Equilibrium Calculation of Gaseous Reactive Systems with Simultaneous Species Adsorption

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This work focuses on the calculation of chemical equilibrium in a gaseous reactive system with simultaneous single or multiple species adsorption under isothermal and isobaric conditions. Two different algorithms are developed, following the minimization of Gibbs free energy and the concept of equilibrium constant, respectively. In either case, the problem formulation is converted to a set of nonlinear algebraic equations that are solved using the Newton–Raphson scheme. An example of steam reforming of ethanol with simultaneous CO$_2$ adsorption is used to illustrate the proposed approaches. It is shown that at $T = 500$ °C and $P = 5$ bar, the CO$_2$ removal ratio should exceed 40% to achieve a decent enhancement in hydrogen production and purity. An integrated process that combines the endothermic reforming and the exothermic combustion of CH$_4$ from the off-gas supplemented with simultaneous CO$_2$ adsorption in the reforming process yields a theoretical maximum overall conversion rate of 86.3% (the corresponding H$_2$ purity out of the reformer is 89.4% on a wet basis, or 96.2% on a dry basis) with little or no external heat supply. The analysis in this work is potentially useful in the design and optimization of adsorption-enhanced reforming reactors for hydrogen generation and other applicable reactive systems.

1. Introduction

Chemical equilibrium in a reactive system is a state where the chemical activity of each species does not exhibit a net change over time. The calculation of chemical equilibrium provides the thermodynamic limit of a chemical process and has been traditionally used in the design and analysis of chemical equipment such as turbines and engines. The advances in chemical equilibrium algorithms have been significantly facilitated by the ever-increasing computational power of modern computers. One milestone in chemical equilibrium calculation is the development of the NASA chemical equilibrium and applications (CEA) code, which is capable of tracking hundreds of species in a gaseous reactive system and has been used in various applications such as rockets, incident/reflected shocks, and Chapman-Jouguet detonations. The so-called Gibbs reactor module that is based on the minimization of Gibbs free energy has also been incorporated in various modern engineering solvers, including Pro/II and Aspen Hysys to predict equilibrium compositions. Currently, thermodynamic analyses based on chemical equilibrium calculations have been found in a variety of applications, such as material interfacial phenomena and biological processes, and reacting nozzle flows to name a few.

More recently, various groups of researchers have shown great interest in the application of chemical equilibrium to processes related to hydrogen generation and fuel cells. Because 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. The generation of hydrogen can be realized through various routes such as steam reforming of hydrocarbons, gasification of coal, chemical looping combustion of coal, water splitting by thermochemical cycle, and electrolytic decomposition of water. In particular, hydrogen generation from biomass has received much attention, because it is a potentially viable, renewable, and carbon-neutral (or even carbon-negative, in conjunction with sequestration) process. Most of these processes involve the water-gas shift (WGS) reaction (CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$). If CO$_2$ can be simultaneously removed as the WGS reaction proceeds, the thermodynamic limitation can be circumvented, and, therefore, the chemical equilibrium shifts to the right, resulting in an enhancement in the extent of the forward reaction and the hydrogen yield.

This work focuses on the development of computational algorithms for chemical equilibrium calculations in gaseous reactive systems with simultaneous single or multiple species adsorption. The algorithms are then applied to the thermodynamic analysis of steam reforming of ethanol. Implications to an integrated autothermal process for hydrogen generation from steam reforming of hydrocarbons are discussed at the end of this work.

2. Chemical Equilibrium Calculation through Nonlinear Optimization

For a closed system under constant temperature and pressure, the Gibbs free energy decreases as equilibrium is approached. Therefore, one approach to equilibrium calculation in an isothermal and isobaric reactive system is to minimize its total Gibbs free energy. The mathematical formulation generally leads to a nonlinear optimization problem, which can be solved using numerical methods. This approach is advantageous over the equilibrium constant method when simultaneously tracking a large number of species is necessary, because it circumvents specifying a set of reactions a priori. To this end, it is worth noting that, although the NASA CEA package is capable of handling various types of equilibrium calculations, no species adsorption is explicitly taken into account in the current code.

The focus of this work is to calculate the chemical equilibrium of a reactive gaseous system with species adsorption, which is a common problem to adsorption-enhanced reactive systems. In the problem formulation, the following assumptions are made:

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Where the reactive system is maintained under isothermal and isobaric conditions; (ii) the gaseous phase obeys the ideal gas law; (iii) there is no heterogeneous reaction on the surface of the adsorbent; and (iv) there is no condensed species in the entire reactive system. Consider such a reactive system with one kilogram of reactants, the Gibbs free energy ($G$) of the entire reactive system is

$$G = \sum_{j=1}^{s} (\mu_j^{(g)} n_j^{(g)} + \mu_j^{(ads)} n_j^{(ads)})$$  \hspace{1cm} (1)

where $s$ is the total number of species, $n_j$ is the amount of species $j$ (in terms of moles), $\mu$ is the chemical potential, and the superscripts $(g)$ and $(ads)$ represent properties related to species in the gas phase and on the surface, respectively. When equilibrium is attained, the following criteria should be satisfied:

$$\mu_j^{(ads)} = \mu_j^{(g)} \quad (for \ j = 1, ..., s)$$  \hspace{1cm} (2)

