Thermodynamic Analysis of Fuel Processing

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THERMODYNAMIC ANALYSIS OF FUEL PROCESSING

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Abstract

In most projections of future fuel and power infrastructures, fuel processing plays an important role in providing a pathway for the transition from fossil fuels to alternative energy sources. One example of recent interest is the use of onboard or integrated processing to produce hydrogen from liquid hydrocarbon fuels for use in a fuel cell. However, the quantitative data and analytical techniques needed to assess the efficiency and performance of fuel processors are sparse and unorganized, causing difficulties in the development of this technology.

In this paper, a generalized analysis of fuel processors for use in integrated fuel processor-plant systems is presented. The thermodynamic efficiency and energy expenditure of fuel processing are defined and related to other process parameters, and the overall efficiency of the processor-plant system is derived for several cases. The analytical method described can be employed for comparison of different reformer designs using experimental data on component performance, or used in conjunction with a numerical or analytical model to predict the performance characteristics of a hypothetical reformer.

Chemical equilibrium calculations are used to provide a comparison of the limiting behaviors of different techniques for hydrogen production from hydrocarbon fuels, including pyrolysis, steam reforming, partial oxidation (autothermal reforming), and partial oxidation-water shift, as well as to characterize their performance in integrated reformer-plant systems.

Introduction

Fuel processing is a vital part of most practical energy pathways. Traditionally, fuel processing is performed in large, centralized plants (e.g. oil refineries), producing a high-grade fuel that may be used in buildings or vehicles without further modification. However, in the development of cleaner energy technologies, it has been found that cleaner-burning fuels, such as hydrogen or natural gas, often lack the high volumetric energy density that is characteristic of the liquid fuels commonly in use today, as it allows for easier transportation and refueling. Hence, in recent years there has been an increasing focus on local or onboard fuel processing, allowing the production of clean fuels such as hydrogen or alcohols from traditional fuels such as gasoline or coal liquids. The "reforming" of fuels is also an essential part of proposed hydrogen-based energy infrastructures; in such systems, where hydrogen is used as a universal energy carrier, the utilization of other fuels such as ethanol or biomass will require reforming of these fuels to hydrogen-rich gases at some point in the fuel cycle.

These developments represent a new direction for fuel processing technology, which has only recently begun to be studied carefully. The new constraints that are placed on the fuel processors are similar to those applied to engines; these include a balance between efficiency, size and response time, use of readily available fuels, and minimal environmental impact. In the case of onboard reforming, the determination of vehicle performance must also take into account any inefficiencies associated with the processor. All these factors add complexity to the analysis of the fuel cycle, often making it difficult to determine whether a new "environmental" fuel technology is in fact preferable to existing alternatives. The problem is further complicated by the lack of quantitative experimental or analytical results in this area; thus, new designs must be developed almost exclusively by experiment, and it can be difficult even to compare existing experimental data on a common basis.

This study was inspired by the authors' experiences with these difficulties and others during the ongoing development of a compact reformer, based on arc plasma technology, to produce hydrogen gas from hydrocarbons (O'Brien, 1996). The questions that it is intended to address are the following:

1) How can the "energy efficiency" of a fuel processor best be characterized?

2) How can different reformer technologies (e.g. catalytic partial oxidation versus arc plasma-driven partial oxidation) be compared quantitatively as parts of integrated reformer-plant systems?

3) If, as in the plasma reformer case, energy for reforming may be provided by the plant output work, when is it advantageous to do so, rather than to use some of the chemical energy of the input fuel to drive the reformer?

This paper addresses these issues by proposing a thermodynamic framework for analysis of fuel processors as integral parts of fuel-to-work powertrains. By defining characteristic parameters such as process efficiency and energy requirements in a general and consistent way, a basis can be constructed to compare different fuel processor designs, both based on experimental data and numerical simulations, and to determine how different methods of integrating the power requirements of the fuel processor with the plant can affect overall fuel efficiency.

It is helpful to note at the outset both the potential and the limitations of this method of analysis. Carefully constructed definitions of appropriate thermodynamic parameters can greatly simplify the comparison of different reforming reactions or technologies, since they allow quick and reliable determination of limiting system behaviors. However, several important issues cannot be addressed by thermodynamic arguments; these include the required size and weight of a fuel processor for a given desired conversion, response times, costs, and environmental impacts.

Background

In recent months, growing interest in onboard fuel processing for fuel cells in the transportation sector has found its way into the popular literature (*The Economist*, Jan. 1997). Fuel processing for hydrogen-oxygen fuel cells is also being developed for utility-scale plants (Hirschenhofer, 1996). In addition to the numerous fuel cell applications, similar fuel processing techniques are advocated by hydrogen energy proponents as a means of utilizing existing fossil energy resources efficiently within a hydrogen-based energy economy, presumably while renewable hydrogen resources and technologies are being developed (Buchner, 1995).

Various investigations and summaries of the key hydrogen and synthesis gas production reactions are available in the older gas engineering literature (Eastman, 1956; Vorum, 1965; Cox, 1977); however, most of these focus on utility or commercial scale applications. The majority of studies that have been done in the area of fuel processing in recent years focus on "upgrading" of fuels like natural gas to alcohols, aldehydes and liquid hydrocarbons (Mackie, 1991), the demands for thermal efficiency and power density have not been strong in these applications. Hence, very few experimental results or theoretical investigations of integrated reformer-plant systems or reforming of hydrocarbons to light fuels are available (see for example Mitchell, 1994; Geyer, 1996). For these reasons, when the authors began work on reforming of hydrocarbon fuels to hydrogen, the lack of appropriate tools for analysis of and comparison of existing and arriving data in this growing area of research quickly became evident, leading to the current work.

Analysis of Fuel Reforming

The main question to answer in a thermodynamic analysis of fuel reforming is the following: given a plant that utilizes a specific fuel with known efficiency, what is the change in efficiency that is incurred by operating the plant in conjunction with a fuel processor that produces the desired fuel from some other feedstock? If this is known, then the combined fuel processor-plant system can be viewed thermodynamically as an equivalent plant, running on the fuel processor's feedstock, with the appropriately modified efficiency. Thus, the problem is to find an efficiency factor ε, which can be determined from the fuel processor characteristics, such that

$$\eta_{eff} = \varepsilon \eta \tag{1}$$

where η is the thermodynamic efficiency of the plant alone running on its input fuel, and η_{eff} is the effective efficiency of the equivalent plant (including reformer), running on the reformer's input fuel. ε will in general be a function of the input fuel composition, the size and type of energy inputs, and the chemical and physical processes that occur in the reformer.

