

# Analysis of the Thermal Efficiency Limit of the Steam Methane Reforming Process

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**ABSTRACT:** The thermal efficiency limit of the steam methane reforming (SMR) process is analyzed on the basis of energy balance and pinch analysis. The composite heat exchange curves of the SMR process are characterized by internal pinches. These internal pinches determine the process efficiency limit. An analytical solution for the process efficiency limit is derived from energy balance across the composite heat exchange curves. The solution can be used to calculate the process efficiency limit for any given set of reaction and process conditions.

## 1. INTRODUCTION

Steam methane reforming (SMR) is a major hydrogen production process with more than 70 years of history. It converts a hydrocarbon-containing feed (e.g., methane) into hydrogen and carbon oxides by the steam reforming reactions, as shown below in a simplified form



The overall reforming reaction is endothermic and takes place at high temperature (e.g., above 753 K). The process combusts fuel with air to provide the heat for the reaction. Both reforming and combustion take place in a reformer consisting of reformer tubes housed in a large combustion chamber. The fuel is combusted through burners in the chamber, and part of the heat from the combustion is transferred into the process gas within the reformer tubes. The hydrocarbon-containing feed, along with steam (known as process steam), is fed to the reformer tubes and reformed over a catalyst using the heat from the combustion. The effluent from the combustion side of the reformer is known as flue gas, and that from the tube side of the reformer is known as synthesis gas or syngas. The syngas stream contains  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and unconverted  $\text{CH}_4$  and process steam. The syngas from the reformer further goes through a water gas shift reactor where  $\text{CO}$  and steam react to form  $\text{H}_2$  and  $\text{CO}_2$ . The hydrogen in the final syngas is recovered, typically using a pressure swing adsorption (PSA) unit, to arrive at product hydrogen.

A modern SMR process also uses an elaborate heat exchange network. The heat exchange network heats the streams entering the reformer and cools the streams leaving the reformer. It also recovers the heat in the syngas and fuel gas to produce another product of the process—export steam. The export steam is sent to customers for various end uses.

The SMR process can be viewed as an energy conversion process. It converts the energy stored in the hydrocarbon-containing feed and combustion fuel to other energy forms,  $\text{H}_2$  and export steam. The efficiency of this energy conversion process, therefore, can be defined as

$$\eta = \frac{E_{\text{H}_2}/F_{\text{H}_2}}{(E_{\text{raw}} - Q_{\text{exp}})/F_{\text{H}_2}} \quad (1.2)$$

$E_{\text{H}_2}$  in eq 1.2 is the total energy content of the hydrogen product,  $F_{\text{H}_2}$  is the hydrogen production rate,  $E_{\text{raw}}$  is the total energy content of the feed and fuel (raw energy consumption), and  $Q_{\text{exp}}$  stands for the thermal value of the export steam. Note that eq 1.2 does not consider the electric power involved in the process. Therefore, it defines the *thermal*, but not energy, efficiency of the process. The current study is concerned with thermal efficiency only. Also note that this definition implies that the efficiency of export steam production is 100% and all the inefficiency of the SMR process is in the production of hydrogen.

The numerator of eq 1.2 is also the heating value of the hydrogen molecule, i.e.,

$$E_{\text{H}_2}/F_{\text{H}_2} = 12102 \text{ kJ/Nm}^3$$

on the high heating value basis

$$E_{\text{H}_2}/F_{\text{H}_2} = 10240 \text{ kJ/Nm}^3$$

on the low heating value basis

The denominator of eq 1.2 is the *specific energy consumption* of the SMR process, i.e.,

$$\varepsilon = (E_{\text{raw}} - Q_{\text{exp}})/F_{\text{H}_2} \quad (1.3)$$

It is reported that the specific energy consumption for a typical commercial SMR process ranges from 12288 to 13777  $\text{kJ/Nm}^3$  on the low heating value basis.<sup>1</sup> This translates approximately into 13628 to 15204  $\text{kJ/Nm}^3$  on the high heating value basis. Therefore, the efficiency of a typical commercial SMR process ranges approximately from 80 to 90% on the high heat value basis.

There is a considerable gap between the specific energy consumption for hydrogen production and the heating value of hydrogen. The objective of the current study is to develop a method for understanding what the smallest gap one can achieve in theory or what the efficiency limit is for the SMR

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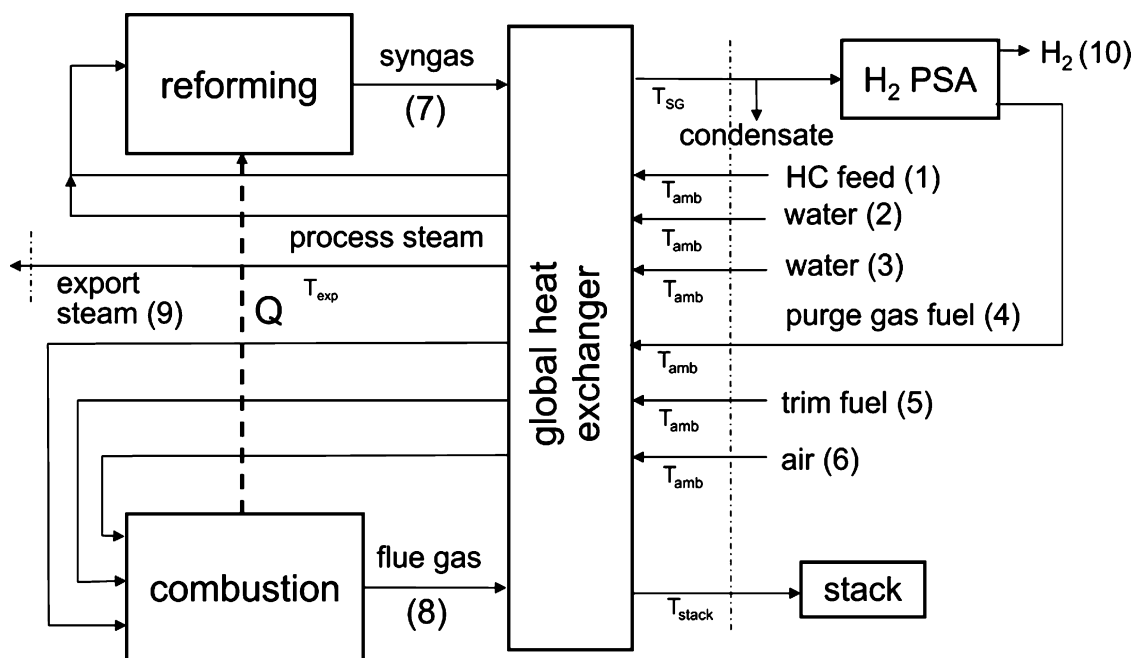