For a gaseous species that obeys the ideal gas law, its chemical potential can be calculated using the following equation:\(^1\)

$$\mu_j^{(g)} = \mu_j^{(0g)} + RT \ln \left( \frac{P}{P_0} \right) + RT \ln \left( \frac{n_j^{(g)}}{n_j^{(g)}} \right) \quad (for \ j = 1, ..., s)$$  \hspace{1cm} (3)

where $T$ and $P$ are temperature and pressure of the system, respectively; $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), the superscript $0$ denotes properties under standard conditions ($P_0 = 1$ bar), and $n_j^{(g)} = \sum_{j=1}^{s} n_j^{(g)}$. A detailed expression for $\mu_j^{(ads)}$ might not be necessary, because the relationship between the gaseous species and the adsorbed species can sometimes be obtained experimentally. Based on the Langmuir isotherm, which is widely used in the analysis of adsorption phenomena, or experimental observations (e.g., equilibrium chemisorption isotherms of CO$_2$ on hydrotalcites), the adsorption/desorption equilibrium typically follows the relationship

$$n_j^{(ads)} = S n_j^{(ads)} \beta_j P_j \quad \frac{n_j^{(ads)} \beta_j n_j^{(g)}}{1 + \sum_{j=1}^{s} \beta_j P_j} \quad (for \ j = 1, ..., s)$$  \hspace{1cm} (4)

where $n_j^{(ads)}$ is the actual adsorbed amount of species $j$ (in terms of moles), $n_j^{(ads)}$ the saturated surface concentration (in units of mol/m$^2$), $S$ the total surface area of the adsorbent, $\beta$ a constant for species $j$ under isothermal conditions, and $P_j$ the partial pressure of species $j$ in the gas phase. Based on eq 4, the ratio of $n_j^{(ads)}$ to $n_j^{(g)}$ is expressed as follows:

$$r_j = \frac{n_j^{(ads)}}{n_j^{(g)}} = \frac{S n_j^{(ads)} \beta_j P_j}{n_j^{(g)} + \sum_{j=1}^{s} \beta_j n_j^{(g)}} \quad (for \ j = 1, ..., s)$$  \hspace{1cm} (5)

There are two ways to solve the relationship between the equilibrium composition and the amount of adsorbent. One could start with the surface area of the adsorbent and include eq 4 in the optimization problem to solve the equilibrium composition. Alternatively, one could start with $r_j$ and solve the equilibrium composition from the optimization problem. The surface area of the adsorbent is then calculated based on eq 5 and the equilibrium composition. The latter approach is used in this work, because the number of constraints can be significantly reduced in the optimization problem. However, it is important to note that $r_j$ are not independent if multiple species are adsorbed simultaneously. In such a case, $r_j$ should be specified based on the following relationship:

$$\frac{r_j}{r_j} = \frac{n_j^{(ads)} \beta_j}{n_j^{(ads)} \beta_j} \quad (6)$$

To minimize the Gibbs free energy of the entire system described by eq 1, the mass balance should be satisfied at the same time. This is achieved by the so-called atomic balance equations. Let $a_{ij}$ be the number of chemical element $i$ contained in species $j$, the atomic balance equation is

$$\sum_{j=1}^{s} a_{ij} n_j^{(g)} + \sum_{j=1}^{s} a_{ij} n_j^{(ads)} = \sum_{j=1}^{s} a_{ij} n_j^{(g)}(0) \quad (for \ i = 1, ..., e)$$  \hspace{1cm} (7)

where $e$ is the total number of chemical elements in this reactive system. The term $b_j(0)$ is the number of moles of element $i$ per kilogram of reactants ($b_j(0) = \sum_{i=1}^{e} a_{ij} n_j^{(g)}(0)$). Note that the effective number of equations in eq 7 is equal to the rank of the atomic matrix, which might be less than $e$ occasionally. In such a case, eq 7 should be replaced by its minimum realization. Interested readers are directed to the open literature for more details. However, the optimization algorithms can still be developed in a similar manner.

