byproduct methane. The net hydrogen yield in Fig. 3-d increases to the multiplicity region from S/C feed ratio of 0.975 mol/mol. Then it is almost constant when S/C feed ratio is in the range of 1.023 to 1.05 mol/mol.

When the S/C feed ratio increases, the heat for water vaporization and the reaction extent for endothermic steam reforming increase. As a result the process heat consumption is high and more carbon has to be generated in the reformer. Accordingly the circulating feed temperature has to increase with the increase of S/C feed ratio for the autothermal operation. Usually, for steam reforming of heptane, high yield of by-product methane means low hydrogen production since 3 mol of hydrogen is consumed for 1 mol of methane formation. Therefore, the net hydrogen yield increases with the increase of S/C feed ratio shown in Fig. 3-d. The exchange of the upper and middle steady states regarding the order of net hydrogen yield is due to the fact that high circulating feed temperature at the upper steady state (around 1000 K) makes the water gas shift reaction unfavorable for the hydrogen production. As a result the net hydrogen yield at the middle steady state is highest and the order of net hydrogen yield from high to low is the middle, upper and lower steady states. The phenomena shown in Fig. 3 are quite complex. Usually, the carbon formation from heptane cracking increases when the S/C feed ratio decreases or reaction temperature increases. In this reaction-regeneration process, because only the burning of carbon in the catalyst regenerator supplies the heat for the highly endothermic reforming reactions, the

S/C feed ratio has to be low and the temperature has to be high.

4 CONCLUSIONS

Two autothermal configurations for a novel ACFBMR have been explored for bifurcation behaviors. The results have shown that there are three steady states for both configurations. For the first reformer-regenerator configuration, generally the higher the autothermal circulating feed temperature, the higher the reformer exit carbon flow rate and the lower the net hydrogen yield. In the region of multiplicity, the order of net hydrogen yield from high to low is the lower, middle and upper temperature steady states, while the order of reformer exit carbon flow rate from high to low is the upper, middle and lower temperature steady states. For the second configuration, the conversion of heptane is always 100% for all the investigated cases. In the multiplicity region, the order of net hydrogen yield from high to low is the middle, upper and lower temperature steady states, while the reformer exit carbon flow rate from high to low is the lower, middle and upper temperature steady states. The bifurcation behavior and its implication for this second configuration are more complex than the first one. These detailed bifurcation behavior investigation over a wide range of parameters is the basis for process optimization of this novel autothermal membrane reformer. The results show that this novel autothermal CFB reformer can be a very efficient producer of pure hydrogen from heavy hydrocarbons. The bifurcation behavior analysis is essential for the design, control and optimization of this novel process..

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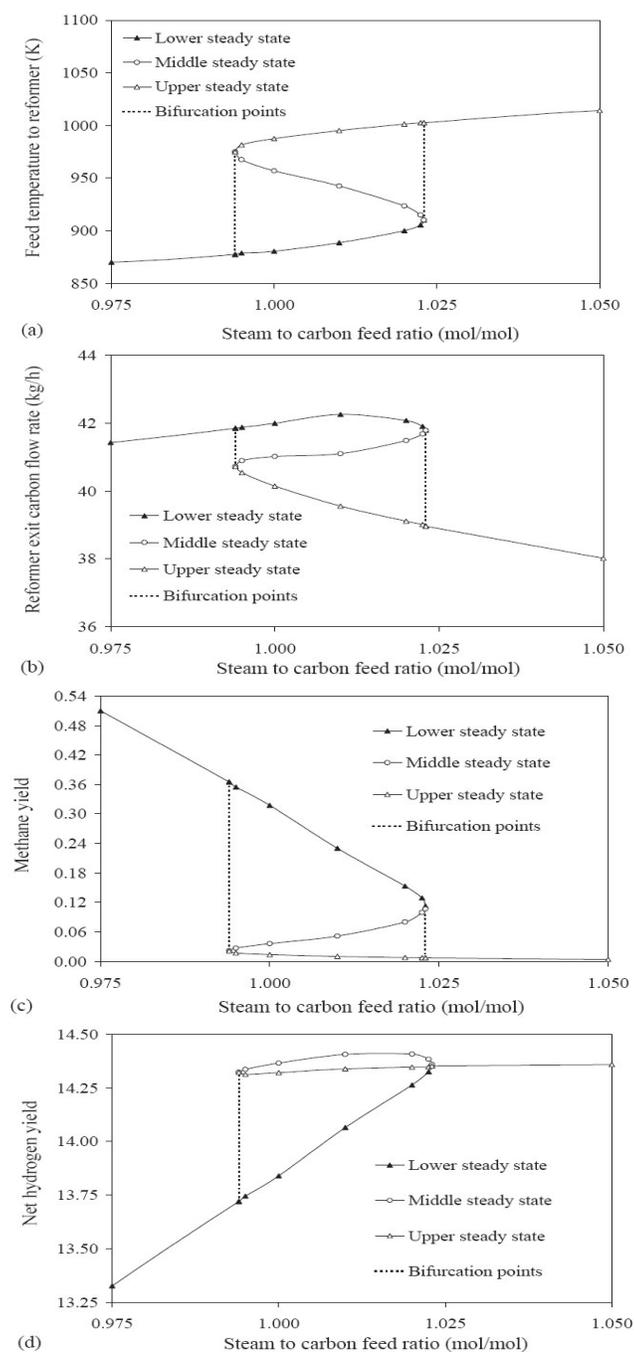


Figure 3: Bifurcation behavior with steam to carbon feed ratio as the bifurcation parameter in the autothermic CFB membrane reformer when catalyst is regenerated after gas-solid separation.