Figure 1. A block diagram of the SMR process. (-----) Process boundary.

process. The study is based on the following consideration. The gap between the specific energy consumption for hydrogen production and the heating value of hydrogen is the heat loss of the process. It consists of the heat loss from syngas and flue gas to the ambient (waste heat) and the heat loss through the surface of all equipment. For given conditions of reforming reactions and combustion, known equipment heat loss, and other fixed process conditions such as the recovery rate of hydrogen from syngas, the process efficiency depends on the heat exchange network design. A better heat exchange system will recover more heat or generate less waste heat from syngas and flue gas, providing better efficiency. Therefore, the focal point of the current study becomes a heat exchange system that provides the best heat recovery, from which the process efficiency limit can be derived.

This approach treats reforming reaction conditions, combustion conditions, other selected process conditions, and equipment heat loss as “given”, although the process efficiency limit is a sensitive function of all of them. Using this approach reduces the number of variables in the analysis greatly so that one can focus on the essential part of the problem (heat exchange) and develop an analytical solution. As a result, the “given” conditions become parameters or design variables in the solution and their impacts on the efficiency limit can be understood via sensitivity calculations.

Efforts have been made to understand the efficiency of the SMR process previously. A study by Lutz et al.<sup>2</sup> reports a thermal efficiency limit around 85%. The analysis is based on global thermal energy balance of the process. The two reactants for reforming, hydrocarbon feed and water, enter the process boundary under the ambient conditions. The heat for preheating and vaporizing the two reactants and for conducting reforming reactions is provided by the heat from combustion. The air for combustion enters the process boundary under the ambient conditions, and the fuel for combustion (“reformate”) is an internal stream comprising unconverted methane, CO, and unrecovered hydrogen from the syngas. The streams leaving the process boundary are product hydrogen and the flue

gas from the combustion. It was assumed that the temperature of the flue gas leaving the process boundary is at 373 K and the water in the flue gas, from both unconverted process steam and combustion, is in the vapor state. There is no export of steam or any other form of energy from the process. Overall, the energy from the hydrocarbon feed is balanced by the energy in product hydrogen and the waste heat in the flue gas. The limiting thermal efficiency is achieved when the requirement of the combustion fuel (“reformate”) is at its minimum. There are several limitations in this analysis. First, the results only apply to the SMR process without export steam. Second, fixing the conditions of the flue gas leaving the process boundary (e.g., 373 K, water in vapor state) makes the efficiency limit from the analysis subject to the selected conditions, therefore, arbitrary. Third, the analysis assumes “perfect heat exchange” that only matches energy or heat exchange duties but ignores heat exchange temperature profiles. Although this assumption may not invalidate the results of the analysis, it is an assumption that invites erroneous results, as discussed later.

There are other efforts in understanding and optimizing the SMR process efficiency. All of them use specific heat exchange network designs.<sup>3–5</sup> For example, Simpson and Lutz<sup>3</sup> conducted an exergy analysis of the SMR process. The study employs a specific heat exchange network. Minimum temperature approaches were assigned to all heat exchangers. The best efficiency of the process is achieved when the minimum amount of fuel is used, corresponding to the temperature approaches in these heat exchangers at their minimums.

There is generally a dilemma in these types of studies in terms of how to represent heat exchange. A specific heat exchange network design is normally used so that the problem is mathematically well-defined. However, using a specific design defines the heat recovery capability of the process, and the resulting efficiency is specific to the heat exchange network only. Unless the design avoids any local pinches, the efficiency, though the best to the design, is not general, intrinsic, or the best to the SMR process. On the other hand, if one avoids the specifics by using a simple energy or heat exchange duty

balance for heat exchange, as in Lutz et al.,<sup>1</sup> there is a risk of obtaining erroneous results if there is a temperature cross in the heat exchange system, as will be illustrated in section 3. This dilemma is circumvented in the current study using a pinch analysis tool—a global heat exchanger.<sup>6,7</sup>

All previous studies are based on numerical simulations and provide numerical answers only. No analytical solutions or expressions for efficiency calculations, to our knowledge, have been reported.

## 2. DEVELOPMENT OF THE ANALYSIS METHOD AND ANALYTICAL SOLUTION

**2.1. Representation of the SMR Process.** The SMR process for this study is represented by a block diagram, as shown in Figure 1. The boundary of the process is shown by two dot-dashed lines. The streams entering the process include hydrocarbon (HC) feed, two water streams, purge gas fuel, trim fuel, and air, all at the ambient temperature. The streams leaving the process include syngas at  $T_{SG}$ , flue gas at  $T_{stack}$  and export steam at  $T_{exp}$ . There are two water streams in the representation, one for the steam used for reforming reactions (water (2)) and the other for export steam (water (3)). In practice, these may be a single stream going to a common steam drum for steam generation. Splitting it into two streams facilitates analysis; energy-wise or heat exchange duty-wise, it will have no impact on the results. Likewise, in reality, the process steam and HC feed are heated separately first and then combined before being heated together to the final temperature. They are treated as two separate streams here up to the final preheat temperature to simplify the analysis.