Based on the aforementioned analysis, the calculation of equilibrium compositions is formulated as the following non-linear optimization problem:

$$\min_{n_j^{(g)}, n_j^{(ads)}} G = \sum_{j=1}^{s} (\mu_j^{(g)} n_j^{(g)} + \mu_j^{(ads)} n_j^{(ads)}) \quad (8)$$

s.t.

$$0 = \sum_{j=1}^{s} a_{ij} n_j^{(g)} + \sum_{j=1}^{s} a_{ij} n_j^{(ads)} - b_j(0) \quad (for \ i = 1, ..., e)$$

$$\mu_j^{(ads)} = \mu_j^{(g)} \quad (for \ j = 1, ..., s)$$

$$\frac{n_j^{(ads)}}{n_j^{(ads)}} = r_j \quad (for \ j = 1, ..., s)$$

$$\mu_j^{(g)} = \mu_j^{(0g)} + RT \ln \left( \frac{P}{P_0} \right) + RT \ln \left( \frac{n_j^{(g)}}{n_j^{(g)}} \right) \quad (for \ j = 1, ..., s)$$

$$n_j^{(ads)} = \sum_{j=1}^{s} n_j^{(g)}$$

Equation 8 can be simplified by cancelling the terms related to the adsorbed species. The resulting problem is

$$\min_{n_j^{(g)}} G = \sum_{j=1}^{s} (1 + r_j) \mu_j^{(g)} n_j^{(g)} \quad (9)$$

s.t.

$$0 = \sum_{j=1}^{s} (1 + r_j) a_{ij} n_j^{(g)} - b_j(0) \quad (for \ i = 1, ..., e)$$

$$\mu_j^{(g)} = \mu_j^{(0g)} + RT \ln \left( \frac{P}{P_0} \right) + RT \ln \left( \frac{n_j^{(g)}}{n_j^{(g)}} \right) \quad (for \ j = 1, ..., s)$$

$$n_j^{(ads)} = \sum_{j=1}^{s} n_j^{(g)}$$

Strictly speaking, the inequality constraint $n_j \geq 0 \ (j = 1, ..., s)$ should be included in the optimization problem described by
applied, sometimes

multiplier method. First, we define to a set of nonlinear algebraic equations using the Lagrange

an effect on the accuracy of the solution, because the contribu-

tion of $n_j$; of these components to the total Gibbs free energy would be very close to zero. (Note that $\lim_{n_j \to 0} n_j = 0$, based on L'Hopital's rule.) With this in mind, the optimization problem described in eq 9 is then converted to a set of nonlinear algebraic equations using the Lagrange multiplier method. First, we define $f = \sum_{i=1}^{s} \Phi_i(a[i, j]) + \sum_{i=1}^{s} \lambda_i[\sum_{j=1}^{s} (1 + r_j)\phi_i(j) - b_i(0)]$, where $\lambda_i$ are the Lagrange multipliers. The optimal solution to the optimization problem of eq 9 should be determined by solving the following nonlinear algebraic equations:

$$0 = \frac{\partial f}{\partial n_j^{(s)}} = (1 + r_j)\mu_j^{(s)} + \sum_{i=1}^{s} (1 + r_j)a[i, j] \quad (for \ j = 1, \ldots, s)$$

(10a)

$$0 = \frac{\partial f}{\partial \lambda_i} = \sum_{j=1}^{s} (1 + r_j)a[i, j] - b_i(0) \quad (for \ i = 1, \ldots, \epsilon)$$

(10b)

$$\mu_j^{(s)} = \mu_j^{(s)} + RT \ln \left( \frac{P_j}{P^0} \right) - RT \ln \left( \frac{n_j^{(s)}}{n_j^{(0)}} \right) \quad (for \ j = 1, \ldots, s)$$

(10c)

$$n_j^{(s)} = \sum_{i=1}^{s} n_j^{(s)} \quad (for \ i = 1, \ldots, \epsilon)$$

(10d)

The variables to be determined are $n_j^{(s)} (j = 1, \ldots, s)$, $\lambda_i (i = 1, \ldots, \epsilon)$, and $n_j^{(0)}$. These $s + \epsilon + 1$ variables in eqs 10a–10d can be solved using the decent Newton–Raphson method. The central idea of the Newton–Raphson method is to apply multivariable Taylor series expansion to a nonlinear vector function and then use truncated terms that contain only the first-order derivatives to build a linear iterative formula. The formula can be then used to compute the solution with a given initial guess close to the solution; interested readers may refer to specialized books for details. Following a method employed by the NASA CEA package, the iterative variables are chosen to be $\Delta n_j^{(i)} (j = 1, \ldots, s)$, $\Delta n_i^{(0)}$ and $\pi_i = -\lambda_i/RT (i = 1, \ldots, \epsilon)$, to avoid taking the logarithm of negative numbers in the iteration procedure. Here, note that the expression $\pi_i = -\lambda_i/RT (i = 1, \ldots, \epsilon)$ is solved directly at each iteration step.