Out of the many possible methods to calculate this efficiency factor for a given reformer and plant, we would like to find one that has several characteristics: it should be applicable to a wide range of different systems, it should be based on parameters that are easily measured or calculated, and it should include the thermodynamically relevant properties of the reformer, such as work requirements and overall energy efficiency.
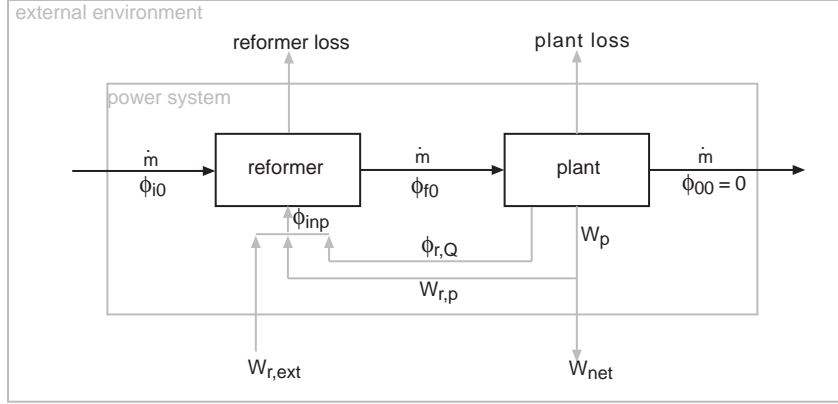
Figure 1. Mass (black) and energy (grey) flows in a generalized reformer-plant system.

Figure 1 is a schematic diagram of a reformer-plant system, including the relevant energy and mass interactions between the reformer, the plant, and the external environment. Black arrows represent mass flows, which carry chemical and thermal energy, while grey arrows represent energy transfers in the form of heat or work. The heat and work "feedbacks" from the plant to the reformer merit some explanation. In an integrated reformer-plant system, some or all of the energy requirements of the reformer may be met using heat and work available from the plant output. For example, waste heat from the plant may be used to preheat reactants for the reformer. The possible work interactions are less evident: in the case of fuel cells, the electrical work produced may be used to provide resistance or plasma heating, or to drive pumps or compressors; the mechanical work of a reciprocating engine might be used to drive a generator or to pressurize reactant flows.

The important values to quantify are the inputs to and outputs of the reformer. Given these mass and energy flows, a set of parameters may be defined that describe the performance of the fuel processor sufficiently to determine its effects on overall system efficiency, while meeting the criteria listed above. These parameters should be based only on the initial and final states of the reforming process, and any energy and mass interactions that occur, so that they may be defined without dependence on any particular reformer, and will not involve any assumptions about the nature of the reforming process.

Adopting a consistent definition of the energy content of the various flows (chemical, thermal, work) allows the appropriate parameters to emerge naturally. In general, the amount of useful chemical and thermal energy stored in a given mixture as a function of its composition and thermodynamic state can be defined as the *availability* of the mixture, with respect to a reference state having the same mass and atomic composition. For the case of a mixture consisting of fuel, oxidizer and an unreactive diluent, a common practice is to calculate the availability per unit mass of fuel with respect to products of complete combustion in thermal and pressure equilibrium with the environment. For a given state s of the mixture, with a composition specified by mass fractions $Y_{n,s}$ of all species n (which are assumed to behave as ideal gases or solutions), temperature T_s, and pressure p_0, the fuel availability is given approximately by

$$\phi_{s0} \approx \sum_n \frac{Y_{n,0}}{Y_{f,i}}\left(h_n(T_0,p_0) - T_0 s_n(T_0,p_0)\right) - \sum_n \frac{Y_{n,s}}{Y_{f,i}}\left(h_n(T_s,p_0) - T_0 s_n(T_s,p_0)\right) \qquad (2)$$

where h_n and s_n are the mass specific enthalpy and entropy of species n, the subscript 0 indicates properties of the reference state, subscript i indicates initial state properties, and $Y_{f,i}$ is the initial mass fraction of fuel. The approximate equality is due to fact that entropy of mixing terms, which are generally small in comparison to the s_n terms, have been neglected. If the state s is identical to the initial state i (e.g. fuel, oxidizer and diluent at T_0 and p_0), ϕ_{s0} reduces to the Gibbs free energy of reaction per unit fuel mass $\Delta G^0_R(T_o, p_o)$. The availability of heat flows may be determined by the above formula, using identical compositions for both states; it is easily seen that high-temperature heat has greater availability than low-temperature heat. The availability of work in the form of mechanical or electrical inputs is simply equal to its magnitude.

It should be noted here that requirements imposed by the plant on its input fuel composition may alter the effective availability of the input and reformed mixtures (for example, a fuel cell that is incapable of oxidizing CO cannot utilize fully the chemical energy of a mixture containing CO). However, these effects depend only on the *plant*, and hence place no restrictions of the generality of this definition with respect to different *reformers*. In determining overall efficiencies for fuel processor-plant systems, only the availability that can be utilized by the plant in question should be considered.

Another common definition of the chemical energy storage is the heating value of the mixture (in this case, the lower heating value (LHV) would commonly be used). There are two main differences between the LHV and the availability as defined here. The first is that the availability accounts for the sensible enthalpy of the mixture (i.e. $T_s \neq T_0$), whereas the LHV does not. This is generally a very small difference, and may be neglected. The second difference is due to the entropy term in the availability. For fuels whose combustion does not involve large changes in entropy, as is the case for most hydrocarbons, the lower heating value and the availability (defined with respect to the same reference state) differ at most by about one percent, so the LHV may be used as a measure of energy storage without significant loss of accuracy. However, for fuels such as H_2 and CO, often the desired output fuels of reformers, this difference can be five to ten percent (with the LHV in general being greater than ϕ_{i0}), and must be considered for a accurate analysis. Table 1 lists the LHV and the availability for complete combustion of several common fuels.

Fuel		LHV [MJ/kg]	ϕ_{i0} [MJ/kg]	Percent difference
Methane	[CH$_4$]	50.16	50.08	0.174
Propane	[C$_3$H$_8$]	46.43	47.12	-1.48
Octane	[C$_8$H$_{18}$]	44.51	45.81	-2.92
Methanol	[CH$_3$OH]	19.94	21.41	-7.34
Ethanol	[C$_2$H$_5$OH]	26.84	28.26	-5.27
Hydrogen	[H$_2$]	121	114	5.50
Carbon Monoxide [CO]		10.11	9.18	9.16

Table 1. Lower heating value versus availability for combustion of some common fuels (data from Lide, 1993)

Taking the availability as our energy measure, one key parameter for fuel processor performance is immediately suggested: the ratio of the availability of the fuel processor's output to that of its input. This *availability ratio*, r, is given by

$$r \equiv \frac{\phi_{f0}}{\phi_{i0}} \tag{3}$$

where ϕ_{f0} is the availability of the reformed state (denoted *r*) of the mixture with respect to the reference state *0*, and ϕ_{i0} is the initial state availability. For example, stoichiometric partial oxidation of methane (one kg oxygen per kg methane) produces 0.25 kilograms hydrogen and 1.75 kilograms carbon monoxide per kilogram of methane, leading to *r* = 0.89.

