Task Report

Fuel Quality Assessment

Addendum to

U.S. Department of Energy
Contract No.
DE-FG36-98CH10942

Final Report
“Biomass Gasification Evaluation of Gas Turbine Combustion”

October 13, 2003

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Summary

This report provides a preliminary assessment of the potential for use in gas turbines and reciprocating gas engines of gases derived from biomass by pyrolysis or partial oxidation with air. Consideration was given to the use of mixtures of these gases with natural gas as a means of improving heating value and ensuring a steady gas supply.

Gas from biomass, and mixtures with natural gas, were compared with natural gas reformates from low temperature partial oxidation or steam reforming. The properties of such reformates were based on computations of gas properties using the ChemCAD computational tools and energy inputs derived from known engine parameters. In general, the biomass derived fuels compare well with reformates, so far as can be judged without engine testing. Mild reforming has potential to produce a more uniform quality of fuel gas from very variable qualities of natural gas, and could possibly be applied to gas from biomass to eliminate organic gases and condensibles other than methane.

Introduction and Background

The major effort of this program focused on the development of a process to produce a gas of medium heating value from a variety of biomass feedstocks. This work was reported in "Biomass Gasification Evaluation of Gas Turbine Combustion" (12/14/2000), and the process is being commercialized. Possible applications of the biogas include its use as a fuel for gas turbines and reciprocating engines. Biogas produced from the Battelle pilot-scale wood gasifier was used successfully to power a small gas turbine, alone and in combination with natural gas, after treatment to remove small amounts of heavy hydrocarbon gases and condensibles. The ability to blend the biogas with natural gas proved valuable in allowing continuous steady load operation when the biogas output was variable. Similar, but smaller, variations in gas output and quality may also occur in industrial scale biogas installations and as a result of seasonal variations in biomass availability. In such cases, consideration of biogas/natural gas rather than sole reliance on biogas can enhance the availability of the power plant and make the utilization of low cost biogas more attractive. Biogas from a pyrolysis based gasifier (as used in the Battelle studies) has hydrogen, carbon monoxide, and methane as its main combustible gases, unlike natural gas which is mainly methane.

In a gas turbine, the inclusion of hydrogen in the fuel increases flame speed and can make it impractical to use standard lean premix combustion systems, so that it is important to know and accommodate the combustion characteristics of both the biogas and blends containing biomass.

The use of biogas in reciprocating engines has received relatively little attention, but reciprocating engines dominate the market for distributed power installations especially in smaller sizes. Reciprocating engines, therefore, represent a large potential sector for the use of biogas, especially in locations where natural gas supplies are limited and costly. A good example is a 2.0 MW power plant which uses a gas produced from biomass by a process similar to that developed by Battelle to power a Jenbacher reciprocating gas engine[1]. In this case, it appears that biomass is the sole energy source, and the gas used has an unusually high heating value for a pure biogas, as shown in Table l.

Table l. Representative Properties of Biogas, Natural Gas, and 50/50 Mixtures

	H_2	CO	CO_2	CH_4	C_2H_6	C_3H_8	N_2	H_2O	LHV MJ/m^3	MW
Natural Gas	0	0	0	95	2.5	0.5	2	0	34.2	16.7
Reference Gas*	28.6	14.3	0	57.1	0	0	0	0		
Biogas ($ABPO_x$)	20	23	8	0	0	0	42	7	4.77	23.4
Biogas (Pyro)	22	38	16	14	3	0	0	7	13.6	22.5
50/50 NG/$ABPO_x$	19	11.5	4	47.5	1.25	0.25	22	3.5	19.5	19.9
50/50 NG/Pyro	11	19	8	54.5	2.75	0.25	1	3.5	23.9	19.5
Biogas (Pyro)[1]	35-40	22-25	20-25	10	0	0	3-5	0	<12	--

Notes: $ABPO_x$ – air blown partial oxidation process

Pyro – Pyrolysis process (Battelle)

Moisture content of biogases corresponds to saturation at 40 C (condition at scrubber outlet)

*Reference Gas analysis is based on reforming 20% of a pure methane fuel supply by steam reforming at stoichiometric conditions and remixing the reformate with the remaining 80% of the supply.

Reciprocating gas engine performance is sensitive to fuel properties, so that knowledge of the gas characteristics is of great importance, as discussed later.

Variations in natural gas quality are also a concern in both gas turbines and reciprocating engines, especially where the supply has received minimal processing. This situation applies in many important market areas, especially in oil and gas field installations and some gas pumping stations. Engine manufacturers must be prepared to match the specific user requirements by special combustor designs for gas turbines and by variations in compression ratio, speed, and output ratings in reciprocating engines. Natural gas reforming has been considered as a means to reduce some of the more troublesome constituents of natural gas and to produce a gas of less variable composition and combustion characteristics. This for example could benefit a user such as a natural gas producer with a multiplicity of engines of different fuel requirements by reducing the range of spare components to be kept in hand. The reformed gases, like biomass, are primarily hydrogen, carbon monoxide and methane plus inert gases.

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[1] Chellini, R., “Jenbacher Engine Running on Wood Gas”, Diesel & Gas Turbine WorldWide, July-Aug 2003, p. 58.

Scope

The scope of this study is to compare the compositions and characteristics of fuel gases prepared from biomass with those made by reforming natural gas, and to form a preliminary judgment about their suitability as engine fuels. Because the reforming processes would likely be required to utilize waste (exhaust) heat from the engines, this necessitates computation of reformer performances outside the range of conditions used in most current applications such as hydrogen production or producer gas production for chemical synthesis.

Preferred Characteristics of Gaseous Fuels for Engines

Gas turbines are in general able to utilize almost any clean combustible gas that does not produce any solid forming combustion product or ash. However, developments in the use of lean premix combustion systems to reduce NO_x formation impose special restrictions. In these systems, the air and gas must be thoroughly mixed before combustion is initiated. When the gas contains components that are readily ignited, spontaneous ignition may occur in the mixing passage ahead of the flame, which may damage hardware, especially in high pressure ratio engines with high compressor delivery temperatures. Fuel components such as the heavier hydrocarbons and hydrogen are therefore undesirable. In the combustion process after the mixing section, these components are important in deciding the heat release and radiation pattern of the flame, and more critically whether or not the flame will be stable. Although undesirable in the premixing stage, hydrogen is valuable here because of its wide range of flammability. Engine manufacturers are cautious about gases containing much hydrogen, but the possible benefits of hydrogen may be worth further study, in light of problems encountered with rough or unstable operation with weak mixtures. The heavier hydrocarbons are readily dealt with by reforming, but hydrogen is formed in the process.

Fuel gases for reciprocating engines should not contain constituents that are prone to auto-ignition, and they should have a high antiknock rating. For lean burn engines (analogous to lean premix situations in gas turbines), the flame speed is very important to ensure high heat release at the beginning of the power stroke and complete burnout of the fuel with environmentally acceptable levels of CO or aldehydes. Knock rating relates to auto ignition because knock occurs when gases ahead of the flame front ignite as pressure and temperature rise. An increase in flame speed reduces the incidence of knock by allowing the flame front to overtake incipient auto ignition centers. Hydrogen is beneficial in this respect. Testing in gasoline engines has shown clear benefits in substituting hydrogen up to about 20% of the fuel heating value.[2]

Antiknock rating of gaseous fuels is expressed in terms of a methane number which is determined experimentally. Methane number correlates well with composition of some

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[2] Anson, D., Hydrogen Fuel and Distributed Generation. Note prepared for DOE Chicago Operations by Battelle, Sept. 2002. Contract No. CCF05515 Proj. Pool 31366.

binary mixtures[3], as shown in Figure 1, and also with limiting compression ratio for a specific engine configuration[4] as shown in Figure 2[4]. It is not generally computable from gas composition, but this has been done empirically for a limited range of compositions of natural gas.[5]

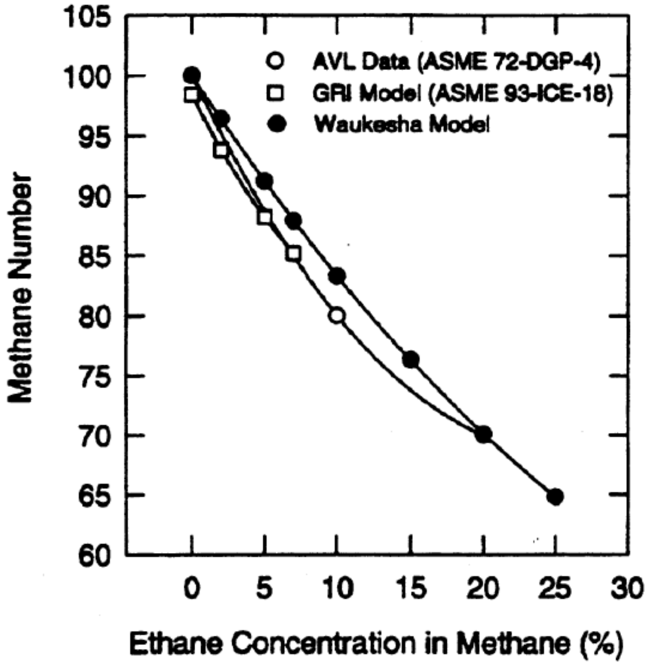

Figure 1. Comparison of the Waukesha Methane Number Model With the AVL and GRI Data

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[3] Calllahan, T. J., et al, "Engine knock Rating of Natural Gases--Expanding the Methane Number Database", ASME Paper Proc. 18th Fall Tech Conf, IC Engine Division.

[4] Callahan, T. J., Ryan, T. W., and King, S. R., "Engine Knock Rating of Natural Gases—Methane Number", ASME Paper 93-ICE-18.

[5] Sarge, et al. (Waukesha), "Method of Determining Knock Resistance Rating for Non-Commercial Grade Natural Gas, U.S. Patent 6,061,637.