The reformer is graphically decomposed into a “reforming” block and a “combustion” block. The reforming block represents the reforming side of the reformer, where reforming reactions occur inside reformer tubes containing a reforming catalyst. The feed to the reforming block consists of steam (“process steam”) and a hydrocarbon feedstock (“HC feed”). The reforming product, known as “syngas”, contains  $H_2$ , CO,  $CO_2$ , unconverted methane, and steam. After the syngas is cooled and the steam in it is condensed out, most of the hydrogen in it is recovered in a pressure swing adsorption separation unit (“ $H_2$  PSA”) as the product. The offgas or purge gas from the  $H_2$  PSA unit is used as a fuel for the process (“purge gas fuel”).

The combustion block represents the combustion side of the reformer. The purge gas fuel and a supplementary hydrocarbon-containing stream known as “trim fuel”, along with air, are introduced to the combustion block, where they are combusted to provide the heat (“ $Q$ ”) for the reforming reactions by heat transfer through the walls of the reformer tubes. The combustion product, known as “flue gas”, is cooled and then released through a stack.

Another simplification in this representation is the omission of the water gas shift reactor. The SMR process generally has a shift reactor. It converts the CO in the syngas to  $CO_2$  using steam and generates more  $H_2$ . The shift reactor is located downstream of the reformer, normally following a boiler, and the reaction takes place at a much lower temperature than the reformer outlet temperature, depending on the type of shift reaction technology to be used. Since the shift reactor is generally sandwiched between two heat exchangers, it is omitted in this representation so that the entire heat exchange system can be represented by a single heat exchanger, which facilitates the analysis significantly. Since the shift reactor

generally operates adiabatically (no enthalpy change),<sup>8</sup> this simplification has no impact on the energy or heat exchange duty balance of the heat exchange system. However, the shift reaction does change the composition of the syngas by several percent points, affecting the dew point of the syngas and the flow rate and composition of the purge gas fuel. This impact is taken into consideration by changing the composition of the syngas stream (stream 7) from that of the reformer effluent to that of a shift reactor effluent. The temperature of the syngas entering the heat exchanger is still the reformer outlet temperature.

A pinch analysis tool<sup>6,7</sup>—global heat exchanger—is used to represent the heat exchange network of the SMR process. There are six cold streams (HC feed, two water streams, purge gas fuel, trim fuel, and air) and two hot streams (syngas and flue gas) entering the heat exchanger. This representation is essential to this study for the following three reasons. First, the global heat exchanger combines all cold streams into a composite cold stream and all hot streams into a composite hot stream. It further matches the highest temperature available from the composite hot stream to the highest temperature needed for the composite cold stream. As a result, it provides the least amount of exergy loss and the best heat recovery. Therefore, the process efficiency derived from such a heat exchange system will be the best efficiency possible as far as heat exchange is concerned. The efficiency from any specific heat exchange network designs will be poorer than that from the global heat exchanger because they cannot exceed the ideal temperature match in the global heat exchanger. It is in this sense that we call the process efficiency derived from the global heat exchanger *the process efficiency limit*.

A typical set of SMR composite heat exchange curves is shown in Figure 2. Such a set of composite curves can be

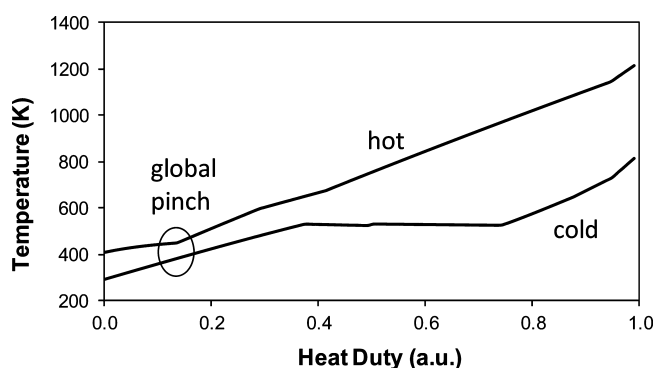


Figure 2. Heat exchanger curves of a global heat exchanger.

readily generated manually or using commercial software such as ASPEN Plus by ASPEN Technology for a given flow rate, composition, temperature, and pressure of all streams entering the heat exchanger. There are several features in these heat exchange curves. The two sloping sections of the composite cold curve correspond to preheating HC feed, water streams, fuel steams, air, and superheating steam. The flat section corresponds to steam generation, a result of the common practice in the SMR industry that generates steam in a steam drum from pure water. The temperature of the flat section is the temperature of the steam drum or saturated steam. There is a bend or elbow in the composite hot curve that creates a global pinch. The temperature approaches on both sides of this pinch point are greater than the temperature approach at the pinch

point. This pinch corresponds to the dew point of the syngas, below which the higher heat capacity of the syngas stream as a result of gradual steam condensation flattens the composite hot curve. Note that this pinch is an internal pinch, as it occurs in the middle of the global heat exchange curves.

The revelation of this internal pinch is the second reason why the global heat exchanger is essential to this study. It shows that treating the heat exchange of the SMR process with a simple energy or heat exchange duty balance can lead to erroneous results. The existence of the internal pinch means that the temperature approach at the pinch point will reach zero before the approaches at the process boundary reach zero. A simple energy balance for heat exchange will generate rational boundary temperatures (e.g., no temperature cross) but ignore the internal temperature approach. Therefore, it may blindly result in temperature cross at the pinch point, violating the second law of the thermodynamics. In other words, for the SMR process, or any processes with an internal pinch for that matter, the efficiency is determined by the second law of thermodynamics, which takes into consideration heat exchange profiles but not the first law of thermodynamics, which only uses the boundary conditions.

Third, as shown below, the temperature approach at the pinch point provides the missing condition in previous studies that one needs to define the problem mathematically, i.e., matching the number of unknowns with that of equations.

**2.2. Attempt to Derive Process Efficiency Limit from Overall Energy Balance.** In the following, it is attempted to derive the process efficiency using one of the previous literature approaches—an overall energy balance across the boundary of the process. This exercise will demonstrate why this approach is inadequate for deriving the process efficiency limit the current study is looking for. The equations developed in this exercise are also needed for the latter sections.