In addition to the chemical energy input to the reformer, other forms of availability input (e.g. mechanical or electrical) must be quantified. The most general way to do this is to determine the total availability transfer from the external environment (including the plant) to the reformer resulting from the sum of all non-chemical availability inputs, regardless of their sources, per unit mass of input fuel (denoted ϕ_{inp} in Figure 1). Energy losses during reforming are *not* included in this sum; they will be found in the difference between ϕ_{i0} and ϕ_{f0}. This input may be normalized by the input fuel availability, leading to a non-chemical energy input parameter defined as

$$w \equiv \frac{\phi_{inp}}{\phi_{i0}} = \frac{\sum \phi_T - \sum W}{\phi_{i0}} \tag{4}$$

where W and ϕ_T represent all the work and thermal availability transfers from the plant and environment to the reformer during reforming of a unit mass of fuel. Since the availability of waste heat is generally low, w will in most cases be dominated by the work term.

The specification of r and w (which implies knowledge of the compositions and temperatures of the initial, reformed and reference states) is sufficient to characterize a given reformer. Although r will not be a single-valued function of w in general, the operation of any reformer must correspond to a particular pair of values of r and w; a complete description of the reformer's operating conditions can thus be translated into a region in the *r-w* plane. Figure 2 indicates the relationships between the energies and states of the reforming process used to derive these parameters.

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The availability ratio can have very different ranges for different systems, and hence is not the best parameter to use for comparisons between different fuel processors. Also, as indicated in Figure 2, r can in principle have values greater than unity. A true energy efficiency for the reformer, η_r, can be defined as

$$\eta_r = \frac{\phi_{i0}}{\phi_{f0} + \phi_{inp}} = \frac{r}{1+w} \qquad (5)$$

While the range of possible values of r depends on w, η_r always lies between zero and one. Any decrease of η_r below one represents a loss in the reforming process, which may be due to inefficiencies in energy transfer (i.e. not all of w reaches the reacting mixture), potentially recoverable heat losses, or reaction irreversibilities. As can be seen from the above relation, r and η_r are identical only when $w = 0$.

Figure 2. Availability diagram of the states of the reforming process. State m is hypothetical.

While w and $r(w)$ or $\eta_r(w)$ are sufficient to specify the performance of the fuel processor, additional information is needed to characterize the performance of the combined fuel processor-plant system. To find an effective efficiency η_{eff} (input chemical energy to output work) for the reformer-plant system, we need to know the fuel-to-work efficiency η of the plant and the portion of w that is supplied from the plant output work. We can characterize this work recirculation by defining a parameter, β, as the fraction of the total non-chemical availability input to the reformer that is taken from the plant output work:

$$\beta \equiv \frac{W_{r,p}}{\phi_{inp}} \qquad (6)$$

The relevant range of β is from zero (no output power from the plant is used by the reformer, e.g. the energy for fuel processing is taken from plant waste heat) to one (all the power necessary to run the reformer is taken form the plant output). Referring to Figure 1, we may now express the effective efficiency of the reformer-plant system in terms of the parameters defined above:

$$\eta_{eff} \equiv \frac{W_{out}}{\phi_{i0}} = r\eta - \beta w = \eta\eta_r + w(\eta\eta_r - \beta) \qquad (7)$$

Two points may be noted based on the above expressions; first, the condition $\beta w < r\eta$ must be met for the effective efficiency to be positive, that is, one cannot recirculate more power than the plant produces, and provided that the first condition is satisfied, any value of β less than $\eta\eta_r$ will lead to an increase in overall system efficiency, while $\beta > \eta\eta_r$ will decrease overall efficiency. If we consider the limiting cases of all fuel processing energy being taken from plant output work ($\beta = 1$) and no fuel processing energy taken from plant output work ($\beta = 0$), we find the full range of possible effective efficiencies of the combined system, and hence the range of values of ε associated with the fuel processor:

$$\varepsilon = r - \frac{\beta w}{\eta}$$

$$r \geq \varepsilon(w, \beta, \eta) \geq r - \frac{w}{\eta} \qquad (8)$$

This set of dimensionless parameters (w, r or η_r, ε or η_{eff}) can be used to quantitatively compare reformers of widely differing designs and characteristics for use with a given plant. If for a particular reformer or reforming process the compositions and temperatures of the initial, reformed and reference (e.g. complete combustion) states are known, along with the total input of energy from the plant and environment to the reformer per unit mass of fuel, the parameters r and w (or η_r and w) as defined above describe the thermodynamic efficiency of the reformer and determine the range of efficiencies obtainable for the reformer-plant system, regardless of the method used to accomplish the reforming reactions. However, these are only definitions; suitable means of determining r, w, and β, and hence ε and η_{eff}, for a particular system must be determined essentially on a case-by-case basis. The following sections will discuss some useful methods for calculating these parameters in idealized or well-characterized situations.

Methods for Determination of Characteristic Reforming Parameters

According to the preceding discussion, a given reformer can be characterized and compared easily to other systems if the values of *w* and *r(w)* can be determined over its range of operating conditions, defining a region in the *w-r* plane for the fuel processor, and a corresponding region in the *w-ε* plane that describes the possible operating conditions of the combined processor-plant system. In order to determine these values, specific knowledge of the reformer and appropriate assumptions must be applied to the problem.

The most unambiguous method of determination of *r* and *w* is direct measurement from an actual reformer. This requires measurement of all work and heat inputs to the system, as well as input and output stream compositions, flow rates and temperatures. Given this data, the efficiency and performance of the reformer for various different plants can be calculated as above and compared clearly to other reformer types, since the relevant parameters have been chosen so as to have no dependence on the nature of the reformer or reforming process.

Another main goal of fuel processor analysis is to be able to calculate directly the performance characteristics of a hypothetical system. In order to do this, a model of the reformer that can predict the output state as a function of the input state and *w* is needed. Such models might range from simple chemical equilibrium models, appropriate for comparing widely differing processes, to complex and computationally intensive chemical kinetic and dynamical models for simulating the effects of minor design changes on the performance of a specific reformer system. Regardless of the level of detail that is desired, various analytical and computational tools are available, making such analysis an effective alternative or precursor to experimental studies, especially where a wide range of situations need to be investigated. Since the reformer and combined system efficiencies are based on fundamental thermodynamic properties of the system, most computational models of reformers will produce results that are sufficient to calculate these quantities for any given plant.

Equilibrium Analysis of Common Reforming Reactions

In many practical cases, the equilibrium state of a reacting mixture is the desired end product of a reforming process, and such reformers are designed so as to drive the chemical reactions involved to equilibrium, preferably in a short time, with minimal energy expenditures (some examples of common fuel processing reactions that fit this description are partial oxidation, steam reforming, and combustion). In this situation, the desired output state of the reformer is uniquely determined if the quantities shown in Figure 1 are specified (i.e. the input state of the reacting mixture and energy interactions with the environment or other systems during reforming). It is therefore possible to calculate easily the characteristic parameters for an *ideal* reformer, that is, one that drives the reacting mixture completely to the desired equilibrium state with no unnecessary energy expenditures. This in turn provides a tool that can be used to compare not different reformers (since all ideal reformers are functionally equivalent by definition) but different reforming *processes*. The resulting reformer and system efficiencies will represent the best achievable values for any reformer design based on driving reactions to equilibrium (catalytic, thermal, etc.), and will depend only on the input state and *w*.