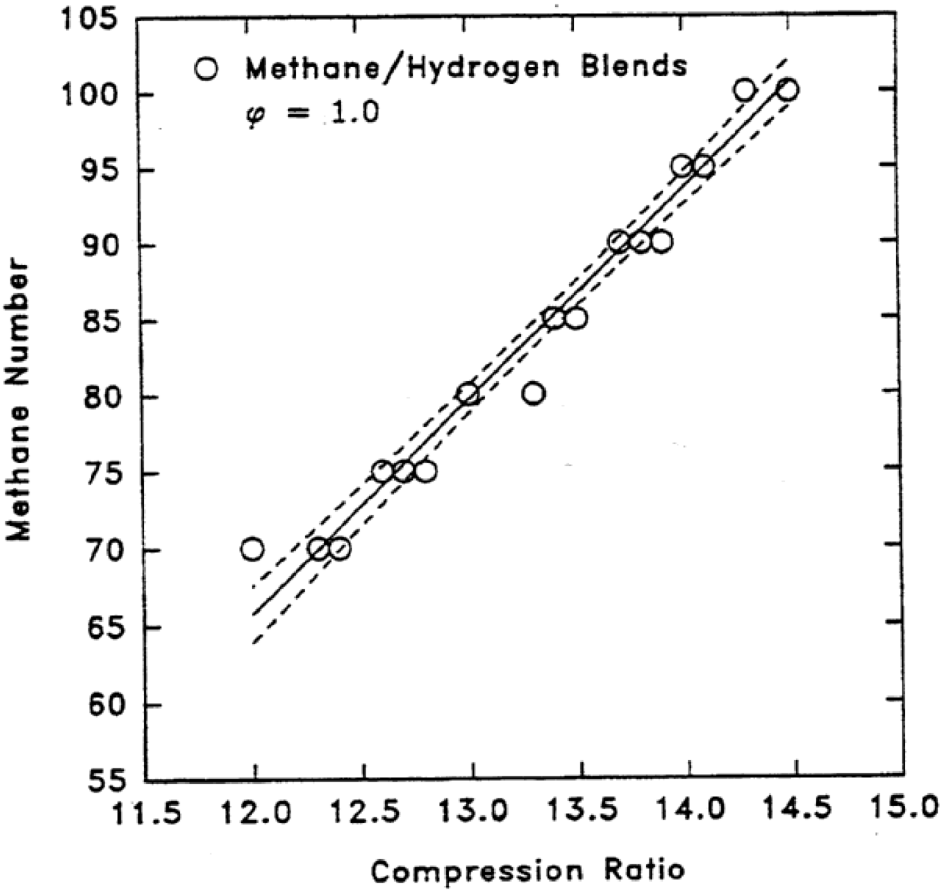

Figure 2. Methane Number Calibration at Φ = 1.0

Biomass Gasifier/Engine Integration

A biomass gasifier would operate independently of the engine it supplies and would be connected by a relatively simple delivery system, as shown in Figure 3. This diagram assumes that the gasifier includes means for cleaning and drying the gas sufficiently to avoid condensation in the delivery section. The delivery section incorporates a surge vessel to absorb short term fluctuations in the biogas supply rate and a flare to deal with overpressure. The isolation valve would be closed during gasifier start up and shown down, and probably would need to be backed by a manually operated valve for safety purposes. A gas compressor would be required only for gas turbine applications which have high pressure requirements, and might

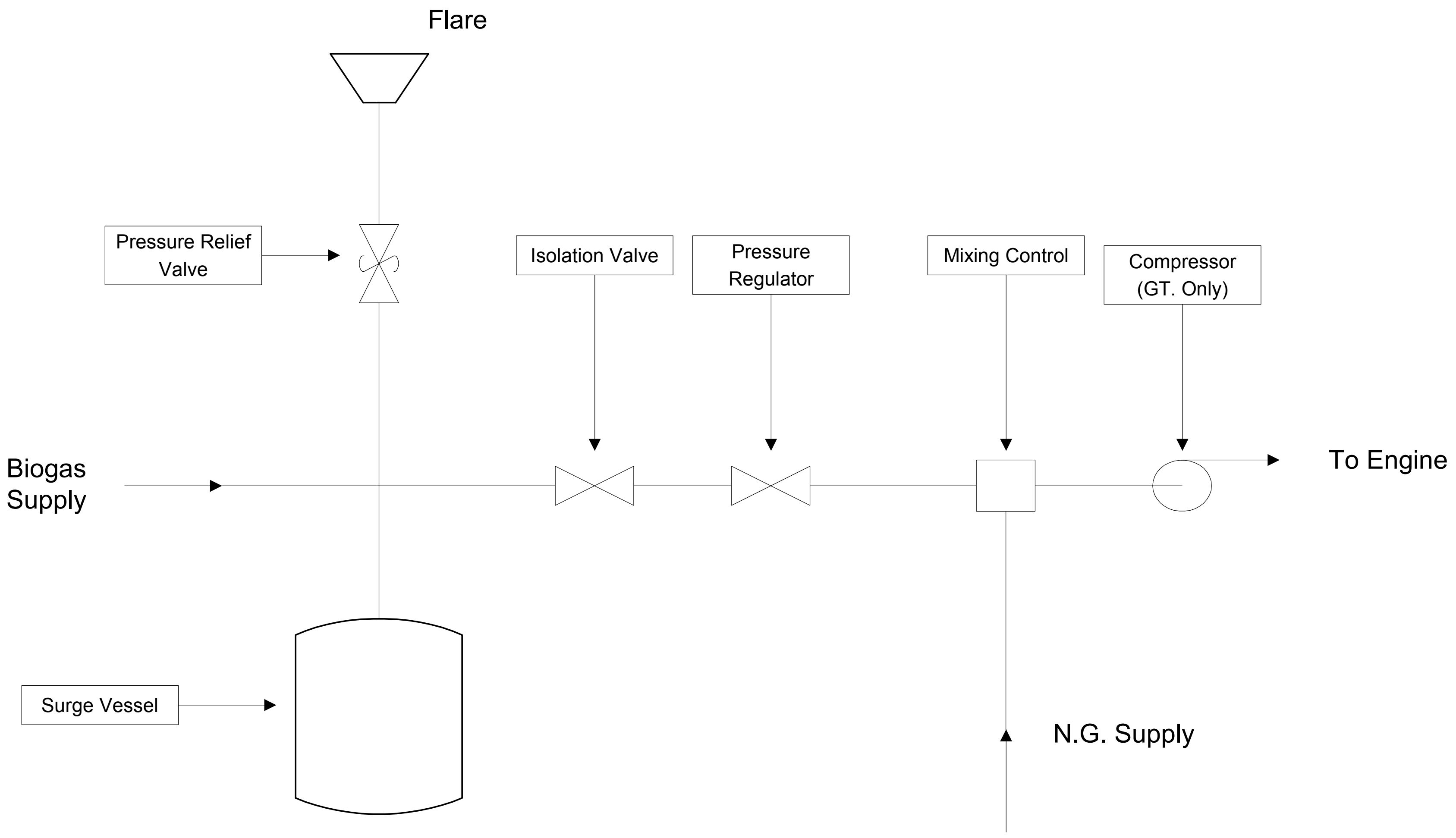

Figure 3. Biogas/Natural Gas Delivery System

incorporate an intercooler or aftercooler. The overall gas supply to the engine would be determined by the engine control system.

Characteristics of Biogas and Biogas Mixtures

Table 2 summarizes the characteristics of biogas, including that prepared by the Battelle pyrolysis route, as they relate to use in internal combustion engines. In reciprocating engines, which have a fixed volumetric capacity, the power output may be limited by the amount of gas that can be included in a stoichiometric mixture filling the cylinder. Supplying more gas would lead to an overrich mixture. The only way of further increasing engine output would be to increase supercharge pressure. Thus in Table 2, the ratio of actual air/fuel ratio to stoichiometric air/fuel ratio (column 7) is a measure of the excess air ratio λ that is possible. To reduce NO_x production, this should be as large as possible, but the final NO_x production rate depends also on other fuel properties such as the adiabatic flame temperature at stoichiometry. Note that the properties listed are for atmospheric pressure and initial temperature, not for engine operating conditions, which will vary from one engine to another.

A hypothetical fuel gas suggested by Caterpillar has been used to set the 100% power standard. A biogas obtained by partial oxidation of biomass with air could not meet this criterion, and is included in Table 2 only as a mixture with natural gas.

Comparing the 50/50 pyrolytic biogas/natural gas mixture with the hypothetical reference gas shows that the flame speed and the power limited excess air ratio are both lower, but the adiabatic flame temperature is also lower. Overall, these differences indicate that NO_x emissions at full power should be similar for all three fuels. The antiknock rating of the reference gas would be expected to be higher because of its superior flame speed and lack of ethane and propane, and this would reduce the permissible compression ratio for pyrolytic biogas and the pyrolytic biogas/natural gas blend.

Compared with the reference natural gas, the pyrolytic biogas would require a lower excess air ratio to make the same power output, but has a higher flame speed. The pyrolytic biogas/natural gas blend, as would be expected, would come closer to the natural gas in terms of power capability, but still has superior flame speed.

Gas derived by partial air oxidation of biomass (air blown biogas) would necessitate relatively severe derating of the engine unless blended with natural gas. It has no ethane or other significant hydrocarbon content and despite 10% hydrogen content in the 50/50 blend, the flame speed is lower than that of natural gas. The blend has a low adiabatic flame temperature so that the need to use less excess air to meet the reference power level would not necessarily lead to more NO_x generation. This is also the case if the airblown biogas blend is compared with natural gas, which has 2.5 times the volumetric heating value.