With the definition of $\pi_i$, eq10a can be converted to dimensionless form,

$$\left(1 + r_j\right)\frac{\mu_j^{(s)}}{RT} - \sum_{i=1}^{s} (1 + r_j)a[i, j] = 0 \quad (for \ j = 1, \ldots, s)$$

(11)

which has the following Newton–Raphson iterative formula:

$$\frac{\partial f}{\partial n_j^{(s)}} = \sum_{i=1}^{s} (1 + r_j)a[i, j] \quad (for \ j = 1, \ldots, s)$$

(12)

or

$$\Delta n_j^{(s)} = \left(1 + r_j\right)\frac{\mu_j^{(s)}}{RT} + \sum_{i=1}^{s} a[i, j] \Delta \pi_i + \Delta n_i^{(0)} \quad (for \ j = 1, \ldots, s)$$

(13)

Similarly, the Newton–Raphson iterative formulas for the other equations can be determined as

$$\sum_{j=1}^{s} (1 + r_j)a[j, j] - \sum_{j=1}^{s} a[j, j]n_j^{(0)} - \sum_{j=1}^{s} (1 + r_j)a[j, j] \Delta n_j^{(s)} = 0 \quad (for \ i = 1, \ldots, \epsilon)$$

(14)

and

$$\sum_{j=1}^{s} n_j^{(s)} - n_j^{(0)} + \sum_{j=1}^{s} n_j^{(s)} \Delta n_j^{(0)} - n_j^{(0)} \Delta n_j^{(0)} = 0 \quad (for \ i = 1, \ldots, \epsilon)$$

(15)

To expedite the calculation, especially when a large number of species are present in the reactive system, the so-called reduced Gibbs iteration scheme has been proposed to significantly reduce the number of variables in the iteration steps.5 The idea is to cancel the $\Delta n_i^{(0)}$ term in eqs 14 and 15, using eq 13. Consequently, eqs 14 and 15 are converted to

$$\sum_{j=1}^{s} \left[ \sum_{k=1}^{s} (1 + r_j)a[j, k]n_k^{(s)} \right] \pi_j + \sum_{j=1}^{s} (1 + r_j)a[j, j] \Delta n_j^{(s)} =$$

$$\left[ \sum_{j=1}^{s} a[j, j]n_j^{(0)} - \sum_{j=1}^{s} (1 + r_j)a[j, j] + \sum_{j=1}^{s} (1 + r_j)a[j, j] \frac{\mu_j^{(s)}}{RT} \right] \quad (for \ i = 1, \ldots, \epsilon)$$

(16)

and

$$\sum_{j=1}^{s} \left[ \sum_{k=1}^{s} a[j, k]p_k^{(s)} \right] \pi_j + \sum_{j=1}^{s} n_j^{(s)} - n_j^{(0)} \Delta n_j^{(s)} =$$

$$\left[ n_j^{(s)} - \frac{\sum_{j=1}^{s} n_j^{(s)} + \sum_{j=1}^{s} n_j^{(s)} \frac{\mu_j^{(s)}}{RT} }{\Delta n_j^{(s)}} \right]$$

(17)

After the aforementioned transformations, the number of variables is reduced from $s + \epsilon + 1$ to $\epsilon + 1$, which is favorable when a large amount of species are to be tracked simultaneously. It can be readily verified that the algorithm reduces to the

![Figure 1. Conversion of C2H4OH to H2 as a function of CO2(s)/CO2(g) (molar ratio of feed = 1:3, P = 5 bar, and T = 500 °C).](image-url)
standard NASA CEA algorithm when there is no adsorption, or $r_j = 0$ (for $j = 1, ..., s$).5

The procedure of the calculation is to calculate the terms on the right-hand side of eqs 16 and 17 with initial guesses of $n_j^{(0)}$ and $n_i^{(0)}$, and then solve $\Delta n_j^{(0)}$ and $\pi_k$ ($k = 1, ..., \epsilon$) using these $\epsilon + 1$ linear equations. Subsequently, $\Delta n_j^{(0)}$ ($j = 1, ..., s$) are calculated using eq 13, based on the value of $\Delta n_i^{(0)}$. The following formulas are then applied to update $n_j^{(0)}$ and $n_i^{(0)}$ to be used in the next iteration step:

\[
(n_j^{(0)})^{(m+1)} = \exp[(\ln n_j^{(0)})^{(m)} + \alpha^{(m)} \Delta (\ln n_j^{(0)})^{(m)}] \\
(n_i^{(0)})^{(m+1)} = \exp[(\ln n_i^{(0)})^{(m)} + \alpha^{(m)} \Delta (\ln n_i^{(0)})^{(m)}]
\]

When the composition is far from equilibrium, a positive $\alpha$ that has a value of $<1$ should be chosen, to avoid divergence. When the composition is close to equilibrium, $\alpha$ is set to have a value of 1. The readers may refer to the NASA CEA technical report8 for more-detailed discussions.