In the following section, this analysis will be applied to several reforming processes commonly used for the production of hydrogen gas from hydrocarbon fuels. The main assumptions implicit in the analysis are: 1) that the reformer is ideal and drives the system from its input state to the thermodynamic equilibrium state that is consistent with the energy addition specified by *w*; and 2) that the plant utilizes exclusively hydrogen as fuel, so that no other species in the output mixture contribute to the useful availability. A particular situation to which these assumptions apply is the use of a reformer to supply a low-temperature fuel cell with hydrogen from a hydrocarbon fuel. (The consideration of poisoning of the plant by reformed fuel components, e.g. loss of effectiveness of fuel cell membranes with exposure to carbon monoxide, will not be included here, as it varies widely with different plant types.)

The four processes that will be considered here are pyrolysis, partial oxidation, steam reforming, and partial oxidation/water shift. All four have some combination of hydrocarbons, oxygen or air, and water as their reactants. For simplicity, gaseous methane and liquid ethanol will be used as a representative hydrocarbon fuels, and air is used as the oxidizer in all cases. The assumptions used in the calculation of the equilibrium state are that, once vaporized, all species behave as ideal gases, and that the energy input *w* can be modeled as a perfectly efficient enthalpy addition. Given a specified input state composition and temperature, for each energy input *w*, an intermediate state is calculated by increasing the enthalpy of the input state by $w\phi_{i0}$ per unit fuel mass. (The input and intermediate

states are equivalent to states *i* and *m* in Figure 2.) The equilibrium state for an adiabatic process (from state *m* to state *f* in Figure 2) is then determined. In the calculations for these examples, the method of element potentials, as implemented in the program STANJAN, was used, along with thermodynamic data from the CHEMKIN thermodynamic database (Reynolds, 1986; Kee, 1989). Hence, for each *w*, the compositions and temperatures of input and equilibrium (reformed) states are determined. The availability ratio *r(w)* and other parameters can then be calculated as above, assuming that *only* the availability of the hydrogen in the output mixture is useful to the plant. All availabilities are calculated with respect to the state of complete stoichiometric combustion of the fuel to water and carbon dioxide (see Table 1 for representative values). The results of these calculations for the four different reactions are presented below.

Pyrolysis

Pyrolysis is the simplest process for hydrogen production from hydrocarbon fuels, used widely in the steel industry; it consists simply of heating the input fuel until thermal decomposition occurs. For saturated hydrocarbons, the most straightforward reactions involved are of the following stoichiometry (unsaturated and oxygenated hydrocarbons have analogous reactions):

$$C_nH_{2n+2} \rightarrow nC + (n+1)H_2$$

The actual product composition is much more complicated than this, usually including various unsaturated hydrocarbons and soot. These reactions are highly endothermic (i.e. *w* must be large in order to produce significant yields of hydrogen), resulting in extremely long reaction timescales at normal process temperatures; typical timescales for pyrolysis of butane range from tens to hundreds of seconds at 800 - 1000 K (Nelson, 1940). While pyrolysis has the advantage of relative simplicity and is adaptable to a wide range of input fuels, it requires very high energy densities and produces large amounts of soot and other heavy hydrocarbon byproducts which, although they are often valuable in themselves, create problems of separation in integrated power systems.

Figure 3. Equilibrium species yields and temperature vs. energy input for pyrolysis of methane.
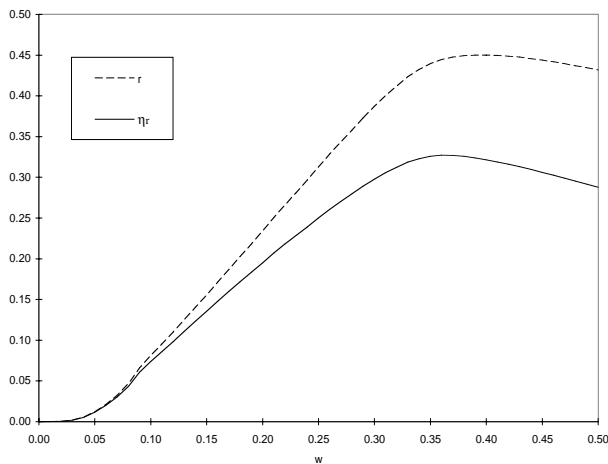
Figure 4. Availability ratio and reforming efficiency vs. energy input for pyrolysis of methane.

Figure 5. Efficiency factor vs. energy input for pyrolysis of methane with a 50 percent efficient plant.

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Pyrolysis of methane to hydrogen (and other byproducts) provides a simple application of this equilibrium-based analysis. Figure 3 shows the results of adiabatic, constant pressure equilibrium calculations as a function of w for the output mixture composition and temperature, and the variation of r and η_r with w is given in Figure 4. The range $0 < w < 0.5$ was chosen for the fuel processor's energy input, which is a reasonable set of values for an onboard or local fuel processor without a large external energy source. In a real process, the formation of heavy hydrocarbon byproducts would be kinetically controlled, so the calculated output levels of acetylene and ethene are probably not realistic; however, these are unimportant for this analysis as they are not considered in the reformed state availability and do not greatly affect the hydrogen yield. As can be seen from the figure, both r and η_r are less than 0.5 over the reasonable range of w values. Hence, from an efficiency standpoint, this process would not be a good choice for an integrated reformer, as it would lead to very low total system efficiencies, even if *none* of the reformer input work was supplied from the plant output. To quantify this conclusion, the range of ε values for a pyrolytic reformer operating with a 50 percent efficient plant is shown in Figure 5 for several different values of β.

Steam Reforming

Steam reforming of hydrocarbons is a very common industrial process. Many reactions are involved due to the presence of oxygen in the system, but the overall chemical transformations can be described in general by

$$CH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)H_2$$
$$C_nH_{2n+2} + 2nH_2O \rightarrow nCO_2 + (3n+1)H_2$$
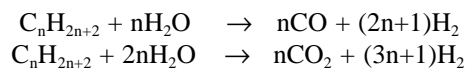
These reactions are also highly endothermic, so steam reforming is usually performed with the aid of a catalyst and at high temperatures. The introduction of the catalyst creates problems of cost, catalyst poisoning (for example, by sulfur in the feedstock), and heat transfer to the catalyst material (Cox, 1977). Catalysts are also in general very fuel-specific, thus limiting the applicability of reformers based on catalyzed reactions. Despite these difficulties, steam reforming has the advantages of inexpensive feed components and the potential for high hydrogen yields (hydrogen is extracted not only from the input fuel, but from the water as well).