For gas turbines, fuel gases of low heating value can be utilized as long as the adiabatic flame temperature is above the design turbine inlet temperature. Normally excess air is used to dilute the combustion products before the turbine inlet. Use of gases with low adiabatic temperatures reduces the amount of diluent air required, but does not eliminate the need for it because some

Table 2. Combustion Related Characteristics of Biogas Fuels and Blends Compared with Natural Gas and Reference Gas

Fuel	Total Inerts $	Stoichiometric A/F	Power Limited A/F	LHV MJ/m^3	Flame Speed cm/S	Total Stoichiometirc C	λ 100% Load	C_2+HC
Natural Gas	1.8	9.8	15.7	34.3	43	1859	1.6*	3.1
Reference Gas	0	6.5	13.8	24	126	1912	2.13	0
Biogas (Pyro)	23	4.3	7.2	13.4	59	1867	1.68	3.0
50/50 NG/Biogas (Pyro)	12.5	7.4	13.8	23.9	56	1861	1.86	3.1
50/50 NG/Biogas (ABPO$_x$)	29.5	7.8	11.0	19.5	29	1796	1.4	1.6
ABPO$_x$	57	3..4	NA	4.8	0	1436	NA	0

excess air is required for cooling turbine components such as combustor liners, rotors, vanes, vane rings, etc. From an emissions standpoint, a low adiabatic flame temperature is beneficial in reducing NO_x, but there is risk of emissions of CO and other partially oxidized species. All of the gases listed in Table l could be utilized, but the air blown partial oxidation biogas has an adiabatic flame temperature around 1430 C at stoichiometric conditions, and an initial temperature at ambient conditions with zero flame speed showing that a flame would not propagate. Allowing for the elevated temperature at the combustor inlet, the adiabatic flame temperature for a stoichiometric mixture would be on the order of 1700 C, which is sufficiently above the design turbine inlet temperatures of industrial scale gas turbines to make the use of air blown partial oxidation type biogas just feasible without any turbine derating, although not without changes in design. For example, the air compression load would be reduced and some of it replaced by an increase in gas compressor duty, as well as the more obvious need for a change in combustor design. With such a low flame temperature, NO_x production would be minimal without lean premix combustion, but the flame speed would be very low and reliable ignition might be difficult to sustain at reduced load. This gas must be regarded as marginal.

Admixture of either biogas type at 50/50 ratio with natural gas leads to a fuel of moderate heating value, with the pyrolysis gas mixture having the higher heating value and flame speed. Without experimentation it is difficult to predict whether these gases could be used successfully in low emission premix combustion systems, and what NO_x levels could be attained. These questions do not appear to have been addressed in depth although field experience may shed light on the subject.

Reforming of Natural Gas

Steam Reforming

Steam prereforming converts higher hydrocarbons to C1-componts with no intermediate products. The typical operating temperature is from 400 to 550°C. The temperature is chosen to avoid hydrocarbon cracking which results in carbon precipitation. Methane reforming is completed in a final stage at higher temperatures and higher steam to carbon ratios are used to suppress carbon precipitation. Below are the reactions that occur.

$C_nH_m + nH_2O \rightarrow nCO + (n + 1/2m)H_2$ $(-\Delta H^\circ_{298} = -1108\text{kJ/mol}, n = 7)$ (1)
$CO + 3H_2 \leftrightarrow CH_4 + H_2O$ $(-\Delta H^\circ_{298} = 206.2\text{ kJ/mol})$ (2)
$CO + H_2O \leftrightarrow CO_2 + H_2$ $(-\Delta H^\circ_{298} = 41.2\text{ kJ/mol})$ (3)

A detailed review of the process is given in a paper by Christensen[6]. Reaction (1) is irreversible whereas the other two reactions establish an equilibrium, which is temperature dependent. Carbon dioxide and water will be present in the product as well as carbon monoxide and hydrogen since reactions (2) and (3) are equilibrium reactions. The reaction mechanism for steam reforming involves the adsorption of the hydrocarbons onto the catalyst surface, leaving of all the carbon-carbon bonds, and leaving only single carbon components (i.e. methane, carbon monoxide). Experiments

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[6] T. S. Christensen – Adiabatic Performing of Hydrocarbons – An Important Step in Syngas Production. Applied Catalysis, A: General, 138 (1996), pp 285-309.

dioxide, carbon monoxide). Experiments have shown that the higher hydrocarbons slowly decrease through the catalyst bed and that no intermediates are created. Because the rates of reactions (2) and (3) are relatively fast, the kinetics of the steam reforming of the higher hydrocarbons is the rate determining step.

The reaction using natural gas as its feed stock is endothermic. Generally, the inlet of the bed is at the highest temperature, where concentration of higher hydrocarbons is highest. However, a number of compact reformers proposed for use with fuel cells include arrangements for heating the reactor to provide a near isothermal reaction zone.(7) With sufficient steam and residence time, all higher hydrocarbons react before exiting the bed. Steam required for the reforming can be generated from the exhaust gases.

The practical temperature range for steam prereforming is dictated by the tendency to deposit carbon onto the catalyst through thermal cracking at high temperatures and by gum formation at lower temperatures. The higher hydrocarbons are more susceptible to such behavior than is methane and it is usual to operate prereformers at temperatures between 250 C and 500 C[2] to reduce sensitivity to variable feedstock composition. Excess steam in the reactor feed is also used to promote oxidation of carbon to CO_2 rather than CO, which could lead to carbon deposition via the Boudouard reaction

$$2\,CO \rightarrow CO_2 + C\ .$$

There is a fuller discussion of this and other factors behind the selection of prereformer operating conditions in the paper by A. J. Dicks cited above. He also states that carbon deposition at high temperatures can apparently be avoided by using precious metal (ruthenium or rhodium) as catalyst rather than nickel. In any case, sulfur removal to about 0.2 ppm or lower is usually necessary to avoid catalyst poisoning and this may involve addition of hydrogen to the reactor feedstock to convert organic sulfur forms to H_2S.

To utilize heat from the engine exhaust gases, the reactor inlet temperature must be at a lower temperature. There is ample heat in the exhaust stream to generate steam, but the final stage of superheating is critical to reactor temperature. The exhaust temperature in a supercharged engine depends on the peak combustion temperature and the overall expansion ratio through both the engine and the turbocharger turbine. The exhaust temperature is therefore dependent on the engine compression ratio if the power output is to be kept constant, because the power output will require a constant temperature rise in the cylinder.

Figure 4 illustrates this relationship for conditions representative of high performance modern engines, but it will vary with engine design, and exhaust temperatures may in some cases approach 600 C. Steam temperature can be increased above the exhaust temperature by extracting heat from the exhaust manifold upstream of the supercharger turbines. The amount of

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[7] A. J. Dicks, “Hydrogen Generation from Natural Gas for the Fuel Cell Systems of Tomorrow”, Journal of Power Sources, 61 (1996), pp 113-124, Elsevier.

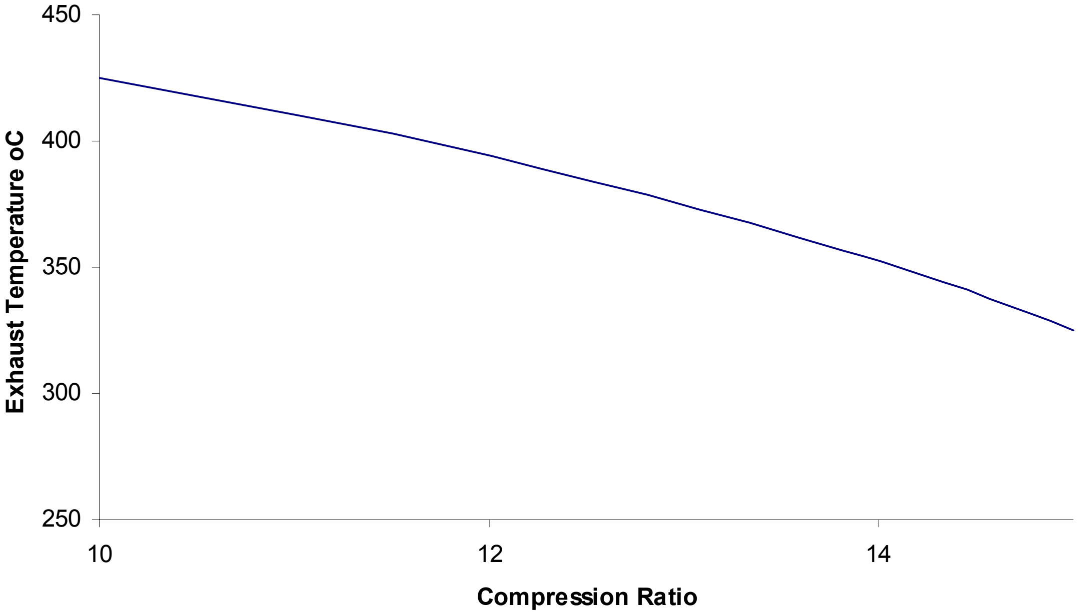

Figure 4. Engine Exhaust Temperature vs Compression Ratio

heat required will be less than 10% of the total heat required in most cases, but because the exhaust temperature falls as compression ratio and boost pressure increase, the availability of high quality exhaust heat decreases as engine efficiency is increased. In setting parameters for the assessment of steam reforming, inlet temperatures to the reformer have been limited to the range 300 to 500 C.

Table 3 presents the results of ChemCAD computations for six reactor inlet conditions of a steam reformer at a steam/carbon ratio of 1:1. The two input gas compositions represent widely different levels of heavy hydrocarbon content and the similarity between output compositions demonstrates the improvement in consistency resulting from reforming. Figures 5 through 10 illustrate the sensitivities of the reforming process to the various operating conditions. Note that if steam reforming is carried out at pressure to meet the required engine combustion conditions, the hydrogen content would be as little as 50% of that for reforming at 2 atmospheres. Because gas compression is usually necessary in gas turbine installations, it may be preferable to reform the natural gas at low pressure and compress the product after cooling. This could double the gas compressor parasitic power load, but under constant total mass flow rate there would be a corresponding drop in the air compressor duty.

Figures 11 and 12 are simple schematics showing how a steam reformer system could be incorporated into the fuel delivery system for gas turbine and reciprocating engine systems. The duct burner shown in Figure 11 is optional, but is a simple way of achieving a high superheat temperature. A more efficient method would be to use low temperature steam for some of the engine cooling duty and to use the heat recovered for superheating. The simple schemes in both Figures 11 and 12 could be improved by closer integration with specific engine systems.