In the aforementioned equations, 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:4

\[
\frac{c_p^{\theta}(T)}{R} = \frac{a_1}{T^2} + \frac{a_2}{T} + a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4
\]

\[
\frac{H^{\theta}(T)}{RT} = -\frac{a_1}{T} + \frac{(a_3/2)}{T} + \frac{a_5}{3} T^2 + \frac{a_6 T^3}{4}
\]

\[
\frac{S^{\theta}(T)}{R} = -\frac{a_1}{2T} - \frac{a_2}{T} + a_3 \ln T + a_4 T + \frac{(a_5/2)}{T} + \frac{a_6}{3} T + \frac{a_7}{4} T^4 + a_9
\]

\[
\frac{\mu_j^{\theta\pi}(0)}{RT} = \frac{H_j^{\theta}(T)}{RT} - \frac{S_j^{\theta}(T)}{R}
\]

where $a_1, ..., a_9$ are constant values for a given species.

**Remark 1.** Regarding the assumptions made in the problem formulation, if the ideal gas law is not adequately accurate (e.g., under very high system pressures), the partial pressure should be replaced by fugacity when the chemical potential is calculated. The formation of condensed species (e.g., the formation of water under low steam/ethanol ratios) is not taken into consideration in the current work and a more-comprehensive algorithm is being developed to have this capability.

**Remark 2.** When the Gibbs minimization problem is solved using the Lagrange multiplier method, only the first-order (necessary) optimality conditions are used. At an optimal solution $n_j^{(0)}$ such that $\partial f/\partial n_j^{(0)} = 0$ ($j = 1, ..., s$), it can be verified that $\partial f/\partial n_j^{(0)} = RT(1 + r_j)(1/n_j^{(0)} - 1/n_j^{(0)}) > 0$ ($j = 1, ..., s$). Given this fact, the computed optimal solution is, indeed, a local minimum. Interested readers are directed to the open literature for global optimization techniques in the calculation of liquid–gas phase and chemical equilibria with possible multiple minima and maxima in the Gibbs free energy.39

In the solution procedure, the initial estimate of $n_j^{(0)}$ is set to be 0.1 and those of $n_i^{(0)}$ are set to be uniformly distributed. This initial guess corresponds to an average molecular weight of 10, which follows the NASA CEA algorithm.4 With these estimates, the optimization converges successfully within a small number of iterations in all cases studied in this work.

### 3. Chemical Equilibrium Calculation Using the Equilibrium Constant Method

Different from the Gibbs minimization method presented in the previous section, the Gibbs energy of the adsorbed species is not required if the amount ratios $r_j$ are available. However, a set of gaseous reactions should be specified before the concept of equilibrium constants can be applied. A reaction scheme can be determined using a set of independent reactions such that any gaseous reaction in this reactive system can be expressed by a linear sum of these basis reactions.40 The minimum number of independent chemical reactions in a reactive system is equal to the number of species minus the rank of the atomic matrix, provided that the former is greater than the latter.37 For example, if the rank of the atomic matrix is $e$, the number of independent reactions is $s - e$. In most cases, $e = e$. Occasionally, $e < e$ when all the row vectors in the atomic matrix are not independent.

Consider a small change in the Gibbs free energy in the gaseous phase under isothermal and isobaric conditions:

\[
\delta G^{\theta\pi} = \sum_{j=1}^{e} \mu_j^{\theta\pi} \delta n_j^{\pi} = \sum_{i=1}^{l} \mu_j^{\theta\pi} \sum_{j=1}^{e} v_j \delta z_j
\]

where $v_j$ is the stoichiometric coefficient of species $j$ and $z_j$ is the reaction extent in the $i$th reaction. Then, $\delta G^{\theta\pi} = 0$ for any $\delta z_j$ at chemical equilibrium implies

\[
\sum_{j=1}^{e} v_j \delta n_j^{\pi} = 0 \quad (i = 1, ..., s - e)
\]

A combination of eqs 3 and 21 yields

\[
\sum_{j=1}^{e} v_j \left[ \frac{\mu_j^{\theta\pi}}{RT} + \ln \left( \frac{P_j}{P_j^{\theta\pi}} \right) + \ln \left( \frac{n_i^{\theta\pi}}{n_i^{\pi}} \right) \right] = 0 \quad (i = 1, ..., s - e)
\]

or

\[
\prod_{j=1}^{e} \left[ \frac{P_j^{\theta\pi} n_i^{\pi}} {P_j n_i^{\theta\pi}} \right] = \exp \left[ -\sum_{j=1}^{e} v_j \frac{\mu_j^{\theta\pi}}{RT} \right] = K_p
\]

which is just the so-called equilibrium constant method.1

The Newton–Raphson iterative formula for eq 22 is

\[
\sum_{j=1}^{e} v_j \Delta \ln n_j^{\pi} - \sum_{j=1}^{e} v_j \Delta \ln n_j^{\theta\pi} = -\sum_{j=1}^{e} v_j \frac{\mu_j^{\theta\pi}}{RT} \quad (i = 1, ..., s - e)
\]

As a result, the chemical equilibrium can be solved based on eqs 14, 15, and 24. (Note that the effective number of equations in eq 14 is $e$ if $e < e$. Therefore, the number of variables is equal to the number of equations). The iterative variables are $\Delta n_j^{\theta\pi}$ ($j = 1, ..., s$) and $\Delta n_i^{\theta\pi}$. Although more iterative variables are involved in the equilibrium constant method, a solution procedure similar to that presented in section 2 can be followed.

