Thermodynamic analysis of adsorption enhanced reforming of ethanol

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ABSTRACT

Adsorption enhanced reforming (AER) is a novel hydrogen generation method. To study hydrogen yield and graphite formation in the AER process, a recently developed thermodynamic code for reaction-adsorption systems is extended to account for the formation of condensed species. Parametric analysis of the steam reforming of ethanol is performed to study the effect of adsorption and other parameters (temperature, pressure, steam/carbon ratio and O2/ethanol ratio in the feed) on the yield of hydrogen and the formation of graphite. It is shown that with CO2 adsorption, the hydrogen yield is enhanced while the graphite formation is suppressed. Based on the thermodynamic analysis, AER is a potential low-temperature method for hydrogen generation.

1. Introduction

As reducing the demand on fossil resources has been a public concern, hydrogen, being a potential carrier of clean energy, is now an important topic that may lead into a new era of energy research. Among various industrial techniques, steam reforming of hydrocarbons accounts for about 50% of the hydrogen produced over the world. In the United States, 95% of the hydrogen production is made through steam reforming of methane [1]. In this sense, steam reforming serves as a foundation in America’s transition to a hydrogen economy.

The past decade witnessed a significant development in steam reforming. On the feedstock side, the reforming of biomass-derived hydrocarbons (e.g., bio-ethanol) is widely acknowledged as a potentially viable, renewable and carbon-neutral (or even carbon-negative in conjunction with sequestration) process [2-4]. On the technology side, the steam reforming combined with CO2 removal using adsorption [5-10] or membrane [11] is shown to significantly enhance the yield and purity of hydrogen. When CO2 is removed from the reforming process, the thermodynamic limitation of the water gas shift reaction (CO + H2O = CO2 + H2) is circumvented and therefore, the chemical equilibrium shifts to the right, resulting in an enhancement in the extent of the forward reaction. Removing CO2 from the reactive system enables a relatively lower reforming temperature, thus alleviating the requirement for both the catalyst and the reactor. Moreover, the higher purity in the syngas leaving the reformer makes it easier for downstream hydrogen separation, which is typically achieved through a pressure swing adsorption (or PSA) unit. Extensive experimental and computational studies indicate that reforming with simultaneous CO2 removal is a very promising technique for enhanced hydrogen production [11-14]. Ongoing research is
conducted by various companies such as Chevron, Shell and Intelligent Energy to commercialize these novel reforming technologies [8,15,16].

Despite their wide utilization for hydrogen generation, the reforming processes (including the aforementioned enhanced reforming processes) might be accompanied by unfavorable formation of graphite under certain conditions, which could lead to catalyst deactivation and reformer malfunction due to its accumulative nature [12,17–27]. Studies have shown that the formation of graphite can be suppressed by using high steam/carbon (or S/C) ratios in the feedstock [17,20,24,28], adding oxygen to the feed [20], doping with a trace amount of sulphur, tin, chromium, molybdenum, potassium, and gold on the catalyst [18,23–25,29], adjusting reforming temperatures [30], enhancing support (e.g., alumina, silica, magnesia, zirconia, and ceria [25,31]), and adding sodium [32] etc. However, due to the inherent complexity of various coupled physicochemical phenomena involved in the reforming process, no general fundamental understanding is currently available towards the graphite formation and catalyst deactivation [12,21,26]. Bridging such a gap could germinate solutions to a longer catalyst lifetime, which will lead to significant economical benefits in the reforming process. Thermodynamic modeling has been a powerful tool in the analysis of hydrogen generation and fuel cells [33–37] and may provide insight into graphite-free operating windows for the AER process. However, to the best knowledge of the author, a generic thermodynamic model that accounts for gaseous reaction, adsorption, and formation of condensed species is not yet available. Motivated by this, a comprehensive thermodynamic model is developed in this work to calculate the equilibrium compositions in both the gaseous and the condensed phases of general reaction–adsorption systems. Thermodynamic analysis is carried out for steam reforming of ethanol under various operating conditions and it shows that adsorption enhanced reforming (AER) is advantageous over conventional reforming processes not only in terms of hydrogen yield but also in graphite suppression. Such an analysis might be used to guide the design and operation of an AER process.