Table 3. Steam Reforming Input and Output Quantities, Including Thermal Efficiency for Six Conditions at Steam to Carbon Ratio of 1.0

Methane Number	70				85			
Reactor Temperature (°C)		300	400	500		300	400	500
System Inlet								
Molar flow kmol/min		0.0208	0.0207	0.0204		0.0218	0.0216	0.0214
Mass flow kg/min		0.406	0.403	0.399		0.370	0.367	0.363
Heating values (60 F)								
Gross kJ/kmol		943600	943600	943600		900500	900500	900500
Net kJ/kmol		853200	853200	853200		811600	811600	811600
Std vap 0 C m3/h		27.98	27.77	27.49		29.34	29.09	28.79
System Outlet								
Molar flow kmol/min		0.0464	0.0470	0.0479		0.0455	0.0463	0.0472
Mass flow kg/min		0.819	0.813	0.805		0.771	0.764	0.756
Heating values (60 F)								
Gross kJ/kmol		426100	419600	411600		434400	426800	417900
Net kJ/kmol		363700	358500	352200		370200	364200	357100
Std vap 0 C m3/h		62.34	63.25	64.38		61.25	62.26	63.49
Component mole %	Inlet	Oulet			Inlet	Outlet		
Methane	82.22	46.57	44.47	41.9	95.14	47.25	44.86	42.04
Ethane	7.35	0	0	0	2.68	0	0	0
Propane	2.53	0	0	0	0.29	0	0	0
I-Butane	0.82	0	0	0	0.03	0	0	0
N-Butane	0	0	0	0	0.05	0	0	0
I-Pentane	0.32	0	0	0	0.01	0	0	0
N-Pentane	0	0	0	0	0.01	0	0	0
N-Hexane	0.01	0	0	0	0.01	0	0	0
N-Heptane	0.09	0	0	0	0.01	0	0	0
N-Octane	0	0	0	0	0.01	0	0	0
Hydrogen	0	3.87	8.09	13.19	0	4.65	9.43	15.04
Water	0	43.73	40.64	36.94	0	45.64	42.08	37.92
Carbon Monoxide	0	0.01	0.05	0.17	0	0	0.02	0.09
Carbon Dioxide	2.13	3.8	4.77	5.87	1.01	2.1	3.26	4.58
Nitrogen	4.51	2.03	1.98	1.93	0.75	0.36	0.35	0.34
Oxygen	0	0	0	0	0	0	0	0
kJ/min								
Inlet								
gross		19627	19485	19287		19649	19478	19280
net		17747	17619	17439		17709	17555	17376
Outlet								
gross		19754	19734	19703		19783	19757	19729
net		16861	16860	16860		16859	16859	16859
Efficiency								
gross		**100.65%**	**101.28%**	**102.16%**		**100.68%**	**101.43%**	**102.33%**
net		**95.01%**	**95.70%**	**96.68%**		**95.20%**	**96.03%**	**97.02%**
kJ/m3								
gross		19012	18721	18364		19380	19041	18643
net		16228	15995	15713		16516	16248	15931
%C in methane	73.3%	92.4%	90.2%	87.4%	92.4%	95.7%	93.2%	90.0%
%C in oxides	1.9%	7.6%	9.8%	12.6%	1.0%	4.3%	6.8%	10.0%
CO/CO2 ratio	0.000	0.003	0.010	0.029	0.000	0.000	0.006	0.020