### 4. A Case Study—Steam Reforming of Ethanol with Simultaneous CO$_2$ Adsorption

A reactive system that consists of steam and ethanol is studied in this section. The steam reforming of biomass-generated
The formation of byproducts such as C$_2$H$_4$, C$_3$H$_7$CHO, and CH$_4$.

Computer simulations demonstrate that both algorithms on the surface (i.e., only CO$_2$ adsorption is solved using the algorithms presented in sections because the number of species is nine (9) and the rank of the thermodynamic coefficients, the atomic matrix, and the reaction stoichiometric coefficient matrix are shown in Tables 1, 2, and 3, respectively. Note that the reaction scheme is required only in the equilibrium constant method. In Table 3, a set of six (6) independent reactions are representative of the entire system, because the number of species is nine (9) and the rank of the atomic matrix is three (3).

The conversion rate of ethanol to hydrogen with simultaneous CO$_2$ adsorption can be significantly improved if CO$_2$ is adsorbed.

Calculations in this section will provide a quantitative analysis for hydrogen production. 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.

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Table 1. Coefficients for Thermodynamic Properties

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<th>reaction number</th>
<th>CH$_4$</th>
<th>CO</th>
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<th>C$_2$H$_4$</th>
<th>CH$_3$CHO</th>
<th>C$_2$H$_5$OH</th>
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<tr>
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<td>1.373904396E+05</td>
<td>2.55485150E+03</td>
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<td>6.25179720E-02</td>
<td>7.88808160E-05</td>
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<td>(ads)/H$_2$</td>
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Table 2. Atomic Matrix

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<tbody>
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</table>

Table 3. Reaction Stoichiometric Matrix

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<th>reaction number</th>
<th>CH$_4$</th>
<th>CO</th>
<th>CO$_2$</th>
<th>C$_2$H$_4$</th>
<th>CH$_3$CHO</th>
<th>C$_2$H$_5$OH</th>
<th>H$_2$</th>
<th>H$_2$O</th>
<th>O$_2$</th>
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<td>0</td>
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<td>2</td>
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</tr>
</tbody>
</table>

*Used only in the equilibrium constant method.*

![Figure 2](image-url)
and, therefore, the size of the reactor (see Figure 2 for a plot generated based on eq 5 and the results from the equilibrium calculation). The parameter $\beta_{\text{CO}_2}$ under the operating conditions in this work, is estimated to be 22 bar$^{-1}$, based on the experimental data of promoted hydrotalcites$^{48}$. It is observed that, with no or little CO$_2$ adsorption, the conversion rate of C$_2$H$_5$OH to H$_2$ is only 15.4%, which is consistent with the NASA CEA code.$^4$ When CO$_2$ is adsorbed, the conversion can be significantly enhanced. For example, at CO$_2^{\text{(ads)}/\text{CO}_2^{\text{(g)}}} = 10^2$, the conversion rate of C$_2$H$_5$OH to H$_2$ is 38.9%, or enhanced by a factor of >2. (A list of the compositions under these two conditions is shown in Table 4.) However, further improvement in the conversion of C$_2$H$_5$OH to H$_2$ requires a significant increase in CO$_2^{\text{(ads)}/\text{CO}_2^{\text{(g)}}}$, or the amount of adsorbent. This can be explained by Figure 3, in which it is shown that, as CO$_2$ is adsorbed on the surface, further removal of CO$_2$ from the gas phase becomes more and more difficult.

The gas composition in the product mixture under different CO$_2^{\text{(ads)}/\text{CO}_2^{\text{(g)}}}$ ratios is shown in Figure 4. Under the operating conditions of interest, none of C$_2$H$_4$, CH$_3$CHO, C$_2$H$_5$OH, or O$_2$ has a differentiable fraction in the product mixture. As CO$_2^{\text{(ads)}/\text{CO}_2^{\text{(g)}}}$ increases, the fraction of CO$_2^{\text{(g)}}$ rapidly decreases to a minimal level (at CO$_2^{\text{(ads)}/\text{CO}_2^{\text{(g)}}} = 10^{1-2}$), beyond which a significant reduction in the CO$_2^{\text{(g)}}$ concentration is not obvious. The low partial pressure of CO$_2$ in the gas phase makes effective adsorption difficult. In fact, at CO$_2^{\text{(ads)}/\text{CO}_2^{\text{(g)}}} > 10^3$, the primary carrier of carbon in the gaseous phase is CH$_4$, instead of CO or CO$_2$. When CO$_2$ is gradually adsorbed on the surface, the forward reaction in the reversible WGS reaction CO + H$_2$O $\rightarrow$ CO$_2$ + H$_2$ is favored. As a result, some of the CH$_4$ is converted to CO through the methane reforming reaction CH$_4$ + H$_2$O $\rightarrow$ CO + 3H$_2$. In this sense, the entire system acts as a buffer solution. Because of the coupling of multiple equilibrium phenomena, a complete removal of CO$_2$ is very difficult.