An energy balance across the process boundary, as shown in Figure 1 gives

$$H_1(T_{\text{amb}}) + H_2(T_{\text{amb}}) + H_3(T_{\text{amb}}) + H_4(T_{\text{amb}}) + H_5(T_{\text{amb}}) + H_6(T_{\text{amb}}) = H_7(T_{\text{SG}}) + H_8(T_{\text{stack}}) + H_9(T_{\text{exp}}) \quad (2.1)$$

$H_i$  in eq 2.1 stands for the enthalpy of stream  $i$ , the subscript  $i$  refers to the stream number in Figure 1, and the temperature of a stream is indicated in the parentheses. Since the temperatures in parentheses are all those at which the streams enter or leave the process boundary, they are referred to as “boundary temperatures” and denoted as “ $T_b$ ” alternatively.

The physical meaning of eq 2.1 becomes clear if it is written as

$$Q_{\text{comb}}(T_b) = Q_{\text{ref}}(T_b) + Q_{\text{exp}}(T_b) \quad (2.2)$$

where

$$Q_{\text{comb}}(T_b) = H_4(T_{\text{amb}}) + H_5(T_{\text{amb}}) + H_6(T_{\text{amb}}) - H_8(T_{\text{stack}}) \quad (2.3)$$

$$Q_{\text{ref}}(T_b) = H_7(T_{\text{SG}}) - H_1(T_{\text{amb}}) - H_2(T_{\text{amb}}) \quad (2.4)$$

$$Q_{\text{exp}}(T_b) = H_9(T_{\text{exp}}) - H_3(T_{\text{amb}}) \quad (2.5)$$

Equations 2.3 and 2.4 can be viewed as the heat of combustion and heat of reforming of the process, respectively, defined at the boundary temperatures. Equation 2.5 is the thermal value of

the export steam. Equation 2.2 simply states that the heat of combustion of the process goes into the reforming reactions and the export steam.

If all the terms in eq 2.1 can be solved, the specific energy consumption of the SMR process can be calculated by

$$\varepsilon = \frac{E_1 + E_5 - Q_{\text{exp}}(T_b)}{F_{10}} \quad (2.6)$$

and the process efficiency by eq 1.2. Equation 2.6 is just a specific form of eq 1.3 with respect to Figure 1.  $Q_{\text{exp}}(T_b)$  in eq 2.6 is defined in eq 2.5,  $F_{10}$  is the hydrogen production rate, and  $E_1$  and  $E_5$  are the consumption rates of HC feed and trim fuel, respectively, in terms of their total heating value.  $E_1$  and  $E_5$  can be determined if the compositions and flow rates of HC feed and trim fuel are known. These are also two of the properties necessary for determining the enthalpies of the two streams, i.e.,  $H_1(T_{\text{amb}})$  and  $H_5(T_{\text{amb}})$ , respectively.

For further derivation of the process efficiency limit, let us assume that the following process and reaction conditions are given:

- Rate of hydrogen production
- Recovery of  $H_2$  PSA
- Compositions of HC feed and trim fuel
- Steam-to-carbon ratio for reforming
- Outlet temperature and pressure of the reforming block
- Combustion system pressure
- Excess usage of combustion air (i.e., % $O_2$  in flue gas)
- Heat leak through all equipment (assumed to be zero)
- Temperature, pressure, and flow rate of export steam

The rate of hydrogen production is given because it scales the flow rates of all streams. In theory, it does not impact the process efficiency. All other conditions, however, will impact the process efficiency significantly. They are fixed for the following reasons. First, doing so reduces the number of variables greatly, enabling the derivation of an analytical solution for the process efficiency limit. Once the solution is derived, these conditions can all be parameters in the solution and their impact on the process efficiency can be calculated through sensitivity studies. Second, these conditions are mostly determined by technical limitations or commercial requirements, rather than the thermodynamics of the process, therefore, not intrinsic to the understanding this study is aimed to achieve.

Once these process and reaction conditions are given,  $H_1(T_{\text{amb}})$ ,  $H_2(T_{\text{amb}})$ ,  $H_3(T_{\text{amb}})$ ,  $H_4(T_{\text{amb}})$ , and  $H_9(T_{\text{exp}})$  are determined.  $H_5(T_{\text{amb}})$  and  $H_6(T_{\text{amb}})$  can be determined if the trim fuel flow rate is known.  $H_7(T_{\text{SG}})$  and  $H_8(T_{\text{stack}})$  can be determined if  $T_{\text{SG}}$  and  $T_{\text{stack}}$  are known. In other words, there are three unknowns in eq 2.2: the trim fuel flow rate, the syngas temperature leaving the process boundary ( $T_{\text{SG}}$ ), and the flue gas temperature leaving the process boundary ( $T_{\text{stack}}$ ).

Two unknowns of  $T_{\text{SG}}$  and  $T_{\text{stack}}$  can be reduced into one. As shown in eq 2.1,  $T_{\text{SG}}$  and  $T_{\text{stack}}$  can trade off against each other without impacting the balance of the equation. That is, one can have various  $T_{\text{SG}}-T_{\text{stack}}$  pairs for a constant  $H_7(T_{\text{SG}}) + H_8(T_{\text{stack}})$ . Physically, this means that one can maintain a constant process efficiency by recovering an extra amount of heat from the syngas (therefore, a lower  $T_{\text{SG}}$ ) while letting go the same extra amount of heat in the flue gas as waste heat (therefore, a higher  $T_{\text{stack}}$ ). This trade-off is possible because the current analysis utilizes a global heat exchanger that combines syngas and flue gas into a single composite hot stream. The

heat transfer from the composite hot stream to the composite cold stream does not distinguish whether the heat is from syngas or flue gas. As a result, one can fix either  $T_{SG}$  or  $T_{stack}$  as a design parameter and let the other be an unknown variable, or simply let  $T_{SG} = T_{stack}$  to reduce two unknown variables into one. For this study,  $T_{SG} = T_{stack}$  is chosen and the temperature is denoted as  $T_s$ .