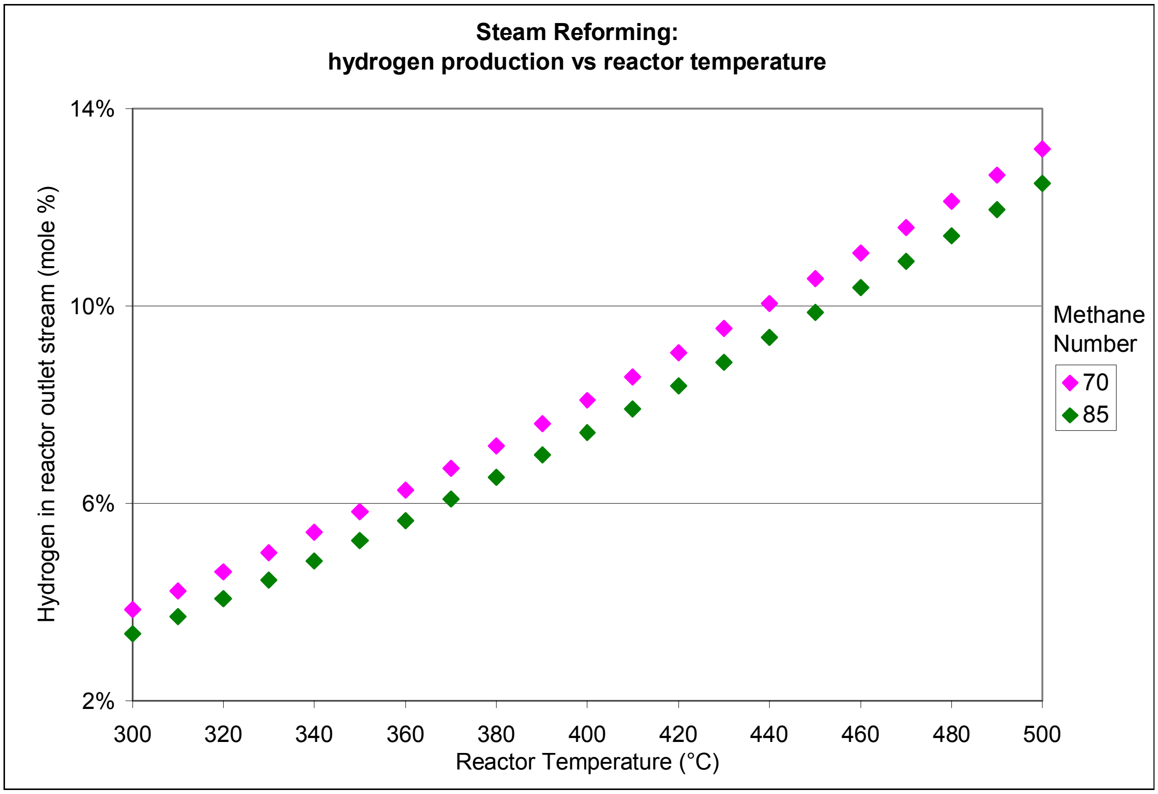

Figure 5. Hydrogen versus Reforming Temperature for Steam to Carbon Ratio of 1

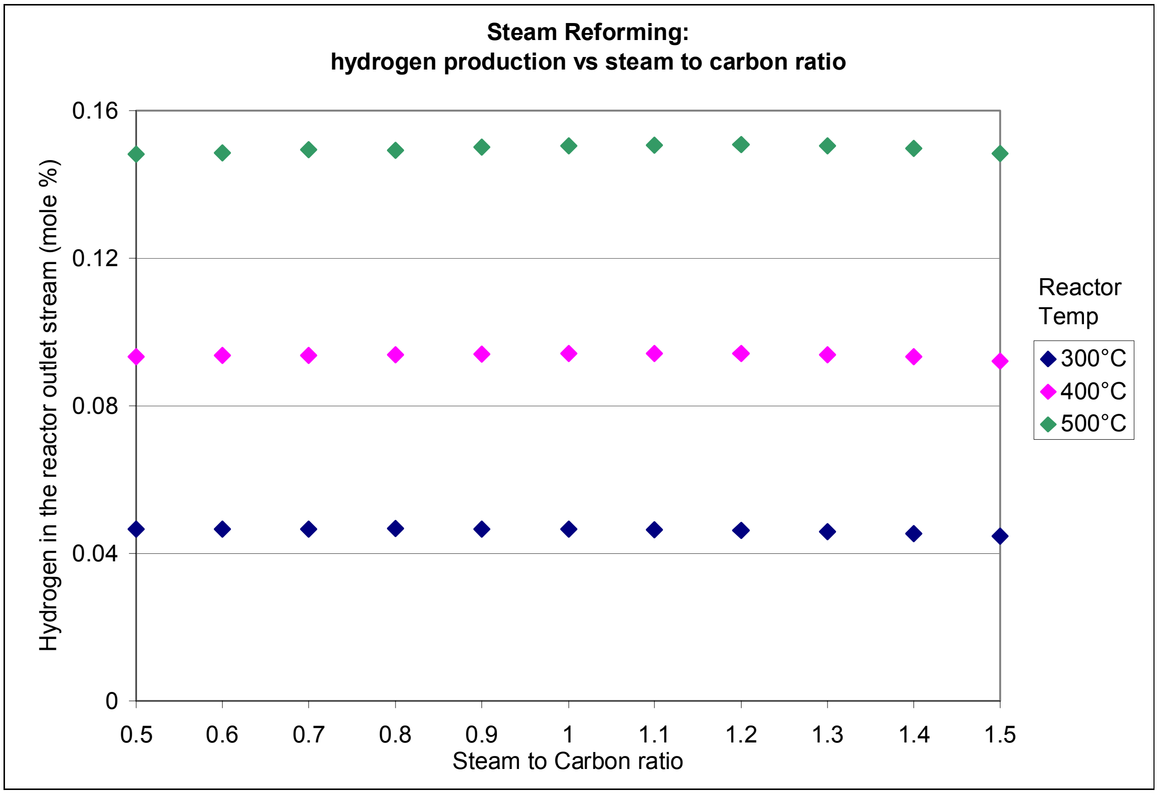

Figure 6. H_2 in Output versus Steam to Carbon Ratio for 85 Methane Number Gas

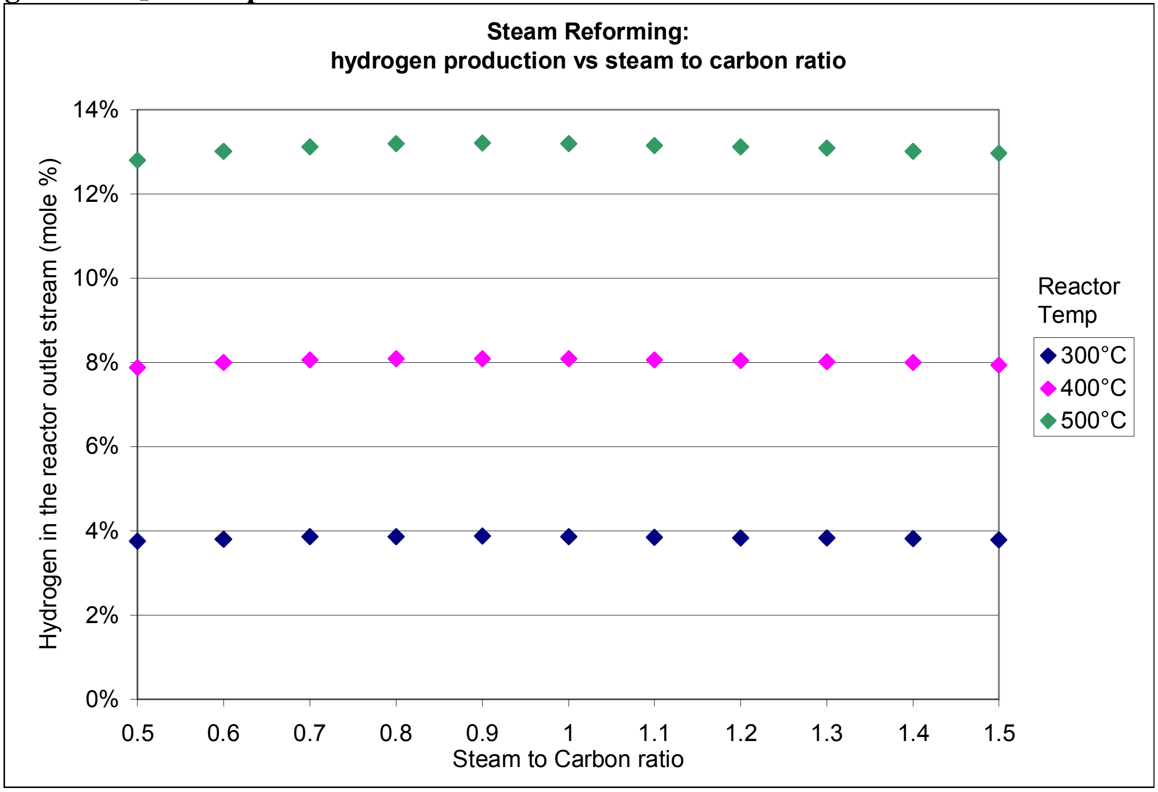

Figure 7. H_2 in Output versus Steam to Carbon Ratio for 70 Methane Number Gas

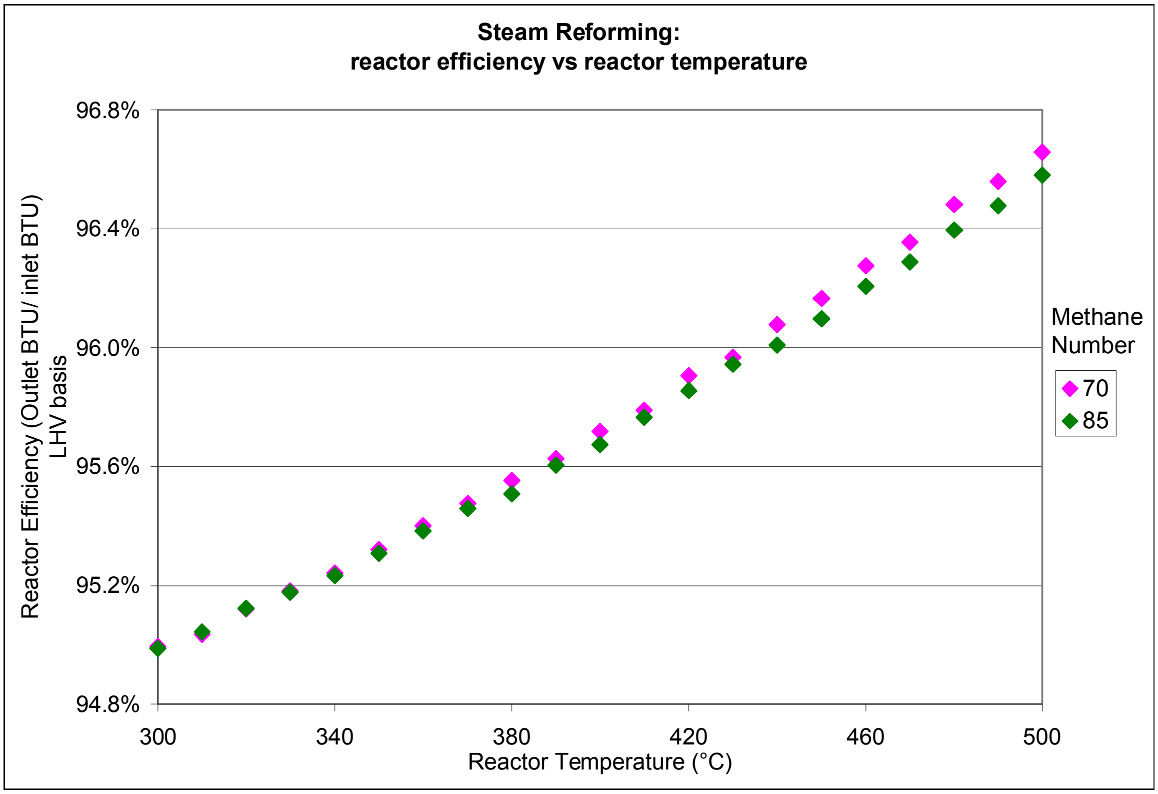

Figure 8. Thermal Efficiency versus Reformer Temperature for Steam to Carbon Ratio of 1

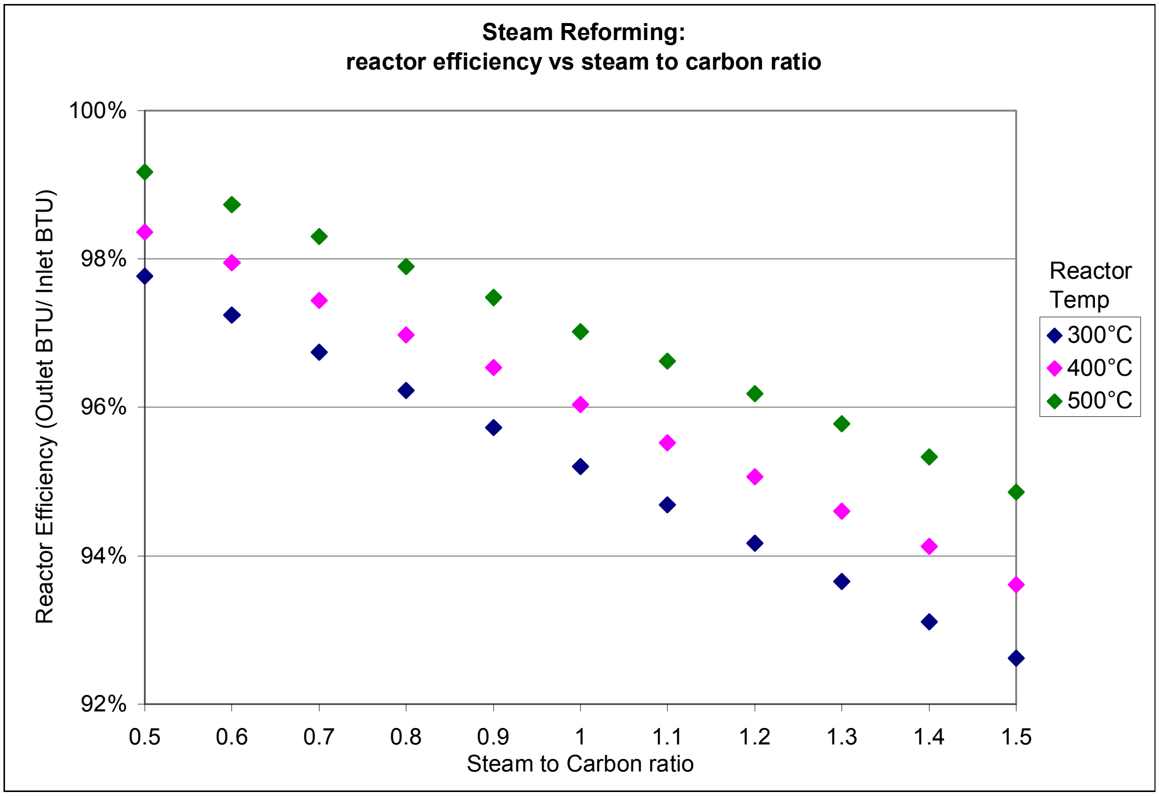

Figure 9a. Thermal Efficiency versus Steam to Carbon Ratio for 85 Methane Number Gas

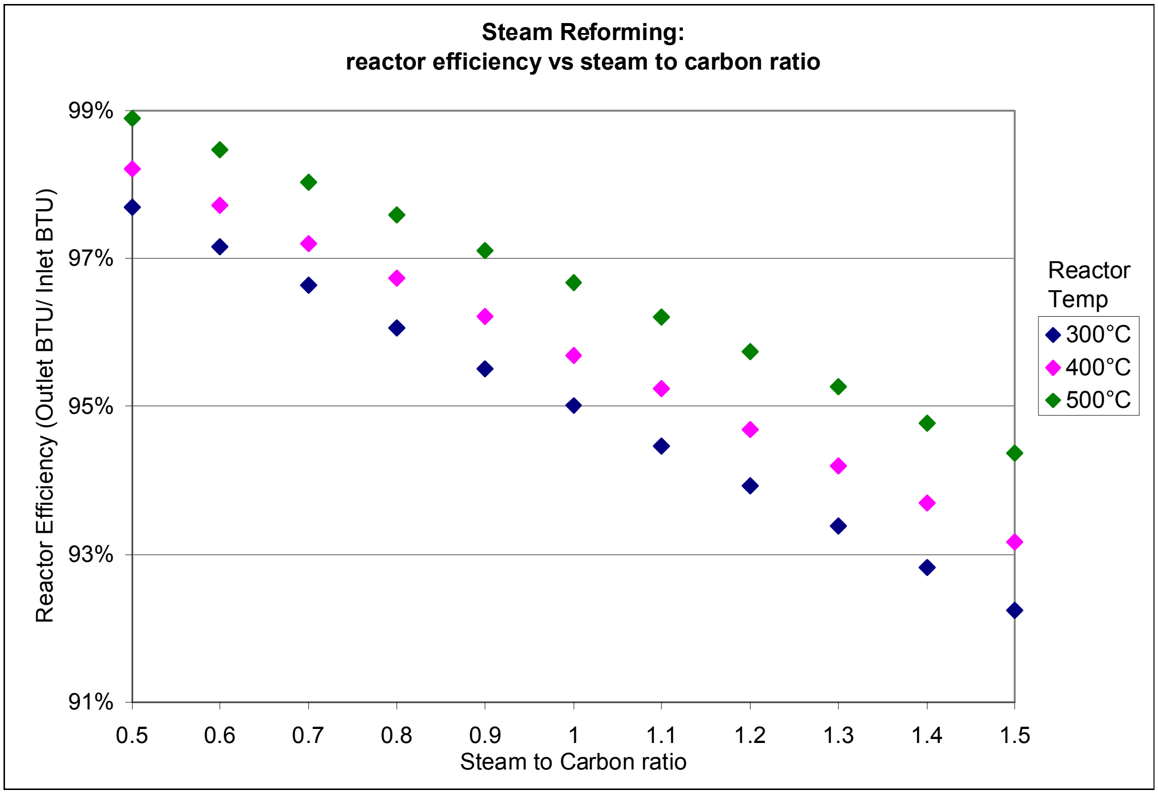

Figure 9b. Thermal Efficiency versus Steam to Carbon Ratio for 70 Methane Number Gas

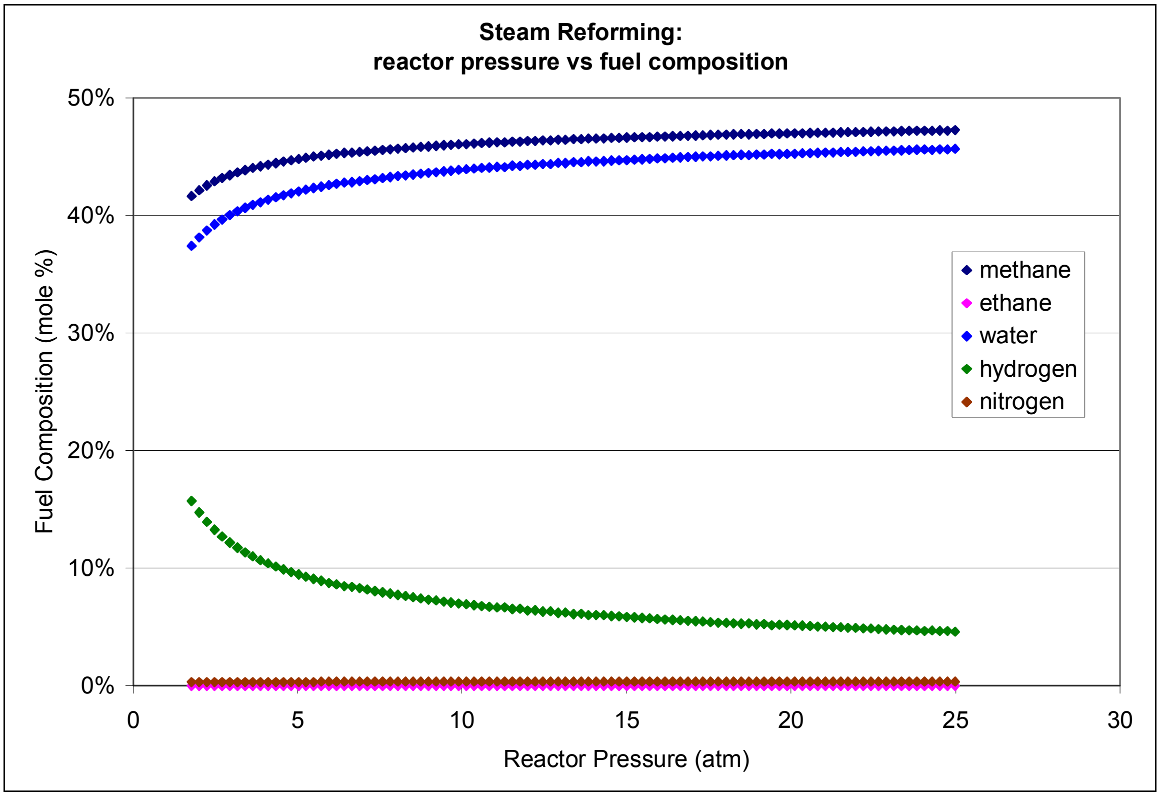

Figure 10a. Effect of Reactor Pressure on Output Gas Composition: Steam Reforming at 1:1 H_2O/C Ratio and 400 C Inlet Temperature – Fuel Methane Number 85

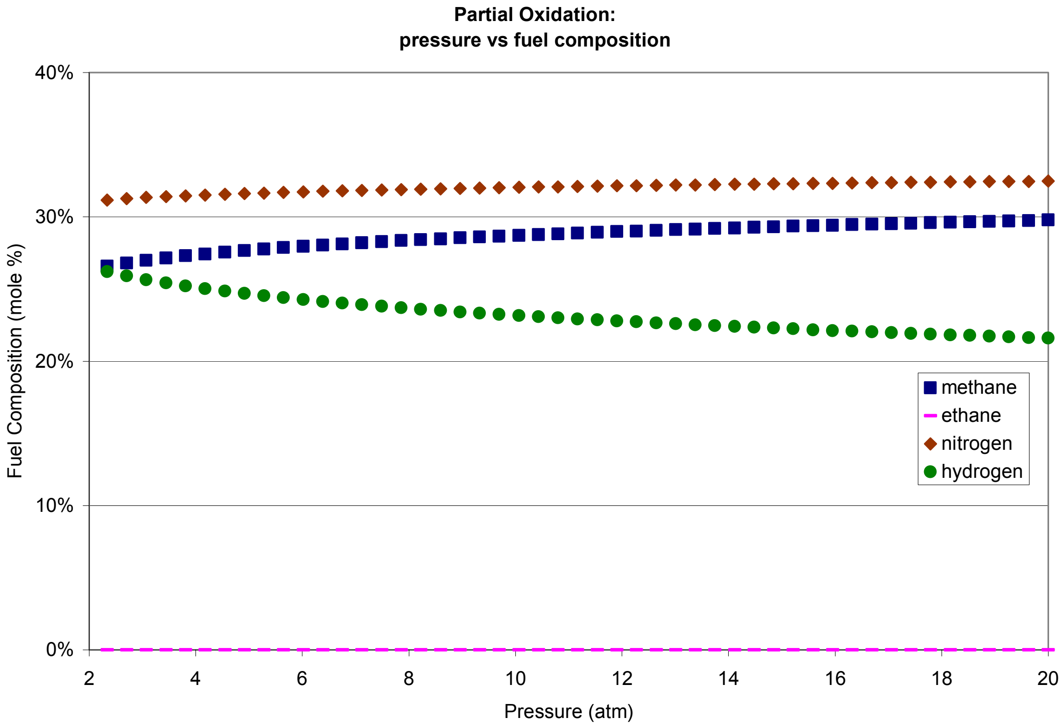

Figure 10b. Effect of Pressure on Partial Oxidation Reforming 85 Methane Number Gas 0.2 O_2/C Ratio 400 C Reactor Temperature

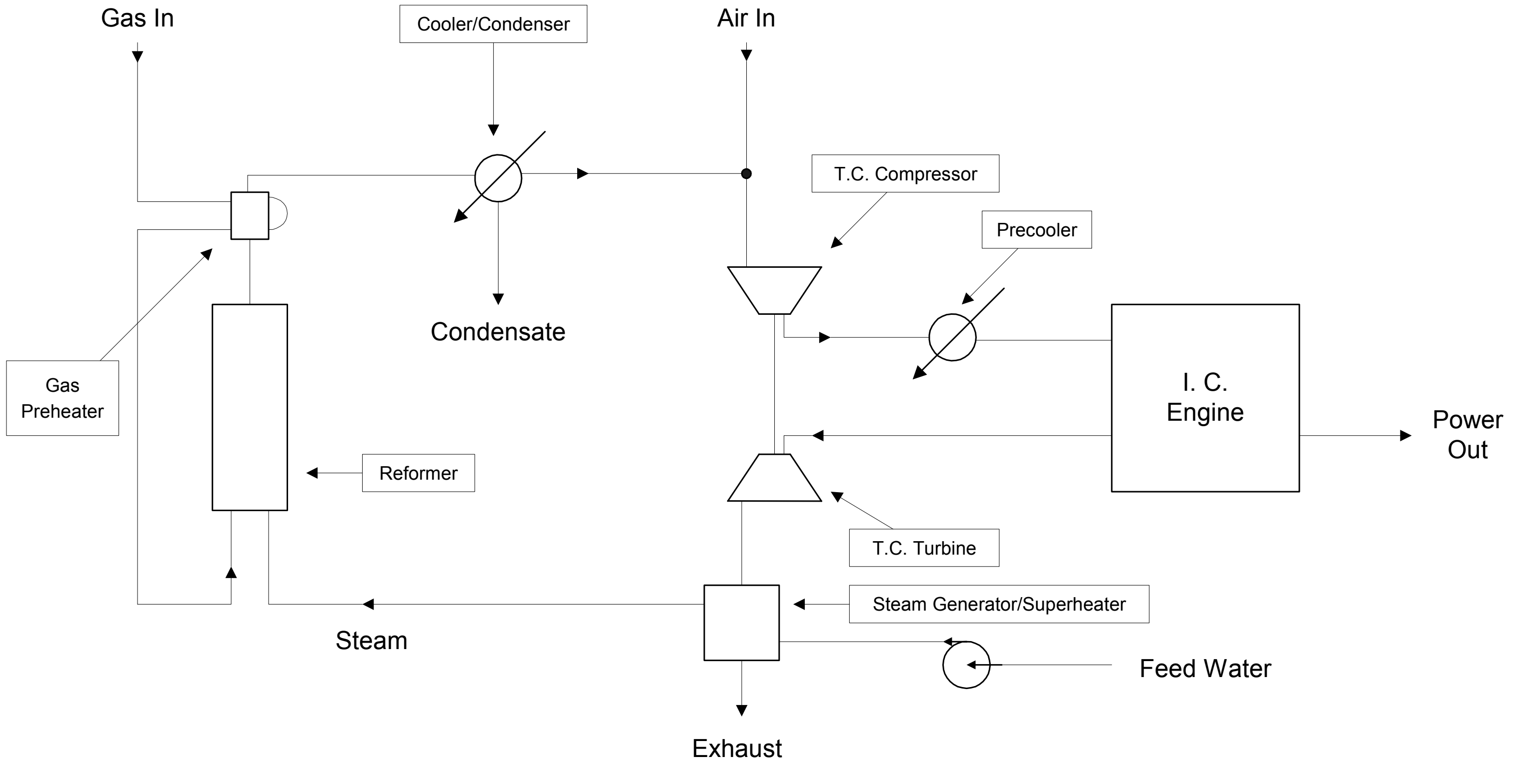

Figure 11. Flow Schematic Integrating Steam Reformer and Reciprocating Engine

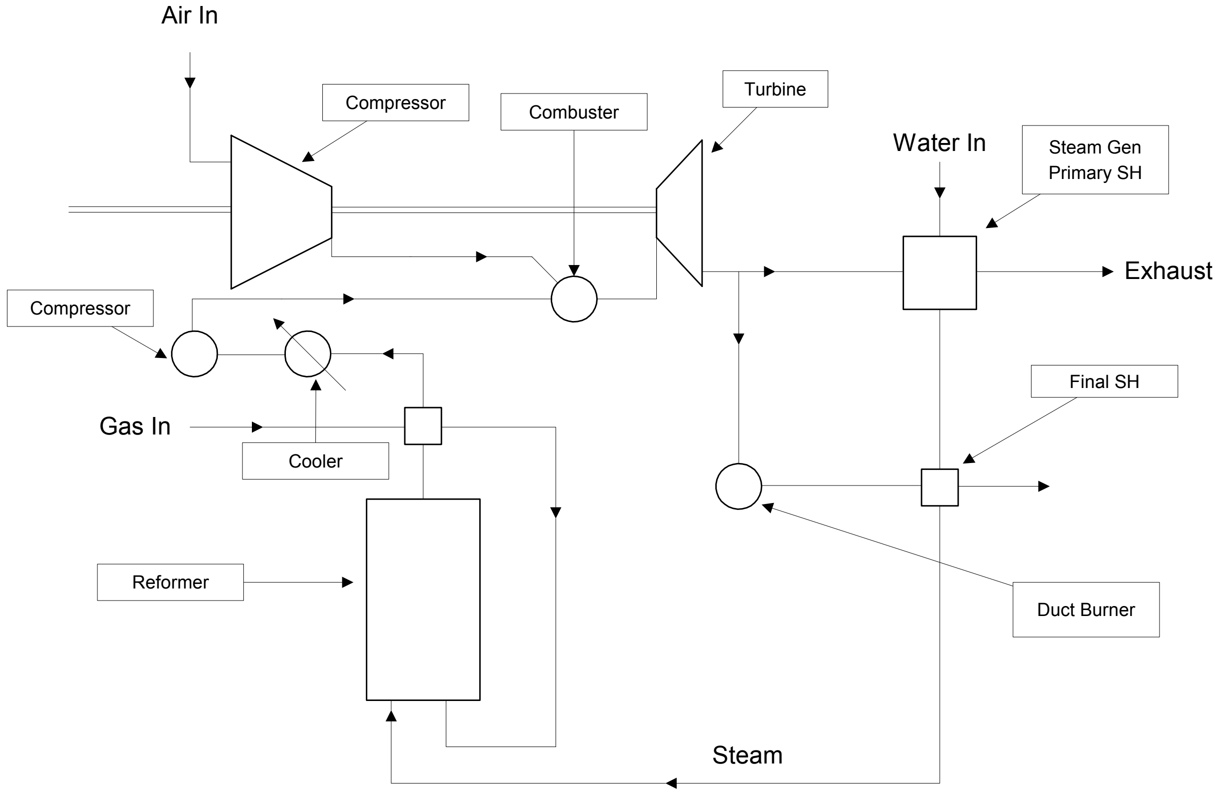

Figure 12. Flow Schematic Integrating Steam Reformer and Gas Turbine

Partial Oxidation Prereforming

Partial Oxidation

Partial oxidation reactors are based on reactions of the general type

$$CnHm + \frac{1}{2}\ n\ O_2 = nCO + \frac{m}{2}\ H_2\ .$$

In practice, this ideal conversion is not attained and both CO_2 and H_2O are also produced. The reaction normally takes place over a catalyst to allow use of lower temperatures, and is exothermic, so that once initiated it may not require an external heat source. For O_2/C molar ratios less than 0.5 some of the hydrocarbons will be left unreacted, and in the case of natural gas which contains higher order hydrocarbons as well as methane, the higher order components will be reformed preferentially. This enables complete destruction of gases such as ethane, propane, and butane with very low O_2/C ratios, as illustrated in Figures 13 and 14. From these figures, it can also be inferred that these components are at first converted to oxides (including H_2O) and that hydrogen production requires higher O_2/C ratios.

As is the case with steam reforming, the final gas composition depends on the reactor temperature which dictates the chemical equilibrium, as well as on the primary oxidative reactions. A good discussion of catalytic partial oxidation of methane/air is given in a recent paper by Lyubousky et al.(8). The lowest O_2/C ratio used in his study was 0.45, which with an inlet temperature of 400 C produced an adiabatic temperature at the catalyst of nearly 1000 C. The reactor temperature decreases in the later stages as endothermic reactions occur to establish chemical equilibrium, but the peak temperature can be critical to catalyst life. The subject of Lyubousky's paper was a novel catalyst substrate giving unusually low light off temperatures, which could be relevant to engine applications.

In Lyubousky's experiments, at the theoretical 0.5 O_2/C ratio required for complete reforming to CO and H_2, almost all of the methane (~96%) was converted to CO or CO_2 and 99.6% of the hydrogen was in elemental form. At 0.45 O_2/C these percentages dropped to ~85% and 98.3% with a significant increase in the amount of water. The efficiency (as defined for this report) rose slightly from 94% to 94.7%. The efficiencies are high because of the high reactor temperatures which favor the CO/CO_2 ratio and the increase at the lower O_2/C ratio is largely result of the incomplete reforming of methane. To attain such high levels of performance thorough premixing of the reactants is essential.

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(8)Lyubousky, M., et al., "Complete and Partial Catalytic Oxidation of Methane over Substrates with Enhanced Transport Properties", Catalysis Today 83 (2003), pp 183-197.

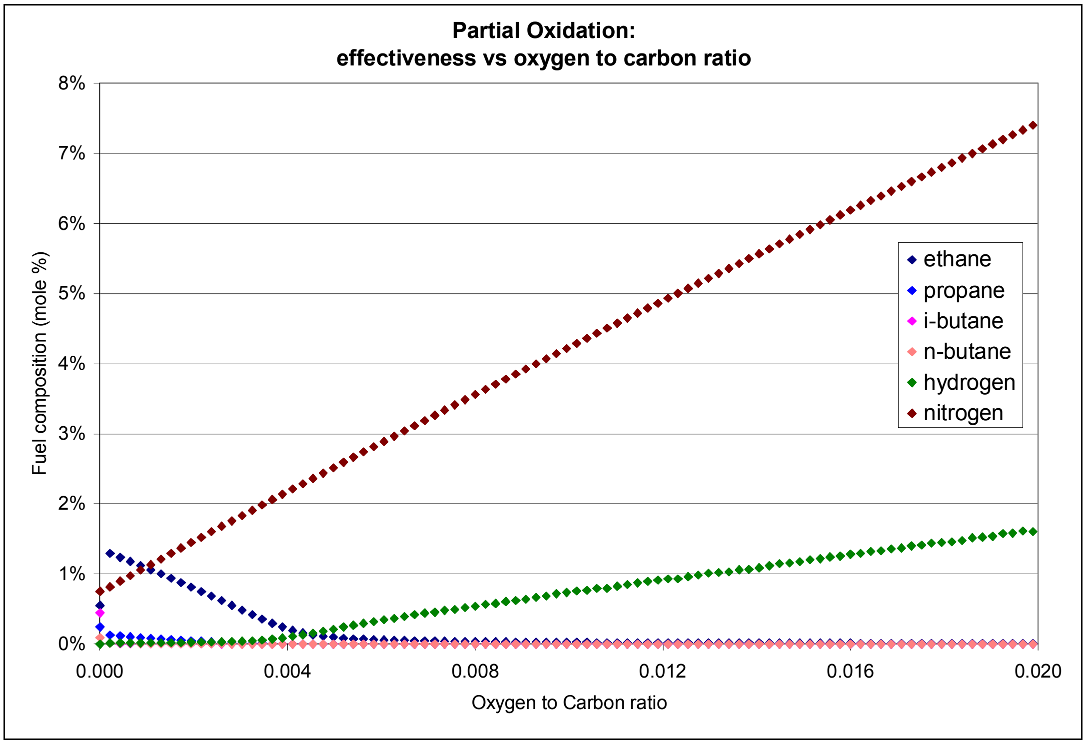

Figure 13. Effectiveness versus Oxygen to Carbon Ratio for 85 Methane Number Gas, Reactor Temperature = 400 C, Balance of Analysis is Methane and Reaction Products

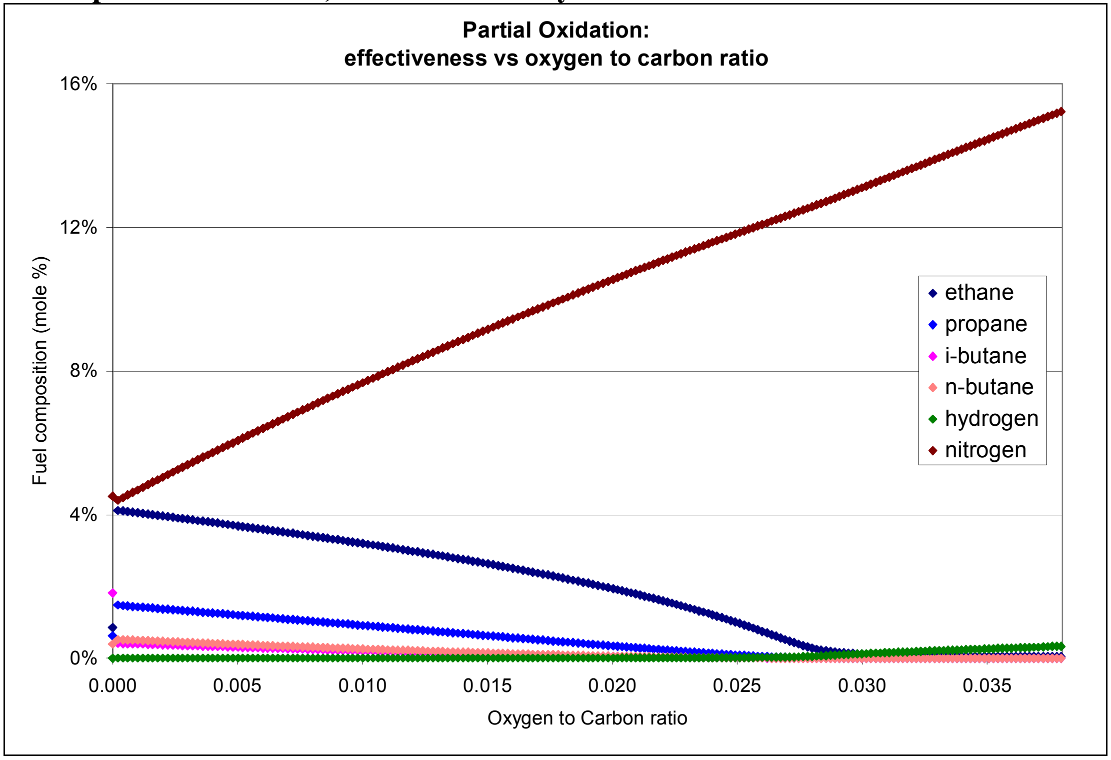

Figure 14. Effectiveness versus Oxygen to Carbon on Ratio for 70 Methane Number Gas, Reactor Temperature = 400 C, Balance of Analysis is Methane and Reaction Products

Table 4 shows how the PO_x reformer performance varies with the oxygen/carbon ratio, for a reactor inlet temperature of 400 C, a gas of methane number 85, and a pressure of 2 ata. To obtain a given hydrogen content in the product gas, up to 30% or more it would be feasible to use a bypass arrangement. For example, 20% H_2 could be obtained either by using a full flow reactor with $O_2/C = 0.15$, or to use an O_2/C ratio of 0.4 or more with a 40% bypass rate. Note, however, that the bypass arrangement would require more air and more parasitic power, and would not eliminate higher hydrocarbons from the fuel to the engine. There would also be a lower overall efficiency. The use of full flow reforming is technically preferable, although use of a bypass would result in a smaller reformer. Another significant advantage of using the lower O_2/C ratio is that the catalyst temperature would be lower and this would extend its life, while the lower temperatures would also reduce the cost of equipment by permitting lower cost materials.

Table 5 is similar to Table 4, but assumes a reactor inlet temperature of 300 C. In the case of the PO_x reformer, there is no difficulty in achieving higher reactor inlet temperatures because high grade heat can be recovered from the reactor exit gases. The choice of inlet temperature is largely dictated by considerations of equipment cost, maintenance cost, especially catalyst life and the possibilities of carbon deposition and other side effects. Figure 15 illustrates graphically the exit temperatures for range of inlet conditions.

In reciprocating engines, the heating value per unit volume of the product gas is important because with the stoichiometric combustion air/fuel ratio it determines the energy density of the mixture that can be delivered to the engine cylinder. Figure 16 shows that the heating value falls steeply with reforming severity. For gas reformed with 0.15 O_2/C ratio, it is 15.8 KJ/cubic meter. For a 40/60 mixture of natural gas and 0.45 O_2/C reformate, it is 18.1 KJ/cubic meter. Both would have similar hydrogen contents.

Figures 17 and 18 display graphically the effect of O_2/C ratio on reactor efficiency and on hydrogen production.

Figures 19 and 20 shows schematically how the partial oxidation reforming process might be incorporated into the fuel delivery systems for gas turbines and reciprocating engines, respectively. The process is assumed to be at low pressure in both cases. Depending on the reactor conditions, the exit gases may be at sufficiently high temperature to warrant further heat recovery, although it is likely to be the case only if the reactor efficiency is low (high O_2/C cases).

Combined Partial Oxidation and Steam Reforming

The simultaneous use of both air and steam as reforming agents has been examined because the heat generated by partial oxidation is a convenient way of increasing the extent of the steam/carbon reactions and the moderating effect of the steam reduces the maximum reactor temperature. Table 6 shows the results for three cases. The reactor exit temperature is only

Table 4

Table 5

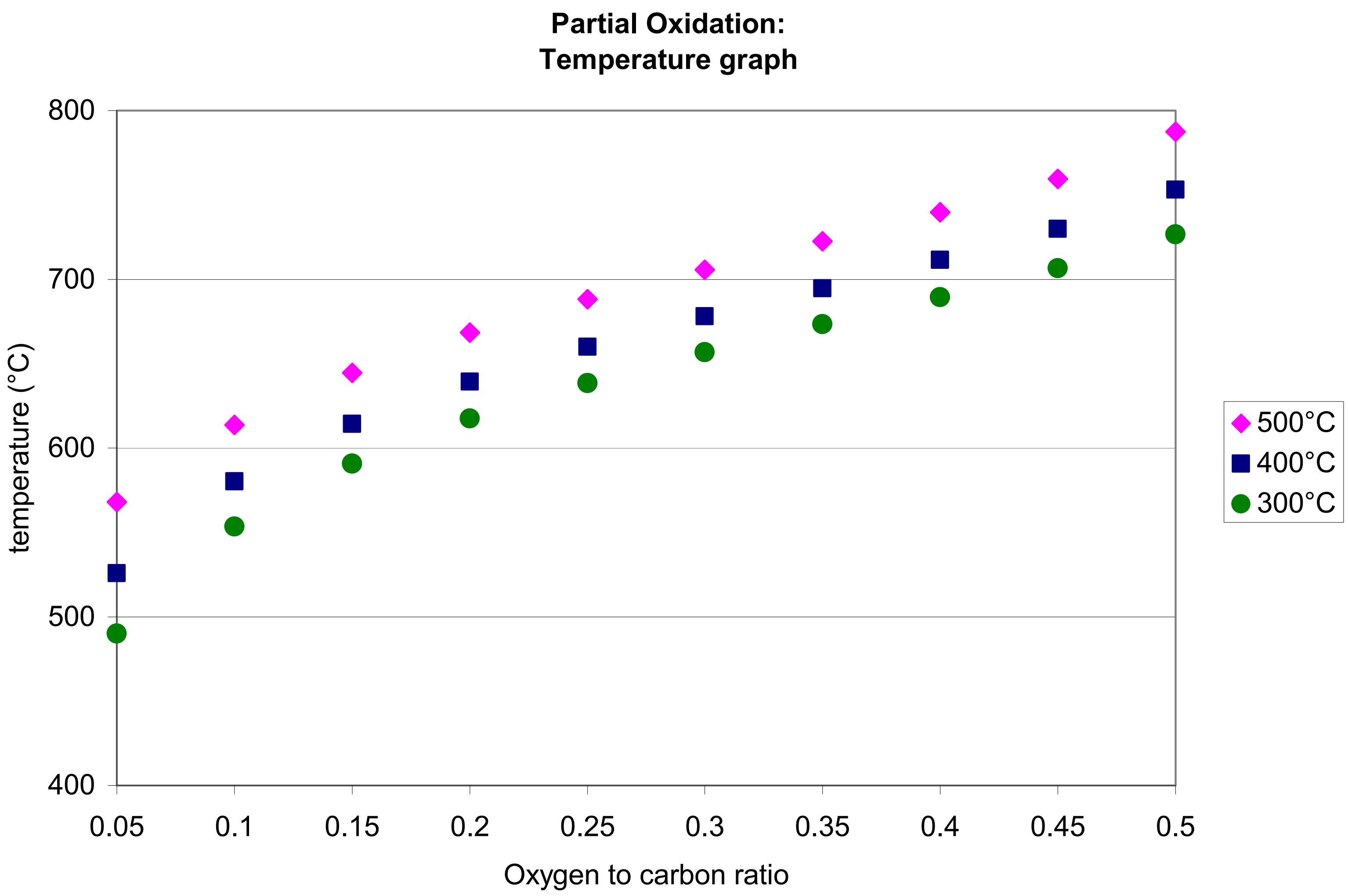

Figure 15. Reactor Exit Temperature as a Function of O_2/C Ratio and Inlet Temperature

