

# Stoichiometric analysis of autothermal fuel processing

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## Abstract

Fuel processing is one of the major processes for generation of hydrogen for fuel cells. Stoichiometric analysis is used to develop a general framework for comparison of fuel reforming data, in the full range of steam reforming (SR) to combustion. This framework is then applied to determine the reforming reaction space for methanol, ethanol, methane, propane, isooctane, dodecane, and hexadecane. A simple approach is proposed for determination of the thermal efficiency for autothermal reforming (ATR) of a generalized fuel based on fuel atomic analysis and oxygen consumption.

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## 1. Introduction

The development of fuel cells is promised to enable the distributed generation of electricity in the near future. However, the infrastructure for production and distribution of hydrogen, the fuel of choice for fuel cells, is currently lacking. Efficient production of hydrogen from fuels that have existing infrastructure (e.g., natural gas or gasoline) would remove a major roadblock for acceptance of fuel cells for distributed power generation.

There are a number of fuel processing technologies for hydrogen generation from hydrocarbon fuels and oxygenates, but in actuality these technologies span combustion and partial oxidation (POX) through steam reforming (SR) [1]. Autothermal reforming (ATR) combines POX and SR, in a single process. POX reaction is exothermic or produces heat, while SR reaction is endothermic and heat must be generated external to the reformer process. Other exothermic reactions that may simultaneously occur in ATR include water gas shift (WGS) and methanation reactions. Typically, ATR reactions are considered to be thermally self-sustaining, and therefore, do not produce or consume external thermal energy. Catalysts are commonly used to enhance the reaction rate of the reforming processes at lower temperatures.

Independent parameters that affect the performance of an ATR reactor are inlet feed temperature, steam-to-carbon ratio (S/C), oxygen-to-carbon ratio (O<sub>2</sub>/C), and pressure. S/C and O<sub>2</sub>/C are defined as the ratio of H<sub>2</sub>O and O<sub>2</sub> feed

to the reaction relative to carbon in the fuel on a molar basis respectively. Dependent parameters include reformat outlet temperature, conversion and reactor heat loss.

In this study, a general framework for comparison of fuel reforming data, in the full range of steam reforming to combustion, is developed based on stoichiometric analysis of autothermal reforming. This framework is then applied to determine the reforming reaction space and efficiency for various hydrocarbon fuels and oxygenates. H<sub>2</sub> yield from fuel processing is determined based on energy and material balance coupled with chemical equilibrium requirements. The assumptions inherent in the ATR energy and material balance are as follows.

- Complete consumption of O<sub>2</sub> without formation of carbon soot, which is a reasonable assumption at a S/C level of 2 or above [2].
- The carbon in the fuel is reformed to CH<sub>4</sub>, CO or CO<sub>2</sub> only. For reforming of methane and oxygenated fuels, CO and CO<sub>2</sub> constitute the only carbon containing reforming products [3].
- SR, WGS and methanation (for non-oxygenated fuels) reactions are assumed to be at equilibrium at ATR outlet temperature. This is again a reasonable assumption based on previous studies [4].
- Adiabatic reaction.

The thermal efficiency of an autothermal reforming process is usually determined by multiplying the hydrogen yield by the ratio of hydrogen and fuel lower heating values (LHV). However, this approach overestimates the efficiency since it neglects to account for the heat input to the reactor.

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Table 1  
Fuel properties

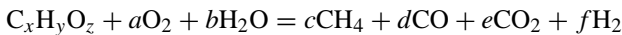
Fuel, $C_xH_yO_z$	$x$	$y$	$z$	Maximum yield = $(y/2) + 2x - z$	$\Delta H_f^\circ$ (kJ/mol) @ 25 °C	LHV (kJ/mol)
Hydrogen	0	2	0	1	0	229.16
Methanol	1	4	1	3	-178.96	663.40
Ethanol	2	6	1	6	-203.59	1251.96
Methane	1	4	0	4	-56.89	785.47
Propane	3	8	0	10	-66.86	2001.89
Isooctane	8	16	0	24	-174.33	4731.24
Dodecane	12	26	0	37	-195.10	7392.41
Hexadecane	16	34	0	49	-248.52	9791.77

The reference point for all enthalpies is 0° absolute.

In a previous study, the efficiency for autothermal reforming of a generalized fuel was determined to be dependent on fuel atomic analysis and fuel heat of formation by assuming maximum efficiency at the thermoneutral point [5]. Other researchers have determined the efficiency of a steam reformer to be only dependent on fuel atomic analysis and S/C by assuming a minimum S/C of 2 [6]. In this study, the efficiency of the fuel processing, in the full range of combustion to steam reforming, is shown to be only dependent on fuel atomic analysis and  $O_2/C$  without any assumptions. Based on this simple approach, the efficiency of autothermal reforming of methane, propane, isooctane, dodecane, and hexadecane is compared.

## 2. Reforming reaction space

ATR reaction stoichiometrics for a generalized fuel,  $C_xH_yO_z$ , can be represented as:



where  $a$  is  $O_{2,Feed}/C_{xH_yO_z,Reformed}$ ,  $b$  the  $H_2O_{Reacted}/C_{xH_yO_z,Reformed}$ ,  $c$  the  $CH_{4,Reformate}/C_{xH_yO_z,Reformed}$ ,  $d$  the  $CO_{Reformate}/C_{xH_yO_z,Reformed}$ ,  $e$  the  $CO_{2,Reformate}/C_{xH_yO_z,Reformed}$ , and  $f$  the  $H_{2,Reformate}/C_{xH_yO_z,Reformed}$ .