Two unknowns still remain, the trim fuel flow rate and  $T_s$ , but there is only one equation (eq 2.1) that is derived from the overall energy balance. One cannot assign one of the unknowns and then use the equation to solve for efficiency. First, this assignment will make the result arbitrary. Second, it may result in temperature cross at the global pinch point, therefore violating the second law of thermodynamics, if the selected value of the flow rate or  $T_s$  is too low, as will be illustrated in section 3. This discussion shows that using overall energy balance is not sufficient to determine the efficiency limit of the SMR process.

**2.3. Derive Process Efficiency Limit Using Energy Balance across the Global Pinch.** The missing condition that mathematically defines the problem is the intrinsic heat exchange capability or constraint of the SMR heat exchange system. This constraint is identified in the current study by carrying out an enthalpy balance across the global heat exchange curves, as shown by the dot-dashed ellipse in Figure 3. The balance envelope crosses the two ends of the global heat

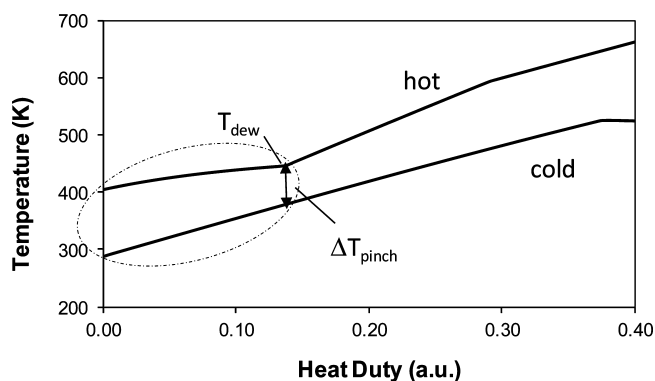


Figure 3. Enthalpy balance across heat exchange curves and the pinch point.

exchange curves on the left-hand side, corresponding to part of the process boundary. The end of the hot composite curve is where syngas and flue gas streams leave the process at  $T_{SG}$  and  $T_{stack}$ , respectively. And the end of the cold composite curve is where the streams enter the process, including HC feed, two water streams, purge gas fuel, trim fuel, and air, all at the ambient temperature. The balance envelope crosses the global pinch point at the right-hand side. This is where the two hot streams mentioned above enter the balance envelope at  $T_{dew}$  (the syngas dew point), and the six cold streams mentioned above leave the balance envelope at  $T'_{dew}$ , where  $T'_{dew} = T_{dew} - \Delta T_{pinch}$ . Note that the pinch point is not a physical boundary where the energy balance envelope is normally drawn but a point inside an imaginary global heat exchanger.

Referring to Figures 1 and 3, the enthalpy balance based on this concept can be written as

$$\begin{aligned} & H_1(T_{amb}) + H_2(T_{amb}) + H_3(T_{amb}) + H_4(T_{amb}) + H_5(T_{amb}) \\ & + H_6(T_{amb}) + H_7(T_{dew}) + H_8(T_{dew}) \\ & = H_1(T'_{dew}) + H_2(T'_{dew}) + H_3(T'_{dew}) + H_4(T'_{dew}) \\ & + H_5(T'_{dew}) + H_6(T'_{dew}) + H_7(T_{SG}) + H_8(T_{stack}) \end{aligned} \quad (2.7)$$

Combining eq 2.7 with eq 2.1 yields

$$\begin{aligned} & H_1(T'_{dew}) + H_2(T'_{dew}) + H_3(T'_{dew}) + H_4(T'_{dew}) \\ & + H_5(T'_{dew}) + H_6(T'_{dew}) \\ & = H_7(T_{dew}) + H_8(T_{dew}) + H_9(T_{exp}) \end{aligned} \quad (2.8)$$

Equation 2.8 is similar to eq 2.1, but all boundary temperatures (except  $T_{exp}$ ) have been replaced by either  $T_{dew}$  or  $T'_{dew}$ . Likewise, eq 2.8 can be rearranged into

$$Q_{comb}(T_{dew}) = Q_{ref}(T_{dew}) + Q_{exp}(T_{dew}) \quad (2.9)$$

where

$$Q_{comb}(T_{dew}) = H_4(T'_{dew}) + H_5(T'_{dew}) + H_6(T'_{dew}) - H_8(T_{dew}) \quad (2.10)$$

$$Q_{ref}(T_{dew}) = H_7(T_{dew}) - H_1(T'_{dew}) - H_2(T'_{dew}) \quad (2.11)$$

$$Q_{exp}(T_{dew}) = H_9(T_{exp}) - H_3(T'_{dew}) \quad (2.12)$$

Equations 2.10 and 2.11 can be viewed as the heat of combustion and heat of reforming of the process, respectively, defined at the pinch point. Equation 2.12 is the thermal value of the export steam referenced to the water at  $T'_{dew}$ .

With the given process and reaction conditions shown previously,  $T_{dew}$ ,  $H_7(T_{dew})$ , and  $H_9(T_{exp})$  are determined. If  $\Delta T_{pinch}$  or  $T'_{dew}$  is treated as a design variable,  $H_1(T'_{dew})$ ,  $H_2(T'_{dew})$ ,  $H_3(T'_{dew})$ , and  $H_4(T'_{dew})$  are determined. If the trim fuel flow rate is known,  $H_5(T'_{dew})$ ,  $H_6(T'_{dew})$ , and  $H_8(T_{dew})$  are determined. This means that the only unknown in eq 2.8 is the trim fuel flow rate. For a given  $\Delta T_{pinch}$ , one can calculate the trim fuel flow rate using eq 2.8, then the specific energy consumption using eq 2.6, and the process efficiency using eq 1.2.

Equation 2.8 is well-defined because  $\Delta T_{pinch}$  is not an arbitrary variable but a heat exchange constraint. The smallest value of  $\Delta T_{pinch}$  is zero, a constraint imposed by the second law of thermodynamics. Zero  $\Delta T_{pinch}$  will give the best efficiency limit of the SMR process, corresponding to an infinitely large heat exchanger. Let us denote the process efficiency limit derived from zero  $\Delta T_{pinch}$  as the *theoretical* efficiency limit. In practice,  $\Delta T_{pinch}$  is a well-known design parameter and its value is determined by the optimal trade-off between the process efficiency and the capital cost of heat exchangers. The efficiency increases with decreasing  $\Delta T_{pinch}$ ; so does the capital cost. A typical design  $\Delta T_{pinch}$  may range from 10 to 30 K.<sup>7</sup> For a given design  $\Delta T_{pinch}$ , the efficiency limit of the SMR process can be calculated from eqs 2.8, 2.6, and 1.2. Let us denote this efficiency limit as the *practical* efficiency limit.

