COMPARISON OF AUTOTHERMAL REFORMING FOR HYDROCARBON FUELS

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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, but in actuality these technologies are points along a spectrum that spans combustion and partial oxidation (POX) through steam reforming (SR) (1). Autothermal reforming (ATR) combines partial oxidation (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_2/C), and pressure. S/C and O_2/C are defined as the ratio of H_2O and O_2 feed to the reaction relative to carbon in the fuel on a molar basis respectively. Dependent parameters include reformate 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 for various hydrocarbons fuels. H_2 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_2 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_4, CO or CO_2 only. For reforming of methane, CO and CO_2 constitute the only carbon containing reforming products (3).
- SR, WGS and methanation (for non-methane 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

Generalized Reforming Reaction Space

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

$$C_xH_YO_Z + a\,O_2 + b\,H_2O = c\,CH_4 + d\,CO + e\,CO_2 + f\,H_2$$

Where,

Table 1 - Fuel Properties

Fuel - $C_XH_YO_Z$	X	Y	Z	Max Yield = (y/2)+2x-z	$\Delta°H_f$ (kJ/mole) @ 25°C	LHV (kJ/mole)
Hydrogen	0	2	0	1	0	229.16
Methanol	1	4	1	3	-178.96	663.40
Ethanol	2	6	1	6	-203.59	1,251.96
Methane	1	4	0	4	-56.89	785.47
Propane	3	8	0	10	-66.86	2,001.89
Isooctane	8	16	0	24	-174.33	4,731.24
Dodecane	12	26	0	37	-195.10	7,392.41
Hexadecane	16	34	0	49	-248.52	9,791.77

The reference point for all enthalpies is 0 degrees absolute.

$a = O_{2,\,Feed} / C_xH_YO_{Z,Reformed}$
$b = H_2O_{Reacted} / C_xH_YO_{Z,Reformed}$
$c = CH_{4,Reformate} / C_xH_YO_{Z,Reformed}$
$d = CO_{Reformate} / C_xH_YO_{Z,Reformed}$
$e = CO_{2,Reformate} / C_xH_YO_{Z,Reformed}$
$f = H_{2,Reformate} / C_xH_YO_{Z,Reformed}$

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:

$b = d+2e-z-2a$
$c = x-d-e$
$f = y/2+b-2c$

Combining all three Equations and rearranging:

$$f = (y/2+2x-z) - 2a - (d+4c) \quad (1)$$

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 yield, Equation (1) reduces to:

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

Table 1 summarizes the values of (y/2+2x-z), standard heat of formation and LHV for a number of fuels and Figure 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:

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

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

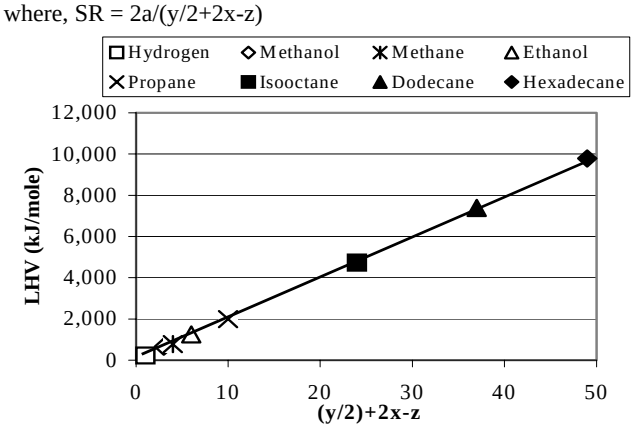

Figure 1. Maximum hydrogen yield for steam reforming of various fuels

Methane Reforming Reaction Space

ATR reaction stoichiometrics for methane fuel can be represented as:

$CH_4 + a\ O_2 + b\ H_2O = c\ CO + d\ CO_2 + e\ H_2$

Where,

$a = O_{2,\ Feed}/(CO+CO_2)_{Reformate} = (O_2/CH_4\ Feed)/X$

$b = H_2O_{Reacted}/(CO+CO_2)_{Reformate}$

$c = CO_{Reformate}/(CO+CO_2)_{Reformate} = (CO/CH_4\ Feed)/X$

$d = CO_{2,Reformate}/(CO+CO_2)_{Reformate} = (CO_2/CH_4\ Feed)/X$

$e = H_{2,Reformate}/(CO+CO_2)_{Reformate} = (H_2/CH_4\ Feed)/X$

$X = CH_4\ Conversion = (CO+CO_2)_{Reformate}/(CO+CO_2+CH_4)_{Reformate}$

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:

$b = e-2 = (H_2/CH_4\ Feed)/X - 2$

$c = 2-2a-b$

$d = 2a+b-1$

If $c=0$ or $CO/CO_2=0$,

$e = 4-2a$

$b = 2-2a$ or $a = 1-0.5b$

$d = 1$

The above means that a plotted versus e versus a will be straight lines. The upper solid line in Figure 2 represent the case of $CO/CO_2=0$.

If $d=0$ or $CO/CO_2=\infty$,

$e = 3-2a$

$b = 1-2a$ or $a = 0.5-0.5b$

$c = 1$

The lower solid line in Figure 2 represents the case of $CO/CO_2=\infty$. In general, it can be shown that for a given CO/CO_2 in the reformate:

$e = A-2a$

Where, $A = [3\ (CO/CO_2)+4]/[(CO/CO_2)\ +1]$

and, $3 \le A \le 4$

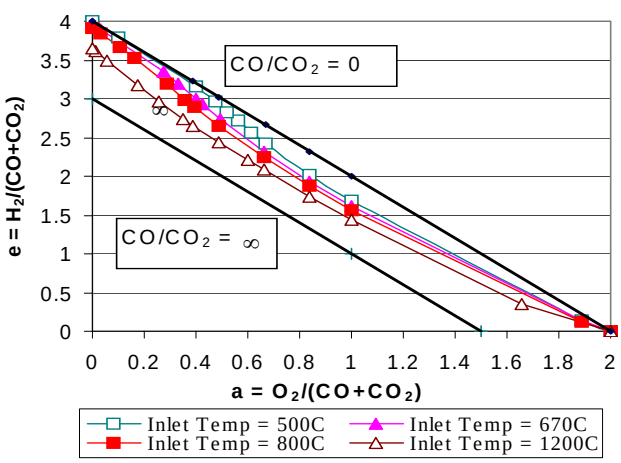

Figure 2. Refrming reaction space for methane at S/C = 6, and P = 97 psig (770 kPa)

ATR Fuel Comparison

Figures 3, 4 and 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 Hydrogen Ratio (HR), the equilateral triangle bounded by HR = 0, SR = 0 and Equation (3) constitutes the ATR reaction space in the full range of combustion to steam reforming for any fuel. 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. 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. Figures 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 Figures 3 to 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 Figures 6 and 7.

Table 2 - Maximum Normalized H_2 Yield for Various Fuels

Fuel	SR	S/C	Pressure psig (kPa)	T in (°C)	T out (°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

Conclusions

The stoichiometric analysis of the autothermal reaction for a generalized fuel is used to determine the reforming reaction space for methane, propane, isooctane, dodecane, and hexadecane, in the full range of steam reforming to combustion. A methodology is shown for normalizing hydrogen yield data to facilitate direct comparison. The hydrogen yield appears to increase with S/C and inlet temperatures for all fuels. The simulation data and conclusions of this paper are applicable to any ATR regardless of size and are independent of feed flowrates.

References

[1] Hagh, B.F. *International Journal of Hydrogen Energy*, **2003**, 28, 1369-1377.

[2] Douvartzides, S.L.; Coutelieris, F.A.; Demin, A.K.; Tsiakaras, P.E. *AIChE Journal*, **2003**, 49, 248-257.

[3] Ming, Q.; Healey, T.; Allen L., Irving, P. *Catalysis Today*, **2002**, 51-64.

[4] Brown, L.F. *International Journal of Hydrogen Energy*, **2001**, 26, 381-397.

[5] Ahmed, S.; Krumpelt, M. *International Journal of Hydrogen Energy*, **2001**, 26, 291-301.