2. Equilibrium of reaction–adsorption systems with formation of condensed species

The aim of this work is to develop a comprehensive thermodynamic model to analyze reaction–adsorption systems coupled by formation of condensed species. In the context of AER of hydrocarbons, the adsorbed species of interest is CO₂, and the condensed species is graphite [5,10,13,14,38,39]. Multi-component adsorption and multi-component condensation might also be included in the current model to handle other condensed species and the adsorption of gaseous species besides CO₂.

The equilibrium algorithm is based on the minimization of the total Gibbs free energy in an isothermal and isobaric system. Different from the equilibrium constant method, the Gibbs minimization approach does not require the specification of a detailed reaction scheme. A list of reactants and their thermodynamic properties suffice for the equilibrium calculation. Interested readers may refer to a previous work for a comparison of both approaches for solving a generic adsorption–reaction system with no condensed species [40]. The condensed species have different forms in the Gibbs free energy and pose a mathematical challenge to the optimization algorithm. In order to calculate the Gibbs free energy, the concept of mole ratio between the gaseous species and the adsorbed species [40] is employed here. According to the Langmuir adsorption/desorption isotherm (and also the equilibrium chemisorption isotherms of CO₂ on hydrotalcites [14,35]), the adsorbed amount of a species follows the relationship below:

\[
\eta_j^{(ads)} = \frac{S \eta_j^{(ads)} \beta_j P_j}{1 + \sum_{j=1}^{nT} \beta_j P_j} = \frac{S \eta_j^{(ads)} \beta_j P_j}{1 + \sum_{j=1}^{nT} \beta_j P_j} (j = 1, \ldots, s)
\]

(1)

![Fig. 1 – Comparison of gas composition of steam reforming of ethanol solved using the current equilibrium code with experimental data [42] under various conditions (S/C = 2, 3, 4, P = 2, 5, 9 bar, T = 700 °C and no CO₂ adsorption).](image)
where \( n_j \) is the amount of species \( j \) in the gas phase ([mole]), \( n_j^{(ads)} \) is the amount of species \( j \) on the adsorbent ([mole]), \( n_{j,\text{sat}}^{(ads)} \) is the saturated surface concentration ([mole/m²]), \( S \) is the total surface area of the adsorbent [m²], \( \beta_j \) is a constant for species \( j \) under isothermal conditions ([bar⁻¹]), \( P_j \) is the partial pressure of species \( j \) in the gas phase, and \( P \) is the system pressure. \( n_j = \sum_{j=1}^{s} n_j \) is the amount of species \( j \) in the system, where \( s \) is the number of gaseous species. For the adsorption of gaseous species on an adsorbent, \( n_{j,\text{sat}}^{(ads)} \) and \( \beta_j \) can be determined experimentally. \( S \) is then derived as the product of the experimentally measured specific surface area of the adsorbent and its weight. From Eq. (1), the ratio of \( n_j^{(ads)} \) to \( n_j \) is expressed as follows:

\[
    r_j = \frac{n_j^{(ads)}}{n_j} = \frac{S n_{j,\text{sat}}^{(ads)} \beta_j P}{n_{j,\text{sat}} + \sum_{j=1}^{s} \beta_j n_j P} \quad (j = 1, \ldots, s)
\]

Because the adsorbed species and its gaseous counterpart have the same chemical potential under chemical equilibrium, the optimization problem is formulated as follows:

\[
    \min_{n_j} G = \sum_{j=1}^{s} \left( 1 + r_j \right) \mu_j n_j + \sum_{j=1}^{s} \mu_j n_j \\
    \text{s.t.} \\
    0 = \sum_{j=1}^{s} \left( 1 + r_j \right) a_{ij} n_j + \sum_{j=1}^{s} a_{ij} n_j - b_i(0) \quad (i = 1, \ldots, \epsilon) \\
    \mu_j = \begin{cases} \\
        \mu_j^0 + RT \ln \frac{P_j}{P} + RT \ln \frac{n_j}{n_j^*} & (j = 1, \ldots, s) \\
        \mu_j^0 & (j = s + 1, \ldots, t) \\
    \end{cases} \\
    n_j = \sum_{j=1}^{s} n_j \\
    r_j = \frac{S n_{j,\text{sat}}^{(ads)} \beta_j P}{n_{j,\text{sat}} + \sum_{j=1}^{s} \beta_j n_j P} \quad (j = 1, \ldots, s) \\
    n_j \geq 0 \quad (j = 1, \ldots, s)
\]

where \( G \) is the Gibbs free energy, \( \mu_j \) is the chemical potential for species \( j \), \( a_{ij} \) is the number of element \( i \) in species \( j \), \( b_i(0) \) is the total number of element \( i \) in the feed mixture, \( n_j(0) = \sum_{j=1}^{s} n_j(0) \), where \( n_j(0) \) is the amount of species \( j \) in the feed, \( n_j^* \) stands for standard conditions, and \( t \) is the total number of species including the condensed material.

The known parameters are \( T, P, S \) and \( n_j(0) \) and the variables to be determined are \( n_j \) \( (j = 1, \ldots, s) \), \( n_j \) \( (j = 1, \ldots, t) \), \( \lambda_i \) \( (i = 1, \ldots, \epsilon) \) and \( n_{j,T} \). Due to the complexity of the problem represented by Eq. 3, one could solve an equivalent problem in which \( T, P, r_j \) \( (j = 1, \ldots, s) \) and \( n_j(0) \) are known while \( S, n_j \) \( (j = 1, \ldots, t) \), \( \lambda_i \) \( (i = 1, \ldots, \epsilon) \) and \( n_{j,T} \) are to be determined [40]. However, it is worth noting that the following relationship:

\[
    \frac{n_j^{(ads)}}{n_j} = \frac{S n_{j,\text{sat}}^{(ads)} \beta_j P}{n_{j,\text{sat}} + \sum_{j=1}^{s} \beta_j n_j P}
\]

should be satisfied when specifying \( r_j \) \( (j = 1, \ldots, s) \) if multiple component adsorption occurs in the system.

It is also worth noting that inequality constraints \( n_j \geq 0 \) \( (j = 1, \ldots, s) \) are handled in the solution procedure by solving in \( n_j \) instead of \( n_j \) [40,41]. To avoid singularity problems when taking logarithms of extremely small positive numbers, any \( n_j \) that is less than \( 10^{-50} \) will be replaced by this number during the iteration process.

The constrained optimization problem represented by Eq. (3) can be solved by the Lagrange multiplier method. Based on this method, an auxiliary function is first defined as follows:

\[
    f = \sum_{j=1}^{s} \left( 1 + r_j \right) \mu_j n_j + \sum_{j=1}^{s} a_{ij} n_j + \sum_{j=1}^{s} \lambda_i \left[ \sum_{j=1}^{s} \left( 1 + r_j \right) a_{ij} n_j + \sum_{j=1}^{s} a_{ij} n_j - b_i(0) \right], \quad \lambda_i \text{ are the Lagrange multipliers for the atomic balance constraints.}
\]

As a result, the optimal solution to the optimization problem of Eq. (3) is determined by solving the following equations:

\[
    \begin{align*}
    0 &= \left( 1 + r_j \right) \left[ \mu_j + \sum_{i=1}^{s} a_{ij} \lambda_i \right] \quad (j = 1, \ldots, s) \\
    0 &= \mu_j + \sum_{i=1}^{s} a_{ij} \lambda_i \quad (j = s + 1, \ldots, t) \\
    0 &= \sum_{j=1}^{s} \left( 1 + r_j \right) a_{ij} n_j + \sum_{j=1}^{s} a_{ij} n_j - b_i(0) \quad (i = 1, \ldots, \epsilon) \\
    \mu_j &= \begin{cases} \\
        \mu_j^0 + RT \ln \frac{P_j}{P} + RT \ln \frac{n_j}{n_j^*} & (j = 1, \ldots, s) \\
        \mu_j^0 & (j = s + 1, \ldots, t) \\
    \end{cases} \\
    n_j &= \sum_{j=1}^{s} n_j \\
    n_{j,T} &= \sum_{j=1}^{s} n_j
\end{align*}
\]