Note that, for the derivation of eq 2.8, the global internal pinch point is at the dew point of the syngas stream. However, the global pinch of the SMR process, i.e., the smallest temperature approach in the global heat exchange curves, can shift, depending on the export steam flow rate and the process

and reaction conditions. In general, when the export steam flow rate is very low, the smallest global internal pinch may shift to the elbow formed by the first sloping section and the flat section on the composite cold curve. Such a case is shown in Figure 4. In this case, eqs 2.8–2.12 will still hold true, but  $T'_{\text{dew}}$

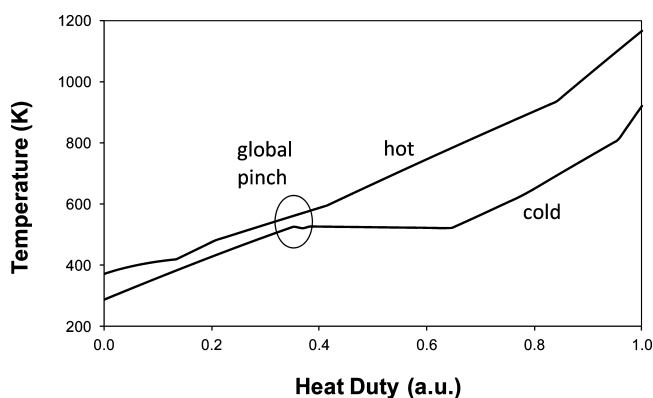


Figure 4. Shifting of the global pinch point at low export steam.

needs to be replaced by the temperature of the elbow on the composite cold curve, i.e., the temperature of the saturated steam or steam drum, and  $T_{\text{dew}}$  replaced by the saturated steam temperature plus  $\Delta T_{\text{pinch}}$ . On the other hand, when the export steam flow rate is very high, the smallest global pinch may shift to the elbow on the hot composite curve formed by the onset of steam condensation in the flue gas. In this case, eqs 2.8 and 2.12 will still hold true, but  $T_{\text{dew}}$  will be the dew point of the flue gas, instead of that of the syngas.

### 3. RESULTS AND DISCUSSION

Equations 2.8, 2.6, and 1.2 are used to calculate the process efficiency limits of the SMR process, and the results are shown in Figure 5. Calculations are conducted for  $\Delta T_{\text{pinch}}$  equal to 0 K

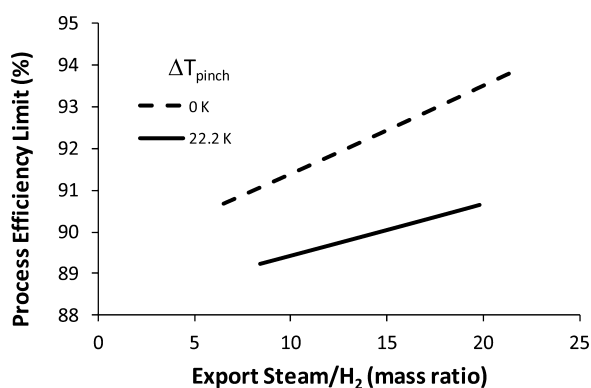


Figure 5. The process efficiency limit as a function of export steam-to-hydrogen mass ratio.

(the theoretical efficiency limit) and 22.2 K (the practical efficiency limit). By convention, the efficiency limits are plotted in Figure 5 as a function of the export steam production rate in mass, normalized by the hydrogen production rate in mass. The process and reaction conditions and design variables used in the calculations are summarized in Table 1. All compositions, flow rates, enthalpies, and heating values necessary for eq 2.8 are obtained using a thermodynamics database and a reforming reaction model. Commercial process software such as ASPEN

Table 1. Selected Process and Reaction Conditions and Design Variables

H <sub>2</sub> PSA recovery (%)	80
steam-to-carbon ratio	3.0
reformer outlet temperature (K)	1144
reformer outlet pressure (MP)	2.8
$T_{\text{dew}}$ (syngas) (K)	437
composition of HC feed	100% CH <sub>4</sub>
composition of trim fuel	100% CH <sub>4</sub>
combustion system pressure	atmospheric
excess air (%)	15
export steam pressure (MP)	3.8
export steam temperature (K)	644
export steam flow rate	varied
heat leak through equipment	0
$\Delta T_{\text{pinch}}$ (K)	0 and 22.2
ambient temperature (K)	289
shift reaction	high temperature shift

Plus by ASPEN Technology can also be used to generate these numbers.

The theoretical efficiency limit (0 K  $\Delta T_{\text{pinch}}$ ) appears to be a linear function of the export steam flow rate. The efficiency limit is better as the export steam increases, ranging from 90.7 to 93.8% on the high heating value basis. As shown by eqs 2.9–2.12,  $Q_{\text{ref}}$  is a constant across the entire range. Therefore, the dependence of the efficiency limit on export steam is determined by the trade-off between export steam production (e.g.,  $Q_{\text{exp}}$ ) and trim fuel consumption (e.g.,  $Q_{\text{comb}}$ ; note that purge gas fuel is a constant). The results indicate that the intrinsic thermodynamics of the SMR process favors higher export steam production.

The efficiency limit line ends on the left-hand side at an export steam-to-hydrogen mass ratio of 6.5. The termination is due to the fact that the trim fuel flow rate has reached zero as export steam decreases. Going further left, the heating value in the purge gas fuel will exceed what the process can consume. Therefore, the efficiency limit line cannot be continued beyond this point unless the excessive purge gas fuel can be exported at its heating value. The practical implication of this observation is that the efficiency of the SMR process is intrinsically poor if export steam is below a minimum and the purge gas fuel has to be consumed by the process itself. This minimum export steam depends on the reaction and process conditions such as those listed in Table 1.