The above assumes that all  $O_2$  is consumed in the ATR without formation of carbon soot. Based on atomic balance for O, C and H, it can be shown that:

$$b = d + 2e - z - 2a$$

$$c = x - d - e$$

$$f = \frac{y}{2} + b - 2c$$

Combining all three equations and rearranging:

$$f = \left( \frac{y}{2} + 2x - z \right) - 2a - (d + 4c) \quad (1)$$

The above equation indicates that maximum theoretical hydrogen yield occurs when all the carbon in the fuel is reformed to  $CO_2$  (i.e., no  $CH_4$  or  $CO$  produced), which is consistent with previous literature [5]. For maximum hydrogen

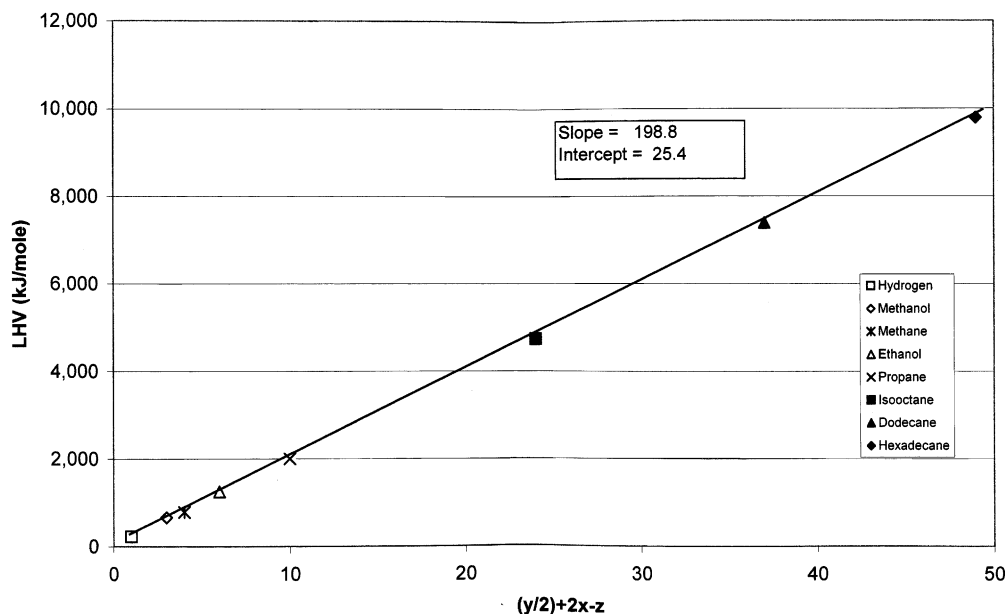


Fig. 1. Maximum hydrogen yield for steam reforming of various fuels.

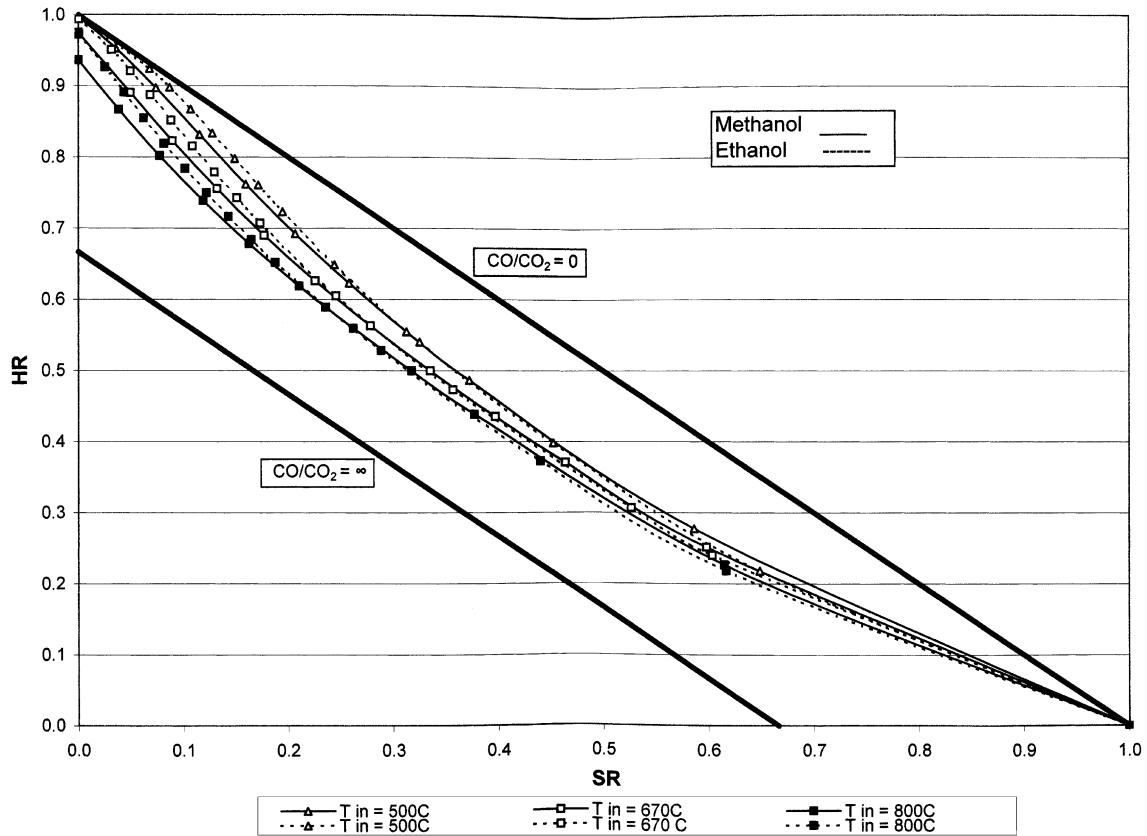


Fig. 2. No methanation, S/C = 3, P = 5 psig (136 kPa).

yield, Eq. (1) reduces to:

$$f_{\max} = \left(\frac{y}{2} + 2x - z\right) - 2a \quad (2)$$

Table 1 summarizes the values of  $(y/2 + 2x - z)$ , standard heat of formation and LHV for a number of fuels and Fig. 1 shows the linear relationship between LHV and  $(y/2 + 2x - z)$ . Defining stoichiometric ratio (SR) as the ratio of oxygen reacted to stoichiometric oxygen required for combustion, the maximum hydrogen yield for any fuel can be represented by the following equation:

$$\frac{f_{\max}}{y/2 + 2x - z} = 1 - SR \quad (3)$$

where  $SR = 2a/(y/2 + 2x - z)$

### 3. Methanol and ethanol

Let us first determine the ATR reaction space for an oxygenated fuel where methanation reaction can be assumed to be negligible [2]. Assuming no  $CH_4$  is produced in the reformer, Eq. (1) reduces to:

$$f = \left[\left(\frac{y}{2} + (A - 2)x - z\right)\right] - 2a \quad (4)$$

where  $A = [3(d/e) + 4]/[(d/e) + 1]$  and,  $3 \leq A \leq 4$ .