The decent Newton–Raphson method is used to solve the above problems, and the iterative variables are chosen to be \( \Delta \ln n_j \) \( (j = 1, \ldots, s) \), \( \Delta \ln n_j \) \( (j = s + 1, \ldots, t) \), \( \Delta \ln n_{j,T} \) and \( x_i = \lambda_i/RT \) \( (i = 1, \ldots, \epsilon) \) which are different from the NASA Chemical Equilibrium with Applications (CEA) code [41]. The following iterative formulas are then derived:

\[
    \begin{align*}
    0 &= -\frac{\mu_j}{RT} + \sum_{i=1}^{s} a_{ij} n_j + \Delta \ln n_j - \Delta \ln n_j \quad (j = 1, \ldots, s) \\
    0 &= \sum_{i=1}^{s} a_{ij} n_j - \frac{\mu_j}{RT} \quad (j = s + 1, \ldots, t) \\
    0 &= \sum_{j=1}^{s} \left( 1 + r_j \right) a_{ij} n_j + \sum_{j=1}^{s} a_{ij} n_j - b_i(0) \\
    &\quad + \sum_{j=1}^{s} \left( 1 + r_j \right) a_{ij} \Delta \ln n_j + \sum_{j=1}^{s} a_{ij} n_j \Delta \ln n_j \quad (i = 1, \ldots, \epsilon) \\
    0 &= \sum_{j=1}^{s} n_j - n_{j,T} + \sum_{j=1}^{s} n_j \Delta \ln n_j - n_j \Delta \ln n_{j,T} \\
    \mu_j &= \begin{cases} \\
        \mu_j^0 + RT \ln \frac{P_j}{P} + RT \ln \frac{n_j}{n_j^*} & (j = 1, \ldots, s) \\
        \mu_j^0 & (j = s + 1, \ldots, t) \\
    \end{cases}
\end{align*}
\]

The “reduced Gibbs iteration” scheme [41] is employed to effectively track a large number of species. The idea is to cancel \( \Delta \ln n_j \) in Eq. (6). Consequently, the following equations are derived:
The solution procedure is described as follows. With initial guesses of \( n_j \) \( (j = 1, \ldots, t) \) and \( n_T \), Eq. (7) is solved to determine \( \Delta \ln n_j \) \( (j = s + 1, \ldots, t) \) and \( \Delta \ln n_T \), \( \Delta \ln n_j \) \( (j = 1, \ldots, s) \) is then determined using the first equation in Eq. (6). Subsequently, \( n_j \) \( (j = s + 1, \ldots, t) \) and \( n_T \) are updated. To avoid divergence of the algorithm, the step size used for updating \( n_j \) \( (j = s + 1, \ldots, t) \) is smaller than \( n_j \) \( (j = 1, \ldots, s) \) and \( n_T \). The iterative procedure continues until the changes in all the correction variables in Eq. (7) fall into specified regions [40]. The thermodynamic data of each species at temperature \( T \), such as the heat capacity, enthalpy, entropy and chemical potential are calculated as functions of temperature [41].

3. Thermodynamic analysis of the effect of CO\(_2\) adsorption on steam reforming of ethanol

A reactive system consisting of steam and ethanol is studied in this section. The steam reforming of biomass-generated ethanol would be a potentially viable and renewable process for hydrogen production [2–4]. Experimental studies have shown that for a system of hydrocarbon (e.g., methane, methanol or ethanol) and steam, the yield and purity of hydrogen can be significantly improved if CO\(_2\) is adsorbed [5–10]. Calculations in this section will provide a quantitative thermodynamic analysis of the AER process.