On the right-hand side, the efficiency limit line extends to an export steam-to-hydrogen mass ratio of 21.5. This observation is somewhat surprising, since this amount of export steam far exceeds what commercial SMR processes offer without duct firing. The current analysis shows that high export steam by the SMR process is possible with deep recovery of the flue gas heat, including its latent heat from steam condensation; the flue gas temperature at the right end of the efficiency limit line is 322 K, below its dew point of 332 K. In practice, the latent heat of the flue gas of the SMR process has never been used, although it can readily account for 5–10 percentage points in the process efficiency. This lack of utilization could be due to the lack of the understanding shown by the current study, and/or due to practical corrosion problems caused by the SO<sub>3</sub> in the flue gas when it is cooled below the sulfur dew point.

Note that the syngas/flue gas temperature leaving the process boundary ( $T_s$ ) for the theoretical efficiency limit curve

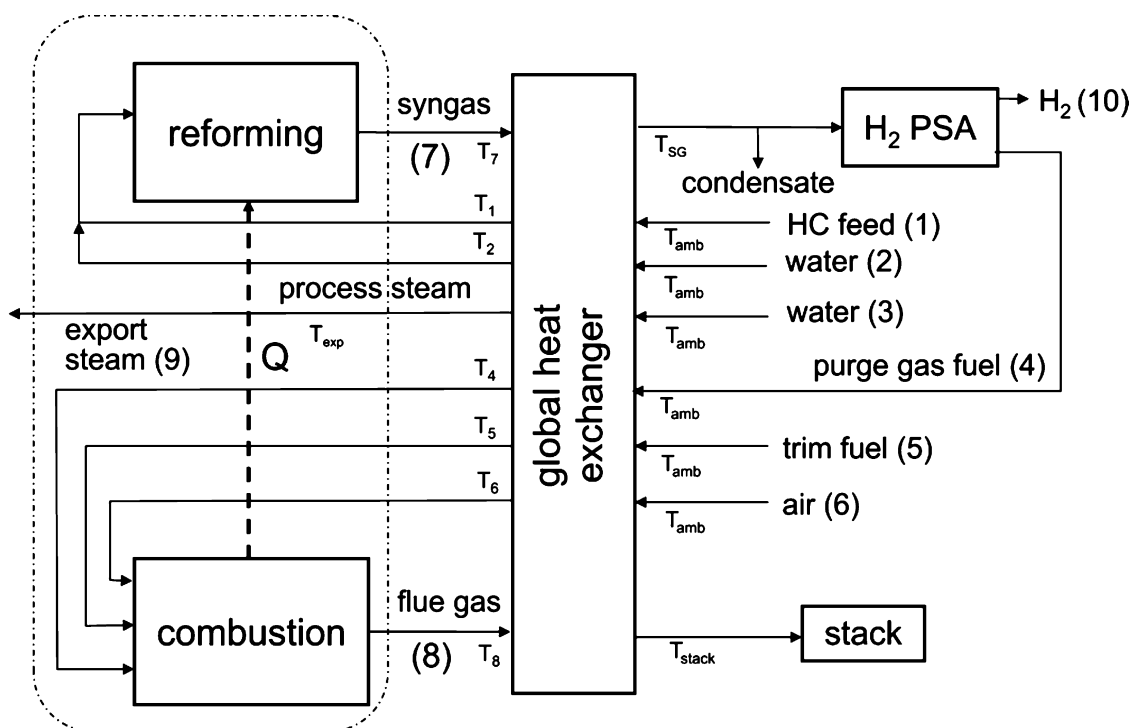


Figure 6. Enthalpy balance around the global heat exchanger.

ranges from 440 to 322 K, from left to right. This temperature range is well above the ambient temperature, yet it corresponds to the theoretical limiting conditions of the process,  $\Delta T_{\text{pinch}} = 0$ . One could conduct a similar efficiency study using the same process and reactions conditions as those in this work. However, if he is guided by the overall energy balance only, he may select syngas/flue gas boundary temperatures reasonably above the ambient temperature but below those in this study. The resulting efficiency will be erroneous because they will have temperature crossing ( $\Delta T_{\text{pinch}} < 0$ ) at the global pinch point.

Figure 5 also depicts the practical efficiency limit as a function of export steam calculated with  $\Delta T_{\text{pinch}}$  equal to 22.2 K. The relationship follows the same trends as the theoretical efficiency limit. The observations discussed above for the theoretical efficiency limit line hold true for the practical efficiency limit line. By allowing 22.2 K in the global pinch, the process loses 1.8–3.2 percentage points of its efficiency. The practical efficiency limit for a 22.2 K  $\Delta T_{\text{pinch}}$  ranges from 88.9 to 90.7%. It is difficult to compare these efficiency numbers with those reported for the commercial processes<sup>1</sup> because the efficiency is a strong function of other reaction and process conditions such as those listed in Table 1. However, for a commercial process with a given set of reaction and process conditions, one can use the method in this study to find out what the practical efficiency limit is and whether there is room for improvement. Similarly, one can use the method in this study to carry out sensitivity studies against reaction and process conditions such as those listed in Table 1 to identify improvement opportunities.

Another interesting observation from the current study is that the efficiency limit of the SMR process is independent of the temperatures at which the cold streams are heated to before they enter into the reformer (both reforming and combustion sides), and the temperature at which the flue gas leaves the reformer. These temperatures are absent in both eq 2.8 and

Table 1. This observation is somewhat surprising because those temperatures are sensitive parameters to efficiency in practical SMR process designs. This surprising observation is due to the fact that the current study deals with the thermodynamic limitations of the SMR process, while the practical design needs to consider equipment design and cost limitations.