Dividing Eq. (4) by  $(y/2 + 2x - z)$ , we would have:

$$HR = \frac{y/2 + (A - 2)x - z}{y/2 + 2x - z} - SR \quad (5)$$

where hydrogen ratio (HR) is defined as the ratio of the moles of  $H_2$  produced per moles of fuel reformed to  $(y/2 + 2x - z)$ . HR is a normalized hydrogen yield, where  $HR = 1$  represents the maximum hydrogen yield for reforming of a given fuel. Eq. (5) shows that on a plot of HR versus SR, lines corresponding to  $CO/CO_2 = 0$ ,  $CO/CO_2 = \infty$ ,  $SR = 0$  and  $HR = 0$  constitute the ATR reaction space in the range of steam reforming to combustion for any fuel where methane is not produced.

Fig. 2 shows the adiabatic reactor operating lines at various reformer inlet temperatures for methanol and ethanol at reactor pressure of 5 psig (136 kPa) and S/C of 3, respectively. This figure shows that lower inlet temperature and higher S/C will result in higher HR for a given SR for both methanol and ethanol.

It is interesting to note that methanol and ethanol have an identical ATR reaction space. This is because  $(y/2 + x - z)/(y/2 + 2x - z)$ , which is the y-intercept for the line representing  $CO/CO_2 = \infty$ , happens to be 0.667 for both methanol and ethanol. Eventhough, Fig. 2 is similar to the reactor operating lines for methane autothermal reforming [1], the value of  $(y/2 + x - z)/(y/2 + 2x - z)$  for methane

is 0.75 and hence the ATR reaction space for methane is somewhat smaller compared to methanol or ethanol.

#### 4. Methane, propane, isooctane, dodecane and hexadecane

Figs. 3–5 show the reaction space and the effect of inlet temperature on  $H_2$  yield for autothermal reforming of a number of fuels at  $S/C = 3$ . In these plots of SR versus HR, the equilateral triangle bounded by  $f = 0$ ,  $SR = 0$  and Eq. (3) constitutes the ATR reaction space in the full range of combustion to steam reforming for any fuel. It is important to mention that the ATR reaction space is independent of conversion,  $S/C$ , pressure, temperature, heat loss, assumption of equilibrium, or choice of fuel. Figs. 3–5 show that higher inlet temperature generally yields more hydrogen with the maximum hydrogen yield shifting to a lower SR at a given  $S/C$ . Table 2 summarizes the maximum  $H_2$  yields and provides the reactor inlet and outlet temperatures for the reforming data shown in Figs. 3–5. These figures show that HR (i.e. normalized hydrogen yield) increases and experiences a maximum with respect to SR for all fuels. The beneficial effects of increasing inlet feed temperature and fuel LHV on the maximum HR are shown in Figs. 6 and 7.

#### 5. Efficiency

The reformer thermal efficiency is commonly obtained by multiplying the hydrogen yield by the ratio of LHV of  $H_2$  to fuel. However, this standard definition may result in efficiencies greater than 100% as discussed elsewhere [6]. In addition to the fuel that is reformed to hydrogen, extra fuel is necessary to supply the required heat for the reforming process. This extra fuel provides external heat to a steam reformer, whereas for an autothermal reformer, the extra fuel is consumed in the reactor to provide internal heat. A more accurate approach, proposed in this study, is to determine the fuel processor efficiency by dividing the hydrogen yield by  $f_{max}$ , which represents the maximum theoretical hydrogen yield at a given oxygen level.

To see how the proposed approach compares to the standard method of determining the fuel processor efficiency, let us express the ratio of hydrogen and fuel LHVs in terms of standard heats of formation of the respective combustion products:

$$\frac{LHV_{H_2}}{LHV_{Fuel}} = \frac{-\Delta H_{f,H_2O(g)}^\circ}{\Delta H_{f,Fuel}^\circ - x\Delta H_{f,CO_2}^\circ - (y/2)\Delta H_{f,H_2O(g)}^\circ} \quad (6)$$

Consider the autothermal reforming of a generalized fuel for maximum hydrogen yield (i.e., no  $CH_4$  or  $CO$

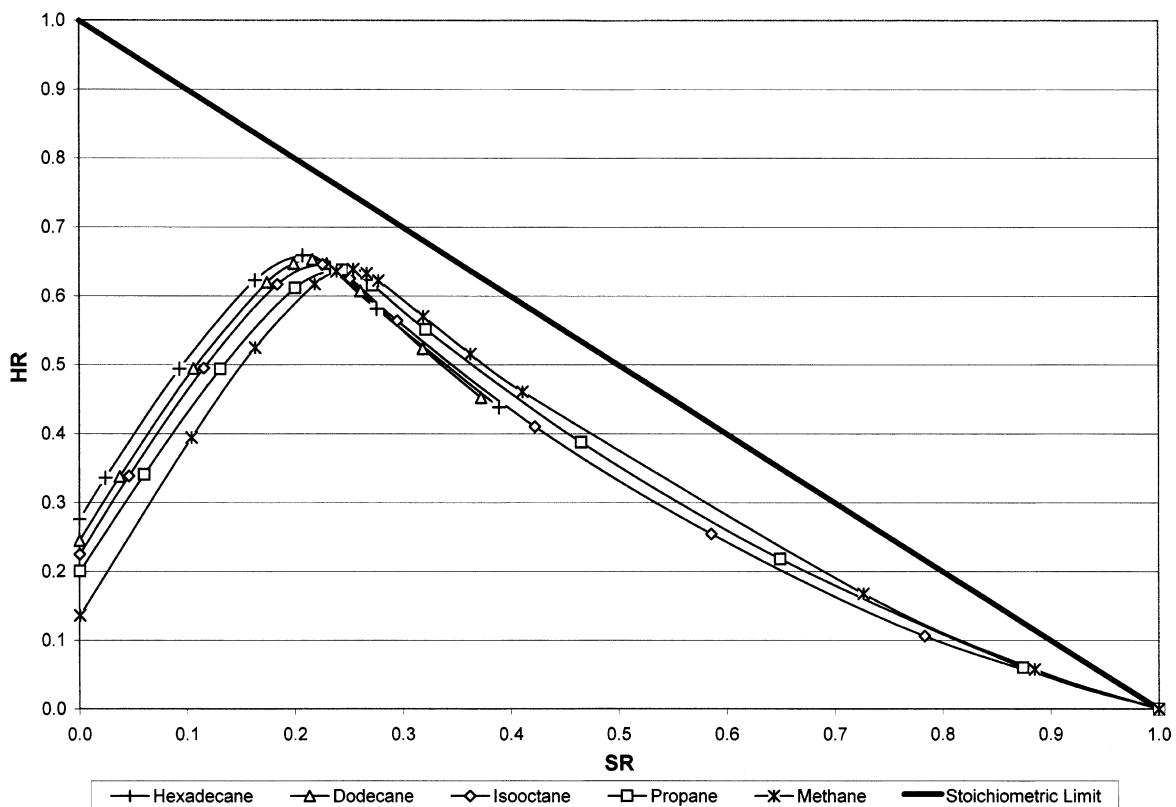


Fig. 3. Fuel reforming, inlet temperature = 500 °C,  $S/C = 3$ ,  $P = 5$  psig (136 kPa).