Even though steam reforming is in general a catalyzed reaction, it is valid to use this equilibrium analysis to compare it to the other methods; the addition of a catalyst cannot change the thermodynamic equilibrium of the system, merely the path towards equilibrium, and the desired final mixture composition for most catalytic reactors is the equilibrium state. We again use methane as the fuel, with the same reference state and initial availability. The additional variable introduced by the presence of water in the input mixture is the *steam-to-carbon ratio s*. In terms of s, the reaction can be described as

$$CH_4 + sH_2O \longrightarrow 4H_2 + CO_2 + (s-2)H_2O$$
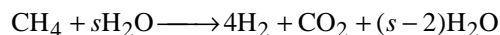
In these calculations, a steam-to-carbon ratio of ten to one was used as a representative value (higher amounts of water lead to greater hydrogen production, and the general characterist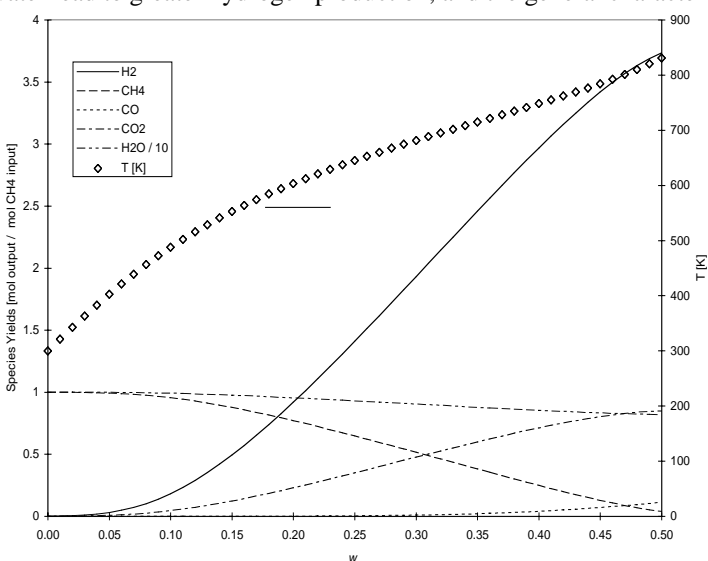ics of the reaction do not change significantly as the steam-to-carbon ratio is varied in a range near this value). The results of the adiabatic equilibrium calculations for output composition and temperature, r and η_r are given in Figures 6 and 7. As can be seen from these plots, steam reforming is a very efficient reaction, with availability ratios of over 90 percent at high enough w. However, it should be noted that the required values of w for good efficiency are high, so that if the source of w is the plant output work, the overall system efficiency remains low, as seen in Figure 8 for $\beta = 1$. Hence, although steam reforming is significantly more efficient than pyrolysis, it is best applied to a system in which the required reformer input energy could be provided by a source such as waste heat from the plant.
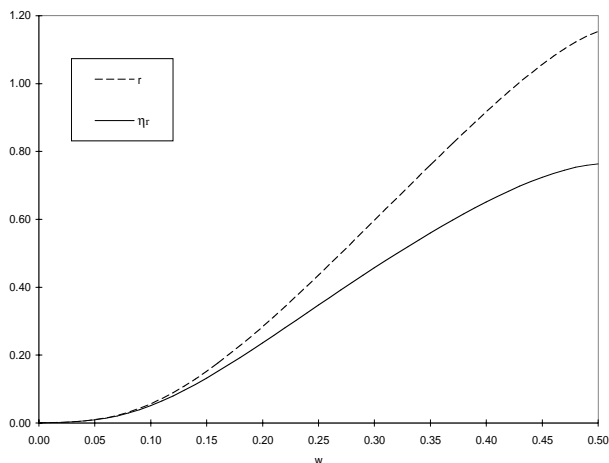

Figure 6. Equilibrium species yields and temperature for steam reforming of methane at $s = 10$.

Figure 7. Availability ratio and reforming efficiency vs. energy input for steam reforming of methane.
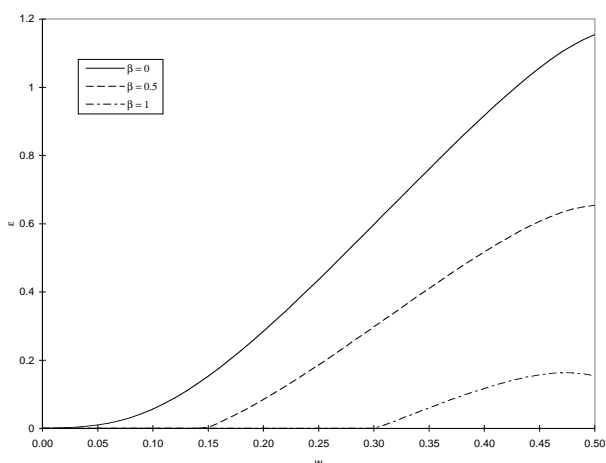
Figure 8. Efficiency factor vs. energy input for steam reforming of methane with a 50 % efficient plant.

Partial Oxidation

In the process of partial oxidation, a small amount of oxygen is admitted to the input mixture, in order to accelerate the decomposition of the hydrocarbons by oxidizing carbon to carbon monoxide or carbon dioxide. The overall stoichiometry is as follows:

$$C_nH_{2n+2} + {}^n/_2O_2 \quad \rightarrow \quad nCO + (n+1)H_2$$
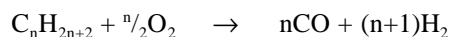
The actual reaction process is more complicated; it consists of initial rapid combustion of the fuel until the oxygen is consumed, followed by slower reforming of the resulting mixture to H_2 and CO with water acting as the oxidizer,
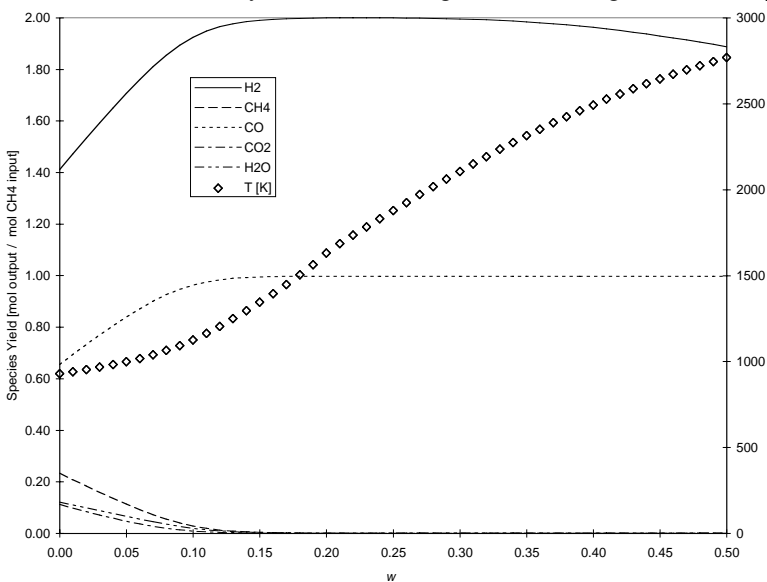
Figure 9. Equilibrium species yields and temperatures for partial oxidation of methane at $\Phi = 4.0$.

in a manner similar to steam reforming (O'Brien, 1996). In contrast to the processes described above, partial oxidation is an exothermic reaction. Hence the energy input required to drive this reaction towards equilibrium does not increase proportionally to the throughput. In fact, the reaction may be self-sustaining under certain circumstances, allowing for high degrees of conversion at low energy inputs. As with the previous two methods, it requires high operating temperatures, but the reaction timescales are considerably smaller. Partial oxidation is carried out both in catalytic and high-temperature non-catalytic systems.