The heat exchange system of the SMR process serves two purposes: (1) *recovering* the heat from the hot syngas and flue gas to generate export steam and (2) *recycling* the heat from the hot syngas and flue gas back to the reformer. The heat recovery is part of the overall energy balance of the process, therefore impacting the process efficiency. This balance is best shown by eq 2.8. The heat available from the hot streams at  $T_{\text{dew}}$  ( $H_7(T_{\text{dew}})$  and  $H_8(T_{\text{dew}})$ ) is greater than the heat needed to heat the cold streams to  $T'_{\text{dew}}$  ( $H_1(T'_{\text{dew}})$ ,  $H_2(T'_{\text{dew}})$ ,  $H_4(T'_{\text{dew}})$ ,  $H_5(T'_{\text{dew}})$ , and  $H_6(T'_{\text{dew}})$ ). This difference is the heat recovered by the heat exchange system to generate export steam ( $H_9(T_{\text{exp}}) - H_3(T'_{\text{dew}})$ ).

To understand the heat recycling role of the heat exchange system, let us carry out an enthalpy balance around the reformer, as shown by the dot-dashed rectangle in Figure 6 below.

The resulting enthalpy balance is

$$H_7(T_7) + H_8(T_8) = H_1(T_1) + H_2(T_2) + H_4(T_4) + H_5(T_5) + H_6(T_6) \quad (3.1)$$

The flow rates and compositions of all streams in eq 3.1 are determined by the reaction and process conditions given in Table 1 plus the trim fuel flow calculated using eq 2.8. The reformer outlet temperature ( $T_7$ ) is also given in Table 1. The undetermined variables in eq 3.1 are the temperatures at which the cold streams are heated to before they enter into the reformer ( $T_1$ ,  $T_2$ ,  $T_4$ ,  $T_5$ , and  $T_6$  or preheating temperatures) and the temperature at which the flue gas leaves the reformer ( $T_8$  or bridge wall temperature). These temperatures determine

the sensible heat content in the respective streams. Equation 3.1 shows that the preheating temperatures and the bridgewall temperature balance each other out completely; higher preheating temperatures result in a higher bridgewall temperature, and the heat for achieving these higher preheating temperatures is provided by the flue gas with the resulting higher bridgewall temperature. In other words, eq 3.1 represents a heat recycling loop. There is no net energy consumption or generation in this loop, and the preheating and bridgewall temperatures can go as high as the equipment limitations allow to or the process conditions require. This heat recycle is needed to maintain the high temperature requirements of reformer operation. Since the heat recycle does not involve any energy consumption or generation, the preheating temperatures have no impact on the process efficiency.

However, higher preheating temperatures do need a greater heat exchanger surface area. In practice, preheating temperatures are determined by equipment design conditions and cost. For example, HC feed and process steam are generally heated to  $\sim 811$  K, the temperature at which reforming reactions start to take off. Let us assume to heat them to 533 K only. Then, there will be no reactions in the entrance part of the reformer tubes but just sensible heating. This means that the reformer needs to be designed bigger to accommodate the additional duty for sensible heating. Due to the higher cost of reformer tubes, this is a higher cost option than heating these two streams to 811 K in heat exchangers. An alternative to increasing reformer size is to combust more fuel. The higher temperature in the combustion chamber from additional fuel combustion will increase the heat transfer to the tubes, therefore providing the additional heat duty. However, this option will result in poor process efficiency due to the extra fuel consumption.

In general, although preheating temperatures and the bridgewall temperature do not play a role in the process efficiency limit calculations, they are important design parameters of the SMR process. They are designed to minimize the total capital cost of reformer and heat exchange systems. For some reaction and process conditions, this minimization may not interfere with designing the process to its practical efficiency limit by the thermodynamics underlying eq 2.8. For other conditions, this interference may occur, and the final cost optimization involving both capital and operation (i.e., efficiency) may lead to a process efficiency that deviates from the linear trend shown in Figure 4.

#### 4. SUMMARY

The key for analyzing the efficiency limit of a process is to identify a proper heat exchange constraint. For the SMR process, this constraint is an internal global pinch in the composite heat exchange curves of the process. The existence of this internal global pinch makes it impossible to understand the efficiency limit of the SMR process using a simple energy balance around the process boundary. With this constraint, an analytical solution for the efficiency limit is derived. The results show that the efficiency limit is a linear function of the amount of export steam, increasing with increasing export steam. This linear trend extends to very large export steam production, much larger than that offered by current commercial SMR processes. And the latent heat of the flue gas becomes a necessary heat source in this region. The practical process efficiency limit can be calculated for any given set of reaction and process conditions using a practical global internal pinch.

The results can be used to understand the room and opportunities for efficiency improvement.

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##### Notes

The authors declare no competing financial interest.

#### NOMENCLATURE

$E_{\text{H}_2}$  = total heating value of product hydrogen, kJ/s

$E_{\text{raw}}$  = total heating value of feed and fuel, kJ/s

$E_i$  = total heating value of stream  $i$ , kJ/s

$F_i$  = flow rate of stream  $i$ ,  $\text{Nm}^3/\text{s}$

$F_{\text{H}_2}$  = rate of hydrogen production,  $\text{Nm}^3/\text{s}$

$H_i$  = enthalpy of stream  $i$ , kJ/s

$Q_{\text{comb}}$  = heat of combustion, kJ/s

$Q_{\text{exp}}$  = thermal value of the export steam, kJ/s

$Q_{\text{ref}}$  = heat of reforming, kJ/s

$T_{\text{amb}}$  = ambient temperature, K

$T_b$  = boundary temperature, K

$T_{\text{dew}}$  = dew point of syngas, K

$T'_{\text{dew}} = T_{\text{dew}} - \Delta T_{\text{pinch}}$ , K

$T_{\text{exp}}$  = export steam temperature, K

$T_i$  = temperature of stream  $i$  entering or leaving the global heat exchanger, K

$T_s$  = temperature of syngas and flue gas when they are equal, K

$T_{\text{SG}}$  = syngas temperature, K

$T_{\text{stack}}$  = stack temperature, K

$\Delta T_{\text{pinch}}$  = temperature approach at the global pinch point, K

$\varepsilon$  = specific energy consumption of hydrogen production, kJ/ $\text{Nm}^3$

$\eta$  = thermal efficiency

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