In the steam reforming of ethanol, the most common products and by-products would be H\(_2\), CH\(_4\), CO, CO\(_2\) and C

![Fig. 2](image-url) Profiles of H\(_2\) yield and graphite formation in steam reforming of ethanol (a, c) without and (b, d) with CO\(_2\) adsorption \( (P = 5 \text{ bar}, r_{CO_2} = 10^2 \text{ for CO}_2 \text{ adsorption}) \). Profiles of H\(_2\) and graphite are normalized based on the molar amount of ethanol in the feed.
An inclusion of more species would not affect the complexity of this problem because the developed algorithm is based on the reduced Gibbs iteration. One possible reaction scheme, specified based on the minimum number of independent reactions, is listed as follows:

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} & = \text{CH}_4 + \text{CO} + \text{H}_2 \quad (8\text{a}) \\
\text{CH}_4 + \text{H}_2\text{O} & = \text{CO} + 3\text{H}_2 \quad (8\text{b}) \\
\text{CO} + \text{H}_2\text{O} & = \text{CO}_2 + \text{H}_2 \quad (8\text{c}) \\
2\text{CO} & = \text{CO}_2 + \text{C} \quad (8\text{d})
\end{align*}
\]

As mentioned earlier, these reactions are not necessary in the calculation of equilibrium composition using the Gibbs minimization approach. However, they are helpful for the explanation of gas composition change as operating conditions vary.

The developed algorithm is first applied to a conventional steam reforming of ethanol process with no CO\textsubscript{2} adsorption. Profiles of CH\textsubscript{4}, CO and CO\textsubscript{2} in steam reforming of ethanol (a, c, e) without and (b, d, f) with CO\textsubscript{2} adsorption (P = 5 bar, \( r_{\text{CO}_2} = 10^2 \) for CO\textsubscript{2} adsorption). Profiles of CH\textsubscript{4}, CO and CO\textsubscript{2} are normalized based on the molar amount of ethanol in the feed.

Fig. 3 – Profiles of CH\textsubscript{4}, CO and CO\textsubscript{2} in steam reforming of ethanol (a, c, e) without and (b, d, f) with CO\textsubscript{2} adsorption (P = 5 bar, \( r_{\text{CO}_2} = 10^2 \) for CO\textsubscript{2} adsorption). Profiles of CH\textsubscript{4}, CO and CO\textsubscript{2} are normalized based on the molar amount of ethanol in the feed.
(i.e., $r_{\text{CO}_2} = 0$) [42]. In this process, the reforming occurs in a tube reactor where Ni was used as the catalyst. All carbon containing gases in the product gas mixture were analyzed using a NDIR spectrometer. A comparison of model predicted gas composition in the steam reforming of ethanol using Ni as catalyst with experimental data under various pressures and steam/carbon ratios is given in Fig. 1. The model prediction matches the experimental data very well, which partly validates the accuracy of the developed thermodynamic model.

The equilibrium analysis is then made for steam reforming of ethanol with/without CO$_2$ adsorption at various S/C ratios, temperatures and a fixed pressure of 5 bar. In the case of CO$_2$ adsorption, $r_{\text{CO}_2}$ is set to be $10^2$. It is shown in Fig. 2 that in both cases, the yield of hydrogen increases as the S/C ratio or the temperature increases. When CO$_2$ is partly removed from the system by adsorption, the hydrogen yield is improved (by 8–178%). The enhancement in hydrogen yield is more prominent at low temperatures and S/C ratios higher than 1.3. Moreover, while the graphite formation is very severe when the S/C is below 1.3 when no CO$_2$ is adsorbed, it reduces to a minimal level when adequate CO$_2$ adsorption is taken into effect.

The profiles of CH$_4$, CO and CO$_2$ with/without CO$_2$ adsorption are shown in Fig. 3. It is worth noting that $r_{\text{CO}_2} = 10^2$ means the amount of CO$_2$ in the gaseous phase is 1% of the one adsorbed on the surface of the adsorbent. If one compares the CO$_2$ in the gaseous phase in Fig. 3(e) (without adsorption) and (f) (with adsorption), the latter is not exactly 1% but between 1% and 2% of the former. This is because the entire reactive system behaves like a buffer solution [40]. When CO$_2$ is partly adsorbed on the surface of adsorbent, it is generated by other reaction mechanisms, e.g., the water gas shift reaction (Eq. 8c). Because the CO$_2$ generation partly compensates for the removal in the gaseous phase due to adsorption, the total amount of CO$_2$ (in both the gaseous phase and on the surface) is more in the case of AER. This also explains why the CO concentration in the gas phase is reduced to a minimal level when substantial CO$_2$ is removed by adsorption (The CO in Fig. 3(d) is only 2–10% of the one in Fig. 3(b)). The reduction in CO$_2$ and CO favors the water gas shift reaction (Eq. 8c) and the methane reforming reaction (Eq. 8b), leading to an enhancement in the hydrogen yield. Even though the reduction in CO$_2$ is more than the one in CO when CO$_2$ is substantially adsorbed, the carbon formation reaction (Eq. 8d) moves backwards because its equilibrium constant is related to the square of CO concentration.

The steam reforming of ethanol with/without CO$_2$ adsorption at a lower pressure ($P = 1$ bar) is shown in Figs. 4.
and 5. It is observed that without adsorption, the hydrogen yield at chemical equilibrium at 1 bar is higher than the one at 5 bar. This can be explained using Le Chatelier’s principle which suggests that the generation of light gaseous molecules is favored at reduced pressures. However, the amount of graphite formed is also higher at 1 bar. Under this low pressure, both the hydrogen yield and graphite suppression are significantly improved when AER is used. It is noticed that for $r_{CO_2} = 10^2$, the graphite formation is still obvious at higher temperatures (500–600 °C) when the S/C ratio is low, which might be improved by increasing $r_{CO_2}$, or the amount of adsorbent.

A further study of the reforming pressure and adsorption on hydrogen yield and graphite formation is shown in Fig. 6. It clearly shows the evolution of hydrogen yield (Fig. 6(a)) and carbon formation (Fig. 6(b)) as the pressure and $r_{CO_2}$ vary gradually. In the entire range of interest, the yield of hydrogen increases when the pressure is reduced. However, the graphite formation is also promoted. A combination of hydrogen enhancement and graphite suppression can be achieved when

![Fig. 5 – Profiles of CH₄, CO and CO₂ in steam reforming of ethanol (a, c, e) without and (b, d, f) with CO₂ adsorption ($P = 1$ bar, $r_{CO_2} = 10^2$ for CO₂ adsorption). Profiles of CH₄, CO and CO₂ are normalized based on the molar amount of ethanol in the feed.](image-url)
CO₂ is removed from the reactive system by adsorption. Based on Fig. 6(b), a contour of graphite formation is plotted in Fig. 6(c), which reveals that a graphite-free region is guaranteed by sufficient CO₂ adsorption. Based on this thermodynamic analysis, CO₂ adsorption could be an alternative or supplement to the high S/C ratios or high pressures used in the reforming processes to inhibit carbon formation. The required amount of adsorbent per mol of ethanol in the feed at specified rCO₂ and P can be calculated based on Eq. (2), or

\[
S_n^{(ads)}(CO_2)_{sat} = \frac{r_{CO_2} \left( \sum_{j=1}^{n} n_j + \beta_{CO_2} r_{CO_2} P \right)}{\beta_{CO_2} P}
\]

Because \( n^{(ads)}_{CO_2} \) is a physical parameter of the adsorbent that is measured experimentally, the surface area of the adsorbent \( S \) can be readily determined if \( S_n^{(ads)}(CO_2)_{sat} \) is known. The group \( S_n^{(ads)}(CO_2)_{sat} \) based on potassium promoted hydrotalcite (\( \beta_{CO_2} \) is around 22 bar⁻¹ at 500 °C [43]) is shown in Fig. 6(d). It is seen that the amount of adsorbent reduces with increased pressure if \( r_{CO_2} \) and the temperature are fixed. This is primarily due to an increased partial pressure of CO₂ in the gaseous phase, which favors CO₂ adsorption on the adsorbent.