The stoichiometry of the input mixture for the partial oxidation calculations can be characterized by the fuel-to-air equivalence ratio Φ. For methane, stoichiometric partial oxidation (as described by the reaction equation above) occurs at $\Phi = 4.0$. However, in order to drive the reaction further towards hydrogen and carbon monoxide, "partial oxidation" is often carried out at lower equivalence ratios (more oxidizer per unit fuel), allowing combustion of some of the fuel to raise reaction temperatures. Hence, results are presented below in Figures 9 to 17 for reactions with $\Phi = 4.0$, $\Phi = 3.3$ and $\Phi = 2.0$. In the $\Phi = 4.0$ results, one can see that although the equilibrium hydrogen yield reaches the stoichiometric value of 2 moles H_2 per mole CH_4 at low energy input, the availability ratio and reforming efficiency for a hydrogen-fueled plant are still relatively low (60

Figure 10. Availability ratio and reforming efficiency vs. energy input for partial oxidation of methane at $\Phi = 4$.
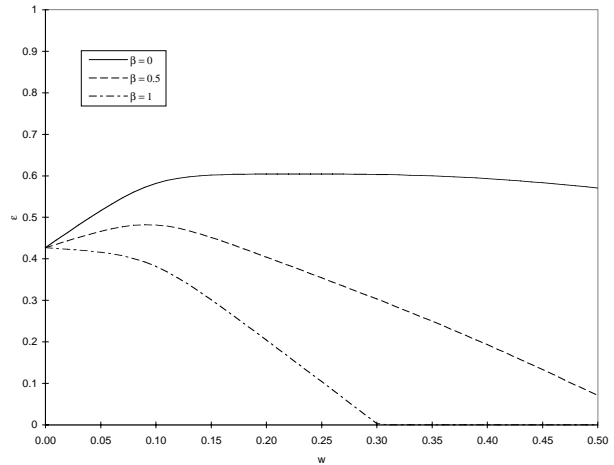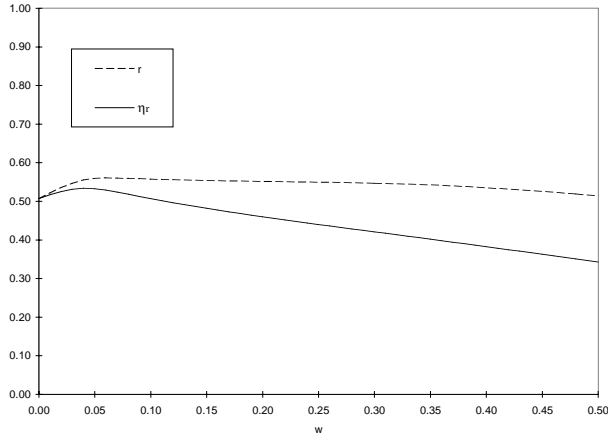

Figure 11. Efficiency factor vs. energy input for partial oxidation of methane at $\Phi = 4$ with a 50 % efficient plant.

percent) due to the large portion of the input fuel availability that is stored in the CO chemical energy in the output mixture.

These results can be used to illustrate an important consideration for integrated reformer-plant systems: a highly efficient reforming process may not be beneficial in an integrated system if it requires a large energy input. For instance, while steam reforming can achieve higher reforming efficiencies than partial oxidation, it reaches these efficiencies only with large energy inputs; hence, the overall system efficiencies remain very low if most of the reforming energy must come from the plant (see Figure 8, $\beta = 1$). In contrast, partial oxidation is most efficient at low w values, resulting in higher overall efficiencies in integrated systems than steam reforming can produce (Figures 10 and 11). A similar comparison can be made among the partial oxidation reactions with different equivalence ratios. As Φ decreases from the stoichiometric value, the maximum of the availability ratio curve both decreases in magnitude and shifts to lower w values. Thus, the $\Phi = 3.3$ process (at $w \approx 0$) can achieve higher overall efficiencies for $\beta \approx 1$ than either of the other two.
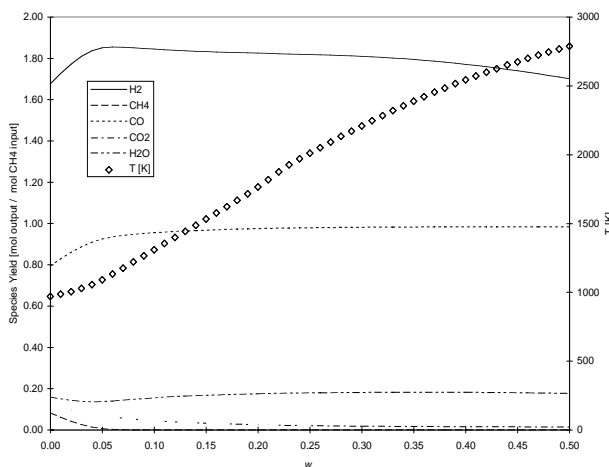
Figure 12. Equilibrium species yields and temperature for partial oxidation of methane at $\Phi = 3.3$.
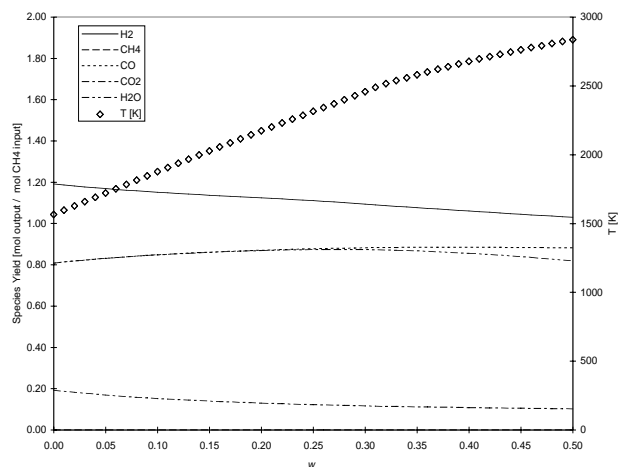
Figure 15. Equilibrium species yields and temperature for partial oxidation of methane at $\Phi = 2.0$.