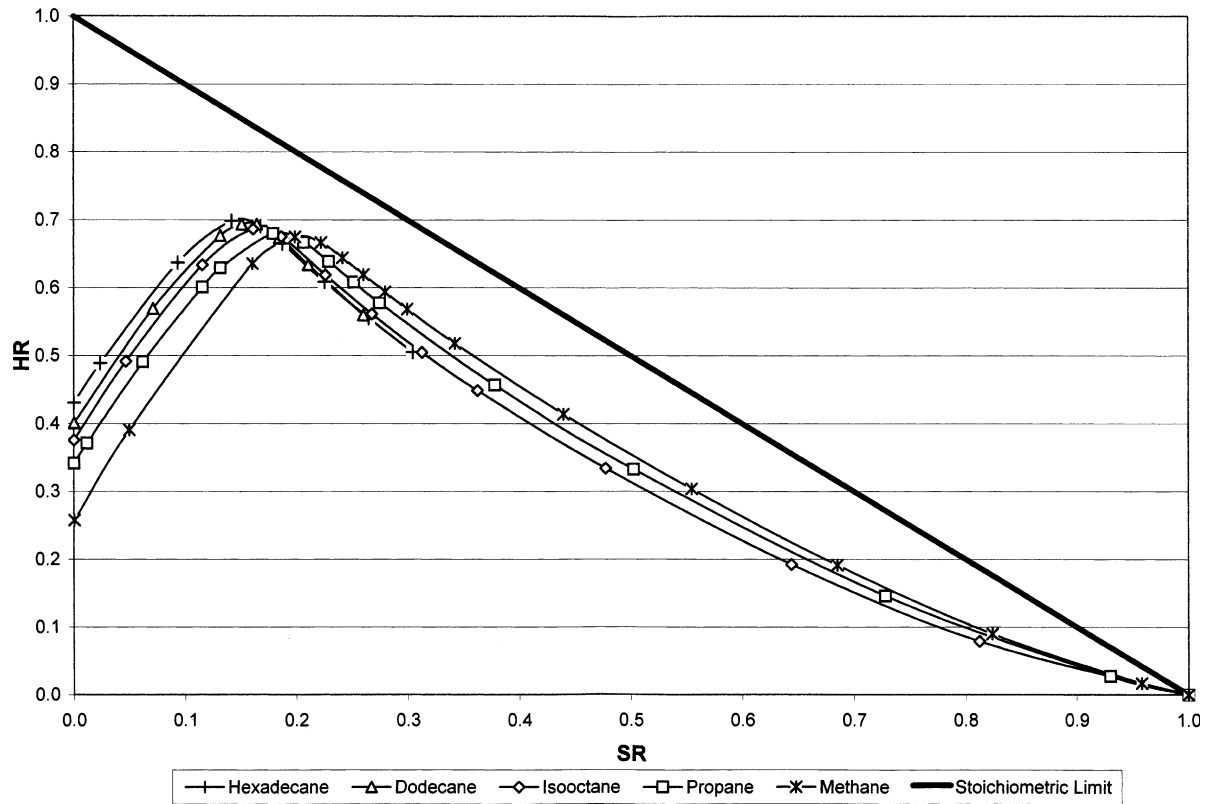


Fig. 4. Fuel reforming, inlet temperature = 670 °C, S/C = 3, P = 5 psig (136 kPa).

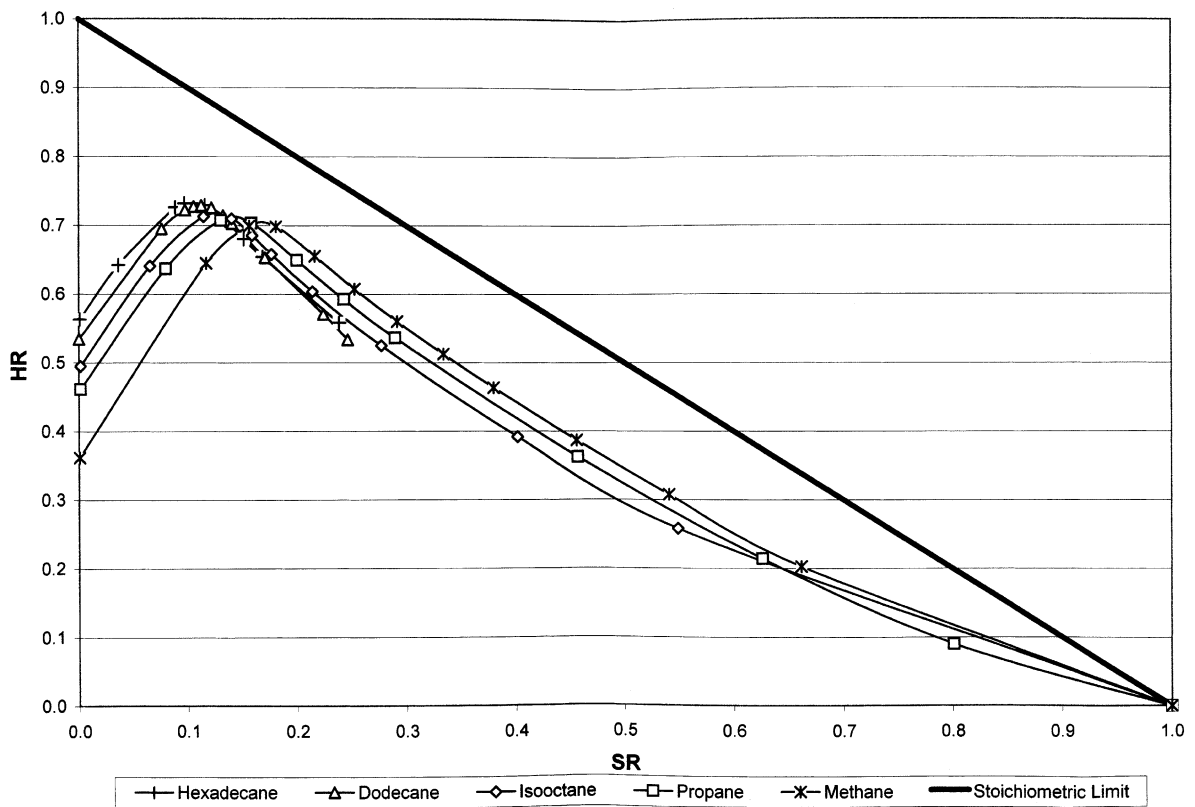
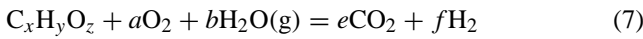


Fig. 5. Fuel reforming, inlet temperature = 800 °C, S/C = 3, P = 5 psig (136 kPa).

Table 2  
Maximum normalized H<sub>2</sub> yield for various fuels

Fuel	SR	S/C	Pressure (psig) (kPa)	T <sub>in</sub> (°C)	T <sub>out</sub> (°C)	Maximum HR
Methane	0.254	3	5 (136)	500	649	0.639
	0.199	3	5 (136)	670	649	0.675
	0.181	3	5 (136)	800	649	0.698
Propane	0.244	3	5 (136)	500	649	0.638
	0.179	3	5 (136)	670	649	0.680
	0.131	3	5 (136)	800	649	0.707
Isooctane	0.226	3	5 (136)	500	649	0.646
	0.162	3	5 (136)	670	649	0.687
	0.115	3	5 (136)	800	649	0.713
Dodecane	0.217	3	5 (136)	500	649	0.653
	0.165	3	5 (136)	670	677	0.694
	0.112	3	5 (136)	800	677	0.729
Hexadecane	0.207	3	5 (136)	500	649	0.659
	0.142	3	5 (136)	670	649	0.699
	0.116	3	5 (136)	800	663	0.729

produced):



The water in Eq. (7) is in form of steam in recognition of high temperatures necessary for fuel reforming. Based on atomic balances for O and C, it can be shown that:

$$b = 2x - z - 2a$$

$$e = x$$

The standard heat of reaction for Eq. (7) is:

$$\Delta H_R^\circ = -\Delta H_{f,Fuel}^\circ + x \Delta H_{f,CO_2}^\circ - (2x - z - 2a) \Delta H_{f,H_2O(g)}^\circ \quad (8)$$

Substituting Eq. (8) into Eq. (6) and assuming that LHV<sub>fuel</sub> and ΔH<sub>R</sub><sup>o</sup> refer to the same state of fuel:

$$\frac{LHV_{H_2}}{LHV_{Fuel}} = \frac{-\Delta H_{f,H_2O(g)}^\circ}{-(y/2 + 2x - z - 2a) \Delta H_{f,H_2O(g)}^\circ - \Delta H_R^\circ} \quad (9)$$

If we divide the numerator and denominator with -ΔH<sub>f,H<sub>2</sub>O(g)</sub><sup>o</sup> and rearrange:

$$\frac{LHV_{H_2}}{LHV_{Fuel} + \Delta H_R^\circ} = \frac{1}{(y/2 + 2x - z)(1 - SR)} \quad (10)$$

The following expression for the thermal efficiency, η, can be obtained by substituting Eq. (3) in (10):

$$\eta = \frac{\text{hydrogen yield} \times LHV_{H_2}}{LHV_{Fuel} + \Delta H_R^\circ} = \frac{f}{f_{max}} \quad (11)$$

where ΔH<sub>R</sub><sup>o</sup> represents the heat necessary to produce maximum hydrogen from autothermal reforming of a given fuel. The efficiency can also be expressed in terms of HR by substituting Eq. (3) into (11):

$$\eta = \frac{HR}{1 - SR} \quad (12)$$

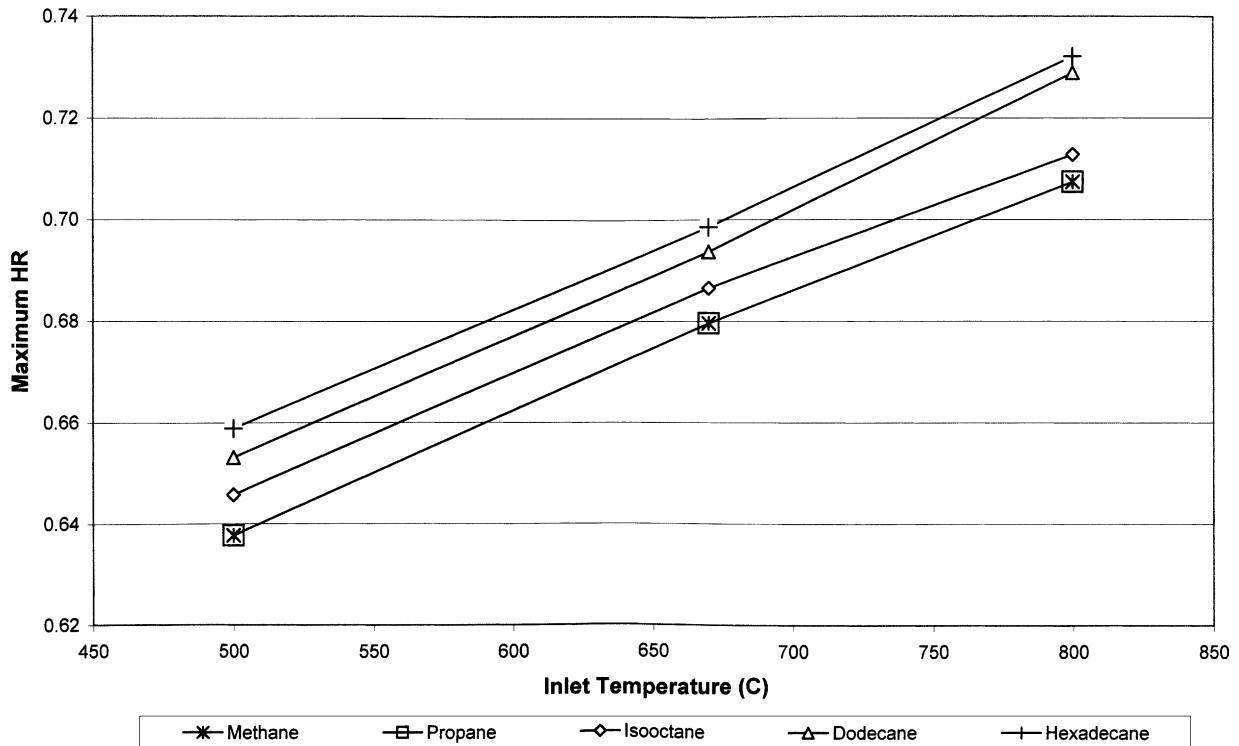


Fig. 6. Fuel reforming, S/C = 3, P = 5 psig (136 kPa).

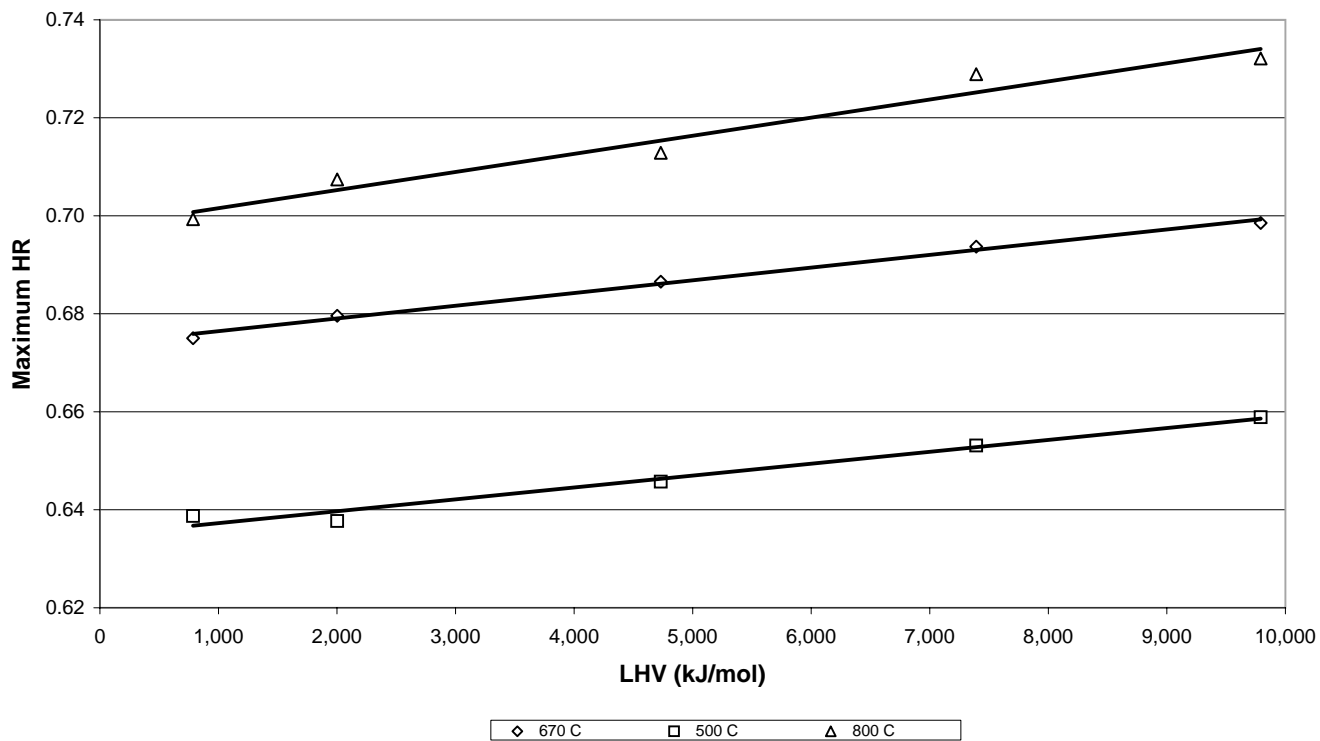


Fig. 7. Fuel reforming, S/C = 3, P = 5 psig (136 kPa).

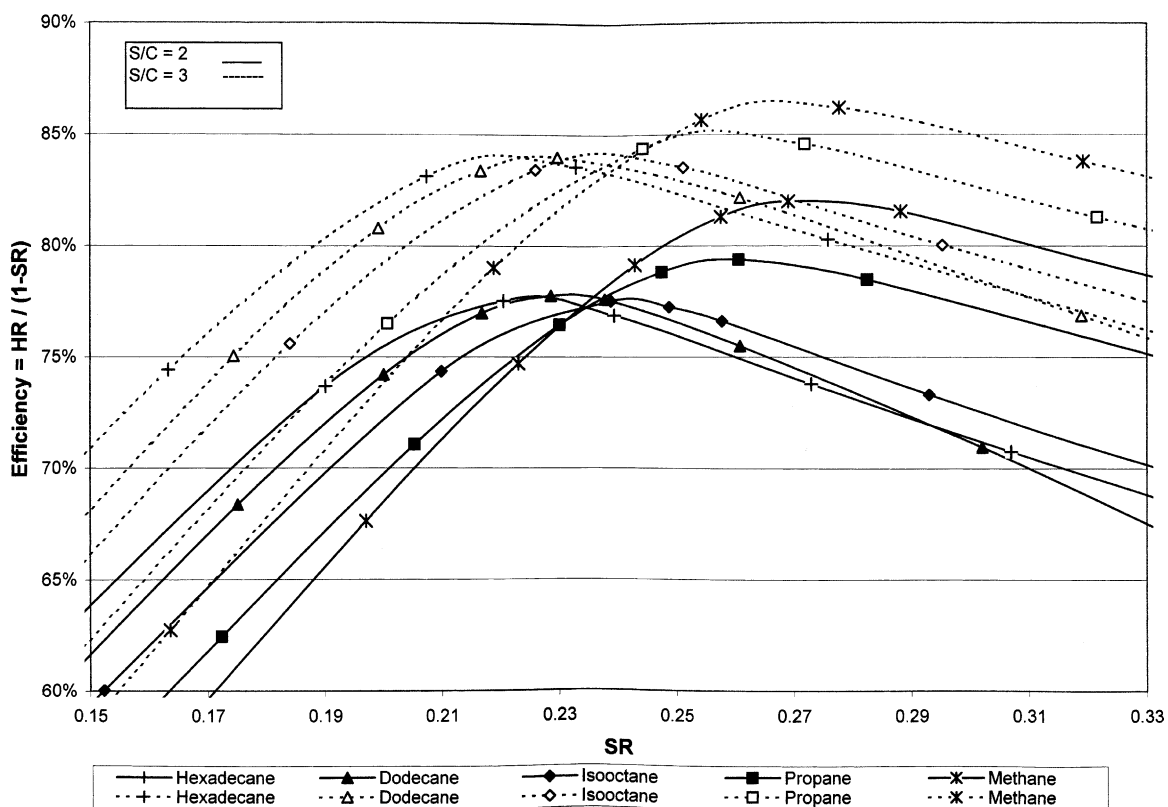


Fig. 8. Fuel reforming, inlet temperature = 500 °C, P = 5 psig (136 kPa).

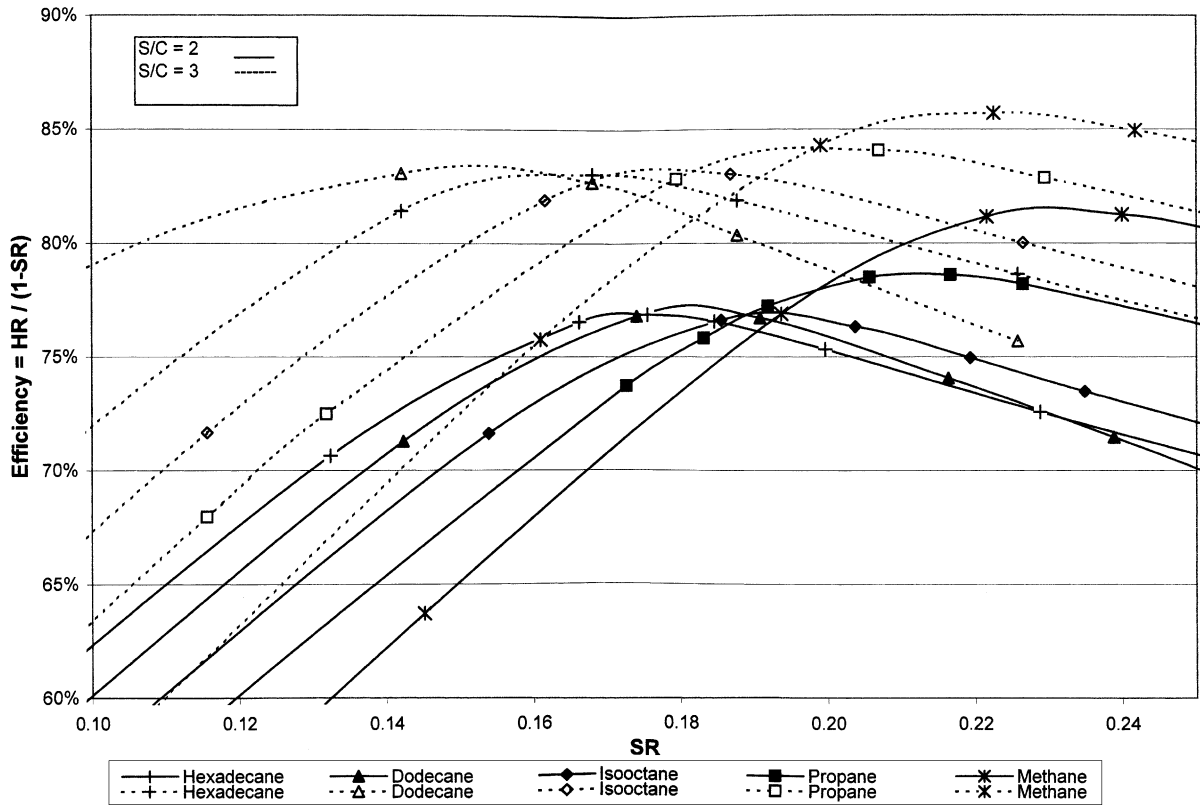


Fig. 9. Fuel reforming, inlet temperature = 670 °C,  $P = 5$  psig (136 kPa).

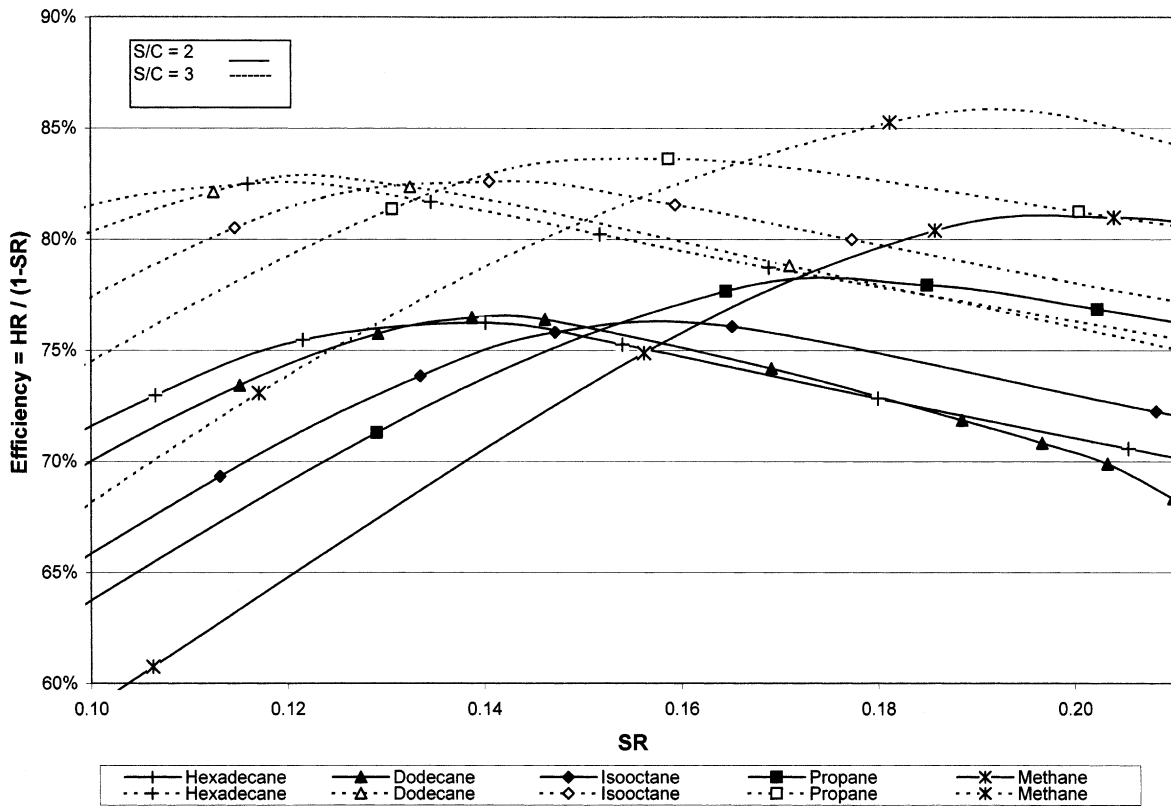


Fig. 10. fuel reforming, inlet temperature = 800 °C,  $P = 5$  psig (136 kPa).



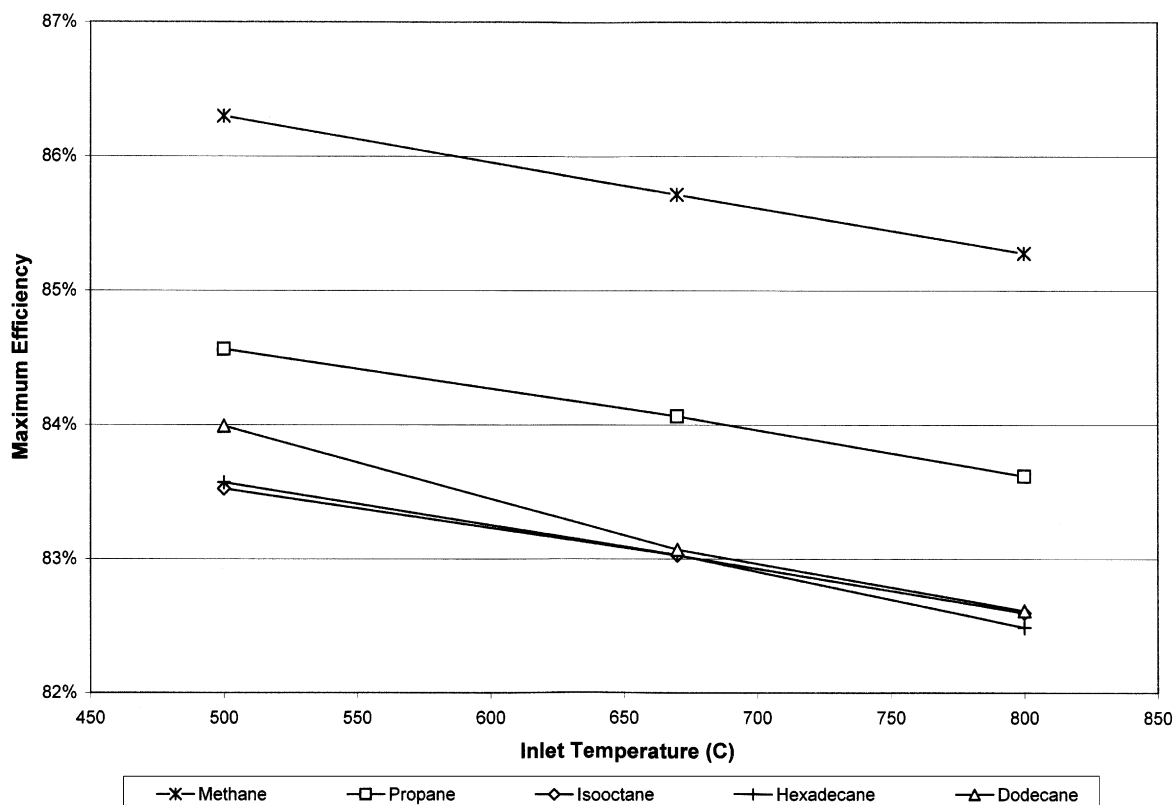


Fig. 11. Fuel reforming, S/C = 3,  $P = 5$  psig (136 kPa).

Figs. 8–10 show the efficiency, as defined by Eq. (12), for hexadecane, dodecane, isooctane, propane and methane as a function of SR for various inlet temperatures at S/C = 3 and 2, assuming adiabatic conditions. Fig. 11 shows that methane has the highest efficiency compared to other fuels, consistent with previous literature [5,6], and the efficiency increases as the inlet temperature decreases. This is somewhat counterintuitive since higher inlet temperatures results in higher hydrogen yield. However, higher inlet temperatures lead to lower SR, which increases the denominator of Eq. (12), hence resulting in lower efficiency.

Eq. (12) does not explicitly show the effect of S/C and water consumption in the reforming process. Substituting Eq. (1) into the numerator of Eq. (11):

$$\eta = 1 - \frac{d + 4c}{f_{\max}} \quad (13)$$

Let us consider the idealized autothermal reforming reaction, where CO and CH<sub>4</sub> are not produced (i.e.,  $\eta = 1$ ):



Using stoichiometric analysis, we can drive the following relationship between water and oxygen consumption:

$$b = \frac{x}{2} \left( \frac{S}{C} + 2 \right) - \frac{z}{2} - a \quad (15)$$

The above equation shows that for a given oxygen feed to the reactor (i.e., SR), water consumption,  $b$ , increases with

S/C. This in turn reduces CO and CH<sub>4</sub> formation in the autothermal reactor by the WGS and reverse methanation reactions, resulting in higher efficiency.

It is important to note the limitations of Eq. (12) for determination of efficiency. The maximum standard heat of reaction for autothermal reforming is not necessarily represented by  $\Delta H^\circ_R$ , as defined by Eq. (8). Due to the exothermic nature of the WGS reaction, the maximum standard heat of reaction would occur when all carbon in the fuel is reformed to CO. The standard heat of reaction also does not include the total heat required for bringing the reactants to the temperature of the reaction. However, the implication of the first limitation is small and the second limitation is mitigated by the inclusion of the oxygen consumed in the autothermal reaction (i.e., SR) in Eq. (12).

## 6. Conclusion

The stoichiometric analysis of the autothermal reaction for a generalized fuel is used to determine the reforming reaction space for methanol, ethanol, methane, propane, isooctane, dodecane, and hexadecane, in the full range of steam reforming to combustion. A simple approach is proposed for determination of the thermal efficiency for autothermal reforming based on fuel atomic analysis and oxygen consumption. The thermal efficiency appears to increase with

S/C and to be inhibited by higher inlet temperatures. The simulation data and conclusions of this paper are applicable to any ATR regardless of size and are independent of feed flowrates.

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