An interesting phenomenon is also observed in this reactive system regarding the specific volume of the product mixture. Note that the calculation is based on a fixed amount of mass (i.e., 1 kg) of the reactant mixture, and therefore, the volume of the product is proportional to the total amount $n^{(g)}$. As shown in Figure 5, the volume of the gas mixture expands by a factor of ~1.37 at equilibrium if there is no CO$_2$ adsorption. According to Le Chatelier’s principle, a low system pressure is preferred
for a high conversion of C2H5OH to H2 at chemical equilibrium, which is consistent with experimental observations.47 When CO2 is gradually adsorbed on the surface, the volume of the product shrinks. After reaching a minimum at a CO2(ads)/CO2(g) ratio of ∼14, the volume of the product increases, even as CO2 is adsorbed. This is because the effect of volume expansion due to methane reforming CH4 + H2O → CO + 3H2 is greater than the shrinking effect caused by CO2 adsorption.

Figure 6 shows the relationship between the conversion rate of C2H5OH to H2, as a function of the CO2 removal ratio, which is defined as the absolute amount of CO2 adsorbed on the surface divided by its theoretical upper limit. It is observed that the enhancement in the H2 production is not significant when the CO2 removal ratio is <40% (corresponding to a CO2(ads)/CO2(g) of ∼13). This is because the effect of volume expansion due to methane reforming CH4 + H2O = CO + 3H2 is greater than the shrinking effect caused by CO2 adsorption.

Figure 7 shows the relationship between the conversion rate of C2H5OH to H2, as a function of the number of equilibrium stages and CO2(ads)/CO2(g) ratios (molar ratio of feed = 1:3, P = 5 bar, and T = 500 °C).

Figure 8 shows the relationship between the conversion rate of C2H5OH to H2, as a function of the CO2 removal ratio, which is defined as the absolute amount of CO2 adsorbed on the surface divided by its theoretical upper limit. It is observed that the enhancement in the H2 production is not significant when the CO2 removal ratio is <40% (corresponding to a CO2(ads)/CO2(g) of ∼13). This is because the methane reforming reaction and the WGS reaction shift only slightly to the right, which is reflected by the fact that the total amount decreases significantly (see Figure 5) and that the fraction of CH4 and H2O might even increase (see the peaks in CH4 and H2O fractions in Figure 4). As the CO2 removal ratio exceeds 40%, the H2 production increases linearly. (A similar phenomenon is observed in H2 purity.) In such a case, there is little CO2 or CO in the gas phase (see Figure 4), and, therefore, the overall reaction in the gas phase is CH4 + 2H2O = CO2 + 4H2. Because the CO2 generation rate is approximately balanced by its adsorption rate, 4 mol of H2 will be generated when 1 mol of CO2 is removed from the gas phase by adsorption. If the result is interpreted in terms of the H2 production and CO2 removal ratio, the slope is 4/3, because the ideal reaction is C2H5OH + 3H2O = 6H2 + 2CO2.

The reactive system in the aforementioned analysis is based on a setting similar to a single-stage reactor, in which the gas phase has a uniform composition and is in equilibrium with the adsorbent. If a reforming reactor is divided into several zones (or stages) and a local chemical equilibrium is maintained in each zone, the overall hydrogen yield at the end of the reactor could be higher. This is because CO2, after being adsorbed on the surface, does not have any effect on the reactive system downstream, which is true in a real reforming reactor. In the next case study, the CO2 is adsorbed using multiple stages in series. This is realized by setting the gas composition at the outlet of one stage to be the inlet composition at the next stage. In addition, the gaseous reactive system at each stage is in local equilibrium with the adsorbent. Four cases are studied in which the stage CO2(ads)/CO2(g) ratios are different. However, the product of CO2(ads)/CO2(g) and the number of stages is fixed, which makes the total adsorbent area approximately the same. A smaller CO2(ads)/CO2(g) at each equilibrium stage corresponds to a shorter time scale for reaction and adsorption equilibrium. In each case, the cumulative adsorbent surface area and the H2 yield
are solved as functions of the number of stages times \( \text{CO}_2 \times 10^5 \text{ J/mol} \). In Figure 10, the heat demand and supply are both negative heat demand (i.e., a heat neutral point occurs at a CO2 removal ratio of 40\%).