Figure 13. Availability ratio and reforming efficiency vs. energy input for partial oxidation of methane at $\Phi = 3.3$.
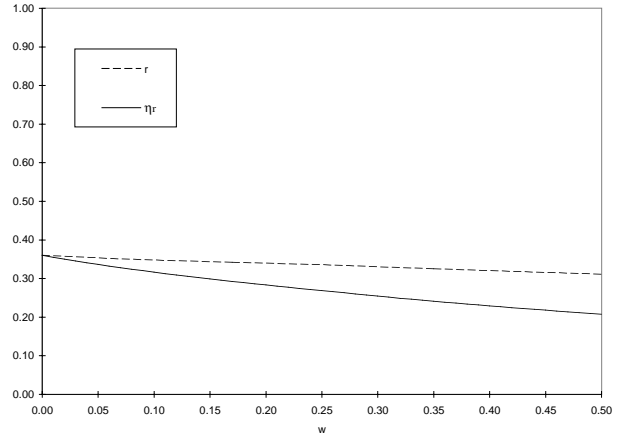

Figure 16. Availability ratio and reforming efficiency vs. energy input for partial oxidation of methane at $\Phi = 2$.
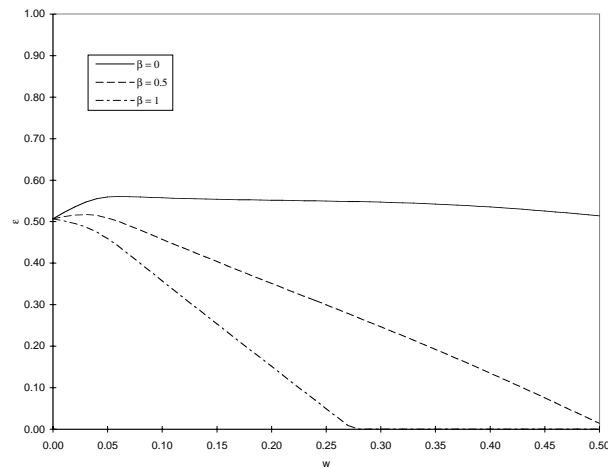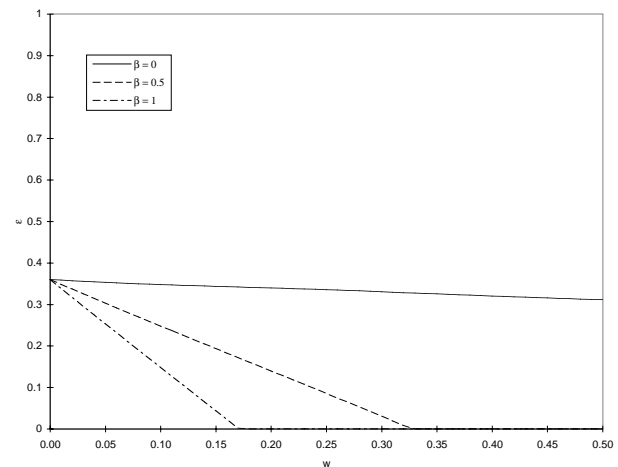

Figure 14. Efficiency factor vs. energy input for partial oxidation of methane at $\Phi = 3.3$ with a 50 % efficient plant.
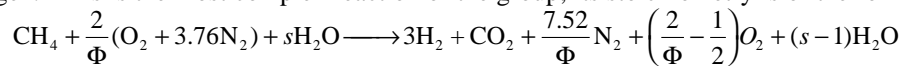

Figure 17. Efficiency factor vs. energy input for partial oxidation of methane at $\Phi = 2$ with a 50 % efficient plant.

Partial Oxidation-Water Shift

A means of overcoming the low reforming efficiency of partial oxidation is to pair the reaction with a *water shift* reaction, in which additional water is used to oxidize the CO to CO_2, transferring the CO availability to the resulting hydrogen. This is the most complex reaction of the group; its stoichiometry is of the form

$$CH_4 + \frac{2}{\Phi}(O_2 + 3.76N_2) + sH_2O \longrightarrow 3H_2 + CO_2 + \frac{7.52}{\Phi}N_2 + \left(\frac{2}{\Phi} - \frac{1}{2}\right)O_2 + (s-1)H_2O$$

with λ and s defined as above. In essence, this reaction is a compromise solution for hydrocarbon to hydrogen reforming, attempting to combine the low energy requirements of partial oxidation with the efficiency of steam reforming.

For methane fuel, using $\Phi = 4$ and $s = 10$ as above, the equilibrium results are shown in Figures 18 to 20. In the optimal range of w around 0.25, the hydrogen yield is near stoichiometric (3 moles H_2 per mole CH_4), and r is near 90 percent (η_r about 70 percent). Figure 20 shows the accessible ε range for partial oxidation/water shift; as may be expected, partial oxidation-water shift falls between partial oxidation and steam reforming in overall efficiency.
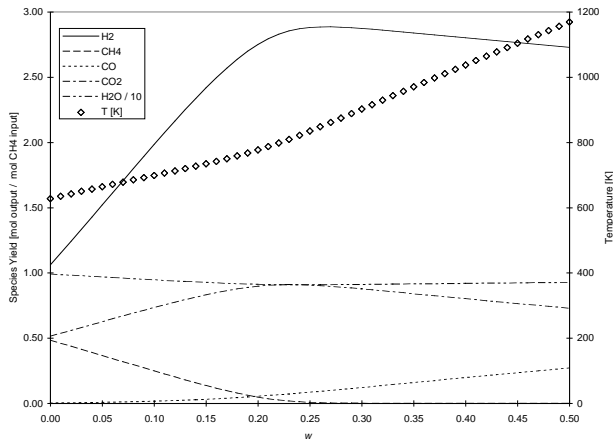
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Figure 18. Equilibrium species yields and temperature for partial oxidation-water shift of methane at $\Phi = 4$ and $s = 10$.
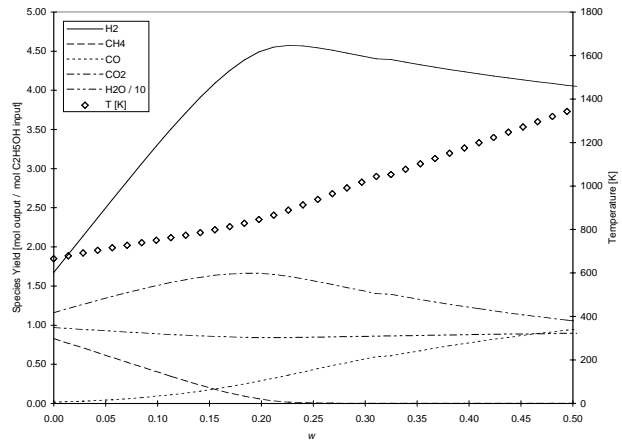