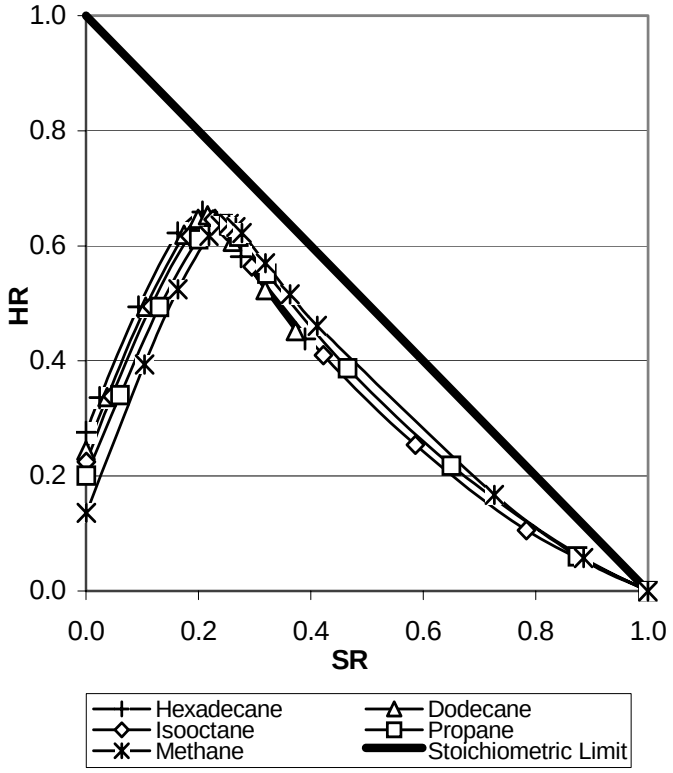

Figure 3. Inlet temperature = 500°C, S/C = 3, P = 5 psig (136 kPa)

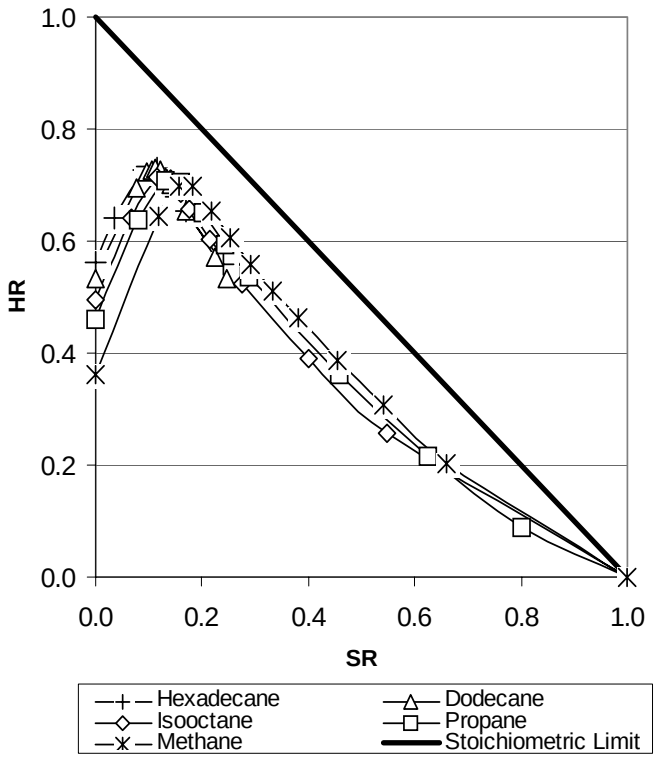

Figure 5. Inlet temperature = 800°C, S/C = 3, P = 5 psig (136 kPa)