Based on this finding, and the fact that the overall gas phase reaction is endothermic at high hydrogen yields, an integrated process design could encompass the heat exchange between the endothermic reforming and exothermic combustion of remaining CO and CH4 in the off-gas downstream of a H2 separation unit. (See Figure 9 for a schematic of this process.) C2H5OH and H2O are preheated by the flue gas before entering the reformer, where H2 is generated and a major portion of CO2 is adsorbed. The product mixture passes through a hydrogen separation unit (e.g., a pressure swing adsorption unit (PSA)), where H2 is separated from unconverted CH4 and H2O, as well as some CO and CO2 (in trace amounts). The CH4 from the H2 separation unit is sent to a combustor, where heat is supplied to the reformer and the feed streams (C2H5OH and H2O) through heat exchange (HE) units. (Interested readers might find more discussions on autotermal processes in the open literature.24,29,49–51) If the heat released from the CO2 adsorption is not taken into account (because it will be released in subsequent CO2 desorption), a plot of the heat demand in the reformer and the heat supply in the combustor versus the CO2 removal ratio is given in Figure 10. Under the current operating conditions, the gaseous reaction could be exothermic (i.e., negative heat demand) at low CO2 removal ratios, where the H2 yields are also low (see Figure 6). However, as the H2 yield increases, the reforming reaction becomes endothermic and the waste heat provided by the combustion of unreacted CH4 and CO decreases. A heat neutral point occurs at a CO2 removal ratio of \(~90\%) in the aforementioned calculation, both reactions occur at 500 \( ^\circ \text{C} \). Therefore, it does not account for preheating of the feed streams to 500 \( ^\circ \text{C} \) or cooling of the flue gases to room temperature or the energy required for the H2 separation unit. Moreover, a heat-transfer efficiency of 100\% between these two processes is assumed. This rough calculation indicates that an 86.3\% theoretical maximum overall conversion of \( \text{C}_2\text{H}_5\text{OH} \) to \( \text{H}_2 \) (the corresponding \( \text{H}_2 \) purity in the product mixture out of the reformer is 89.4\% on a wet basis or 96.2\% on a dry basis; see Table 5 for the composition of other components) can be achieved with little or no external heat supply in the reforming process if combined with simultaneous CO2 adsorption. The reactions in the reformer and the combustor, as well as the overall reaction of the entire process \( (T = 500 \text{ } ^\circ \text{C}) \), are summarized as shown in Chart 1.

Note that the gaseous CO and CO2, in trace amounts, are not listed in Chart 1. The net energy demand of the combined reforming and combustion process is zero at 500 \( ^\circ \text{C} \) if the heat released from CO2 adsorption is not taken into account (\( \Delta H = -\Delta H = 1.64 \times 10^5 \text{ J/mol} \)). In Figure 10, the heat demand and supply are both 1.64 \( \times 10^5 \text{ J} \), because they are based on 1 kg of the ethanol and steam mixture, which contains 10 mol of ethanol and 30 mol of steam). The overall H2 yield could be less if the heat-transfer efficiency and the operating costs are taken into account in this integrated process. A more-detailed engineering calculation, which includes regeneration of CO2, will be presented in a separate work. Note that, although the equilibrium calculation can provide a mean-field analysis and predict the overall trend of a reforming process, it is not adequate to mimic the real operation. Because of the continuous nature of the adsorption enhanced reforming process, a full description requires kinetic models (including the kinetics of reactions and adsorption/desorption as well). Interested readers are directed to the open literature50,52 for research efforts in this direction.

**5. Concluding Remarks**

Two approaches for the calculation of chemical equilibrium in a gaseous reactive system combined with simultaneous species adsorption are developed in this work following algorithms similar to the NASA CEA code. Both algorithms are very effective in solving gaseous reactive systems with simultaneous species adsorption. Whereas the equilibrium constant method requires one to specify a set of independent reactions and solve more nonlinear equations, these reactions are useful in the analysis of various coupled equilibrium phenomena in the entire reactive system.

The algorithms are applied to an enhanced ethanol reforming system where CO2 is partially or fully removed by adsorption. It is shown that, at \( T = 500 \text{ } ^\circ \text{C} \) and \( P = 5 \text{ bar} \), the CO2 removal ratio should exceed 40\% to achieve a decent enhancement in hydrogen production and purity. Whereas the hydrogen production increases linearly with the CO2 removal ratio if the latter is >40\%, the amount of adsorbent (and, therefore, the reactor size required for CO2 increases exponentially. A tradeoff between the H2 production and the reactor size can be achieved by burning CH4 in the offgas from the H2 separation unit to provide heat for the endothermic reforming process. It is shown that a theoretical maximum overall conversion of \( \text{C}_2\text{H}_5\text{OH} \) to H2 of \(~86.3\%\) can be achieved with little or no external heat supply in the reforming process if combined with simultaneous CO2 adsorption (the corresponding H2 purity in the product mixture out of the reformer is 89.4\% on a wet basis or 96.2\% on a dry basis). Although the adsorption of a single species is discussed in the case study, the algorithms can be potentially applied to multiple species adsorption in a similar manner.

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**Literature Cited**