Partial oxidation reforming is a method to heat up the reforming gas by burning part of the fuel using oxygen, thus reducing the energy demand for the reforming process [36]. The AER can be potentially combined with partial oxidation. When oxygen is present in the feed, one more reaction should be included in the reaction scheme described by Eq. (8). The option is not unique. One acceptable reaction independent of all the reactions in Eq. (8) is as follows:

\[
2CO + O_2 = 2CO_2
\]

The effect of O₂ and adsorption on hydrogen yield and graphite formation is shown in Fig. 7. It can be seen that without adsorption, partial oxidation does not lead to significant improvement in the hydrogen yield under the given operating conditions. In fact, at high S/C ratios, the thermodynamic model shows that partial oxidation might result in a reduction in the hydrogen yield (not shown in Fig. 7). However, when partial oxidation is combined with CO₂ adsorption, the hydrogen yield is enhanced. Moreover, partial oxidation suppresses graphite formation. This is because the addition of O₂ in the system converts part of CO into CO₂ (see Eq. 10), and the carbon formation reaction (Eq.

![Fig. 6 - Profiles of (a) hydrogen yield and (b) graphite formation and (d) \( S_n^{(ads)}(CO_2)_{sat} \) and (c) contour of graphite formation as functions of system pressure and CO₂ adsorption (\( P = 1–10 \text{ bar}, T = 500 °C, r_{CO_2} = 10^{-2}–10^3, S/C = 1 \) and \( \beta_{CO_2} = 22 \text{ bar}^{-1} \) based on potassium promoted hydrotalcite [43]). The profiles of hydrogen, graphite and \( S_n^{(ads)}(CO_2)_{sat} \) are normalized based on the molar amount of ethanol in the feed.](image-url)
8d) moves backwards. When the partial oxidation is used in the AER process, the graphite formation can be inhibited with a less amount of adsorbent (see Fig. 6 for a comparison).

4. Concluding remarks

Thermodynamic analyses have been carried out for AER of ethanol. It is shown that adsorption of CO$_2$ suppresses the formation of carbon in the reforming process. When CO$_2$ adsorption is combined with high S/C ratios, increased pressures and partial oxidization, the formation of carbon can be further reduced. Because adsorption also enhances hydrogen yield and purity, AER would be an efficient way of making hydrogen at a reduced temperature as compared to conventional steam reforming.

It is worth noting that even though thermodynamic analysis can be used to explain certain phenomena, it only provides the limit of the reactions. It may only reflect the general trend of a reactor but is not suited for the detailed modeling of a PFR-type reactor (see Ref. [40] for an effort of thermodynamic modeling of gradual CO$_2$ removal along a reactor that is approximated by multiple equilibrium stages). Due to the continuous operation nature of the AER process, a spatiotemporal description of the reactor requires time-dependent distributed kinetic models (including the kinetics of reactions and of CO$_2$ adsorption–desorption as well) coupled by fluid flow and heat transfer. In this way the CO$_2$ breakthrough curve can be captured. Interested readers may refer to literature efforts in this direction [10,13].

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Nomenclature

- $\beta_j$: adsorption parameter of species $j$ in the Langmuir isotherm model, bar$^{-1}$
- $\epsilon$: total number of chemical elements in the reactive system
- $\lambda$: Lagrange multiplier
- $\mu$: chemical potential, J/mol
- $\pi$: $-1/kT$
- $(ads)$: properties of adsorbed species
- $a_{ij}$: number of chemical element $i$ in species $j$
- $G$: Gibbs energy, J
- $i, j, k$: indices
- $n_j$: molar amount of species $j$ in the gas phase, mol
- $n_j^{(ads)}$: molar amount of species $j$ on the surface, mol
- $n_F$: total molar amount in the gas phase, mol
- $n_{s, sat}$: saturated concentration of species $j$ on the adsorbent surface, mol/m$^2$
- $P$: pressure, bar
- $R$: gas constant, 8.314 J/mol/K
- $r_j$: molar ratio of a species in the gas phase to the surface
- $S$: surface area of adsorbent, m$^2$
- $s$: total number of gaseous species
- $T$: temperature, K
- $t$: total number of species

References