Figure 21. Equilibrium species yields and temperature for partial oxidation-water shift of ethanol at $\Phi = 6$ and $s = 10$.
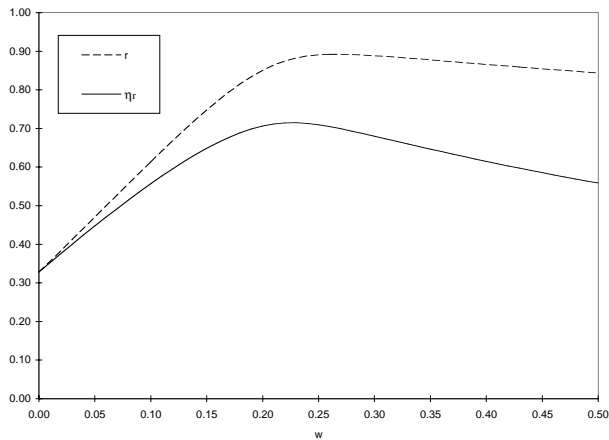

Figure 19. Availability ratio and reforming efficiency for partial oxidation-water shift of methane at $\Phi = 4$ and $s = 10$.
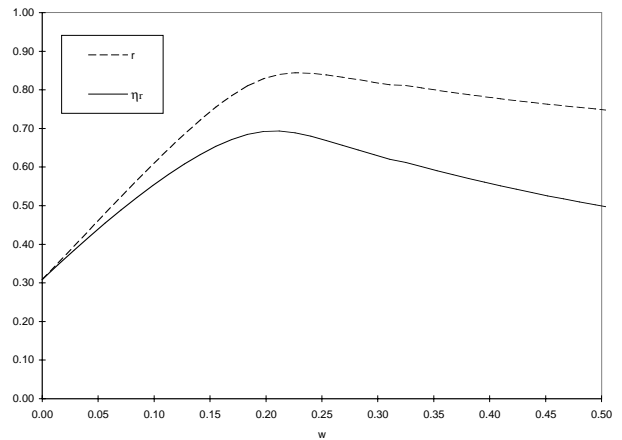

Figure 22. Availability ratio and reforming efficiency for partial oxidation-water shift of ethanol at $\Phi = 6$ and $s = 10$.
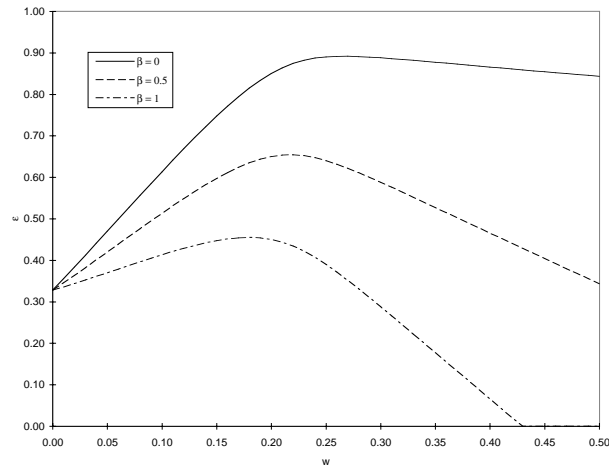

Figure 20. Efficiency factor vs. energy input for partial oxidation-water shift of methane at $\Phi = 4$ and $s = 10$ with a 50 percent efficient plant.
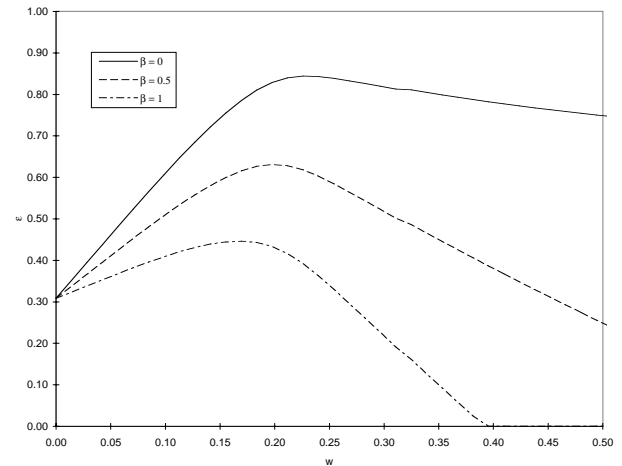

Figure 23. Efficiency factor vs. energy input for partial oxidation-water shift of ethanol at $\Phi = 6$ and $s = 10$ with a 50 percent efficient plant.

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For comparison with the above results for methane, the partial oxidation-water shift calculations were performed with ethanol as the fuel molecule. For ethanol, stoichiometric partial oxidation occurs at $\Phi = 6.0$; the input mixture composition was chosen with $\Phi = 6$ and $s = 10$, to correspond most closely to the methane results. The maximum possible hydrogen yield from this input mixture is 5 moles of hydrogen per mole of ethanol.

As can be seen from Figures 21-23, the behavior of ethanol is very similar to that of methane, and the resulting efficiency factors are almost identical.

Based on the above calculations, we may draw some conclusions about the application of these reforming reactions to integrated reformer-fuel cell systems. Firstly, pyrolysis is a poor choice for integrated reforming, due to its low efficiencies and high energy requirements. Steam reforming is also not a good choice for integrated systems; although it is an extremely efficient process at high enough energy input levels, the energy requirements are too high to allow efficient operation in combination with the fuel cell. Partial oxidation and partial oxidation-water shift have similar efficiencies in integrated systems; any decision between these two would need to take into account other factors, such as desired ranges of w and β or CO tolerance of the fuel cell.

Conclusions

Perhaps the most important point of this analysis is that it is possible to discuss fuel processors in terms of energy efficiency that can be applied to a wide variety of different systems, including catalytic, thermal, and electrical processes. While the integrated reformer-plant efficiency is by no means the only important characteristic of such a system, it can be very helpful in narrowing the field of choices for a particular application, or for comparing very dissimilar technologies in a consistent, quantitative way, and may serve as a starting point to which other, often related, issues such as power density, response times, environmental impacts and cost may be added.

As illustrated via the partial oxidation comparisons, it can be advantageous, from an overall efficiency standpoint, to use some of the plant output work to provide energy to the fuel processor, even if in principle all of the energy requirements of reforming could be met by combustion of additional fuel. One way to rationalize this non-intuitive effect is to consider that the combustion of extra fuel adds to the mass of the reacting mixture that must be heated in order to achieve adequate reaction temperatures. The optimum configuration for a given application is likely to involve supplying reforming energy from a combination of chemical energy and plant work, rather than solely one or the other. For each of the processes discussed above, with reforming work supplied from the plant, there is a particular value of the energy input to the fuel processor that maximizes the efficiency of the overall system, due to the competing effects of adding energy to the reformed fuel and decreasing the net work output of the reformer-plant system.

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