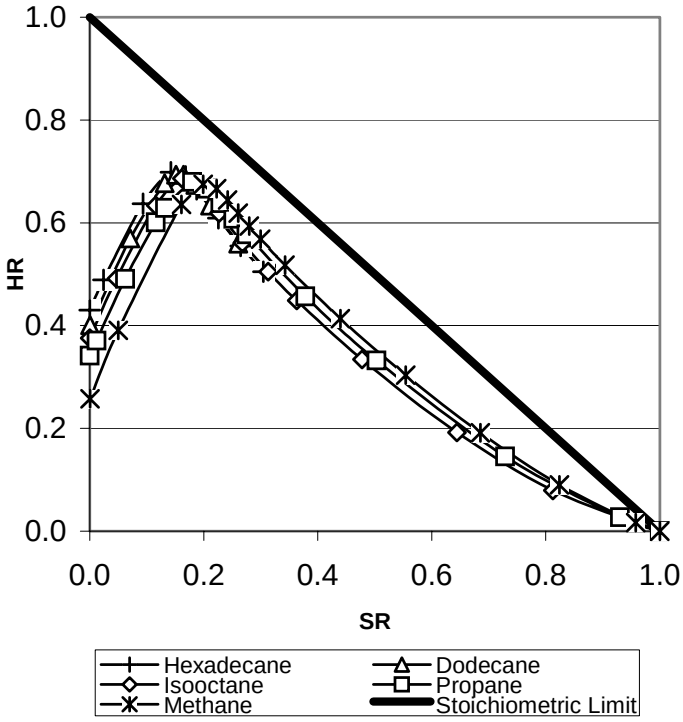

Figure 4. Inlet temperature = 670°C, S/C = 3, P = 5 psig (136 kPa)

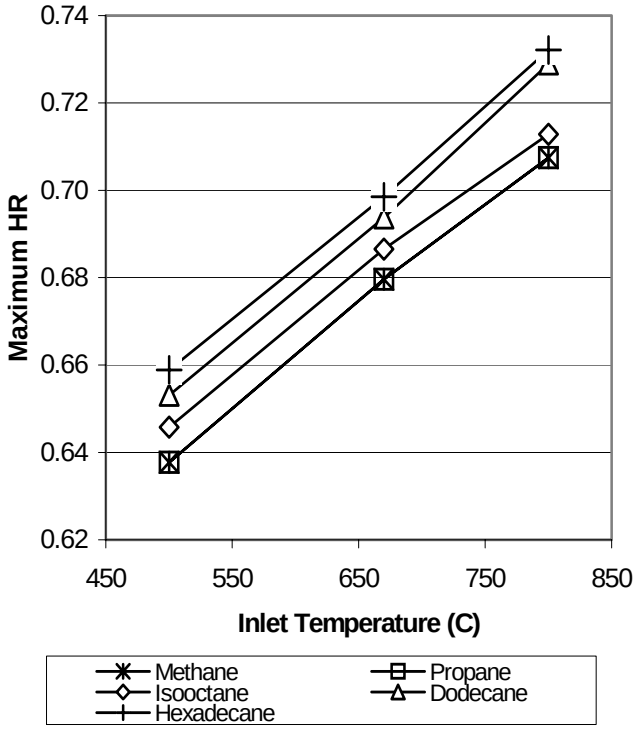

Figure 6. Maximum hydrogen yield at S/C = 3, P = 5 psig (136 kPa)

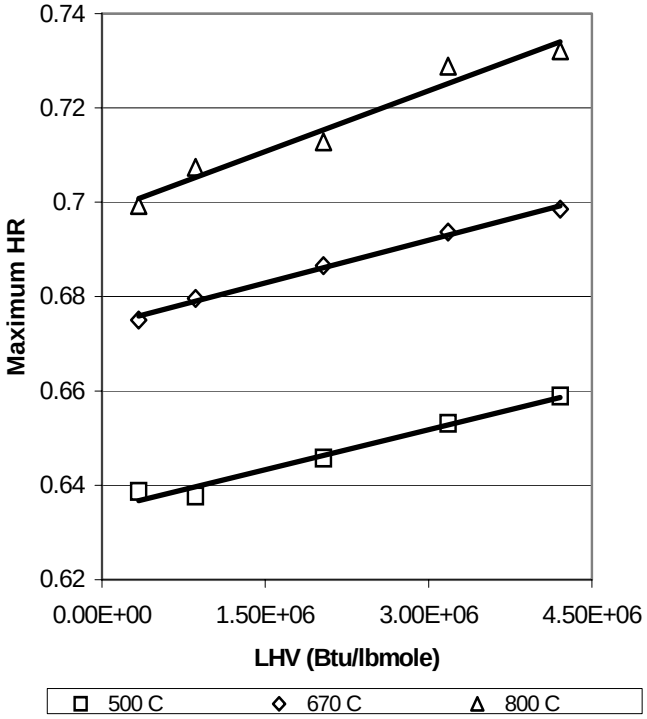

Figure 7. S/C = 3, P = 5 psig (136 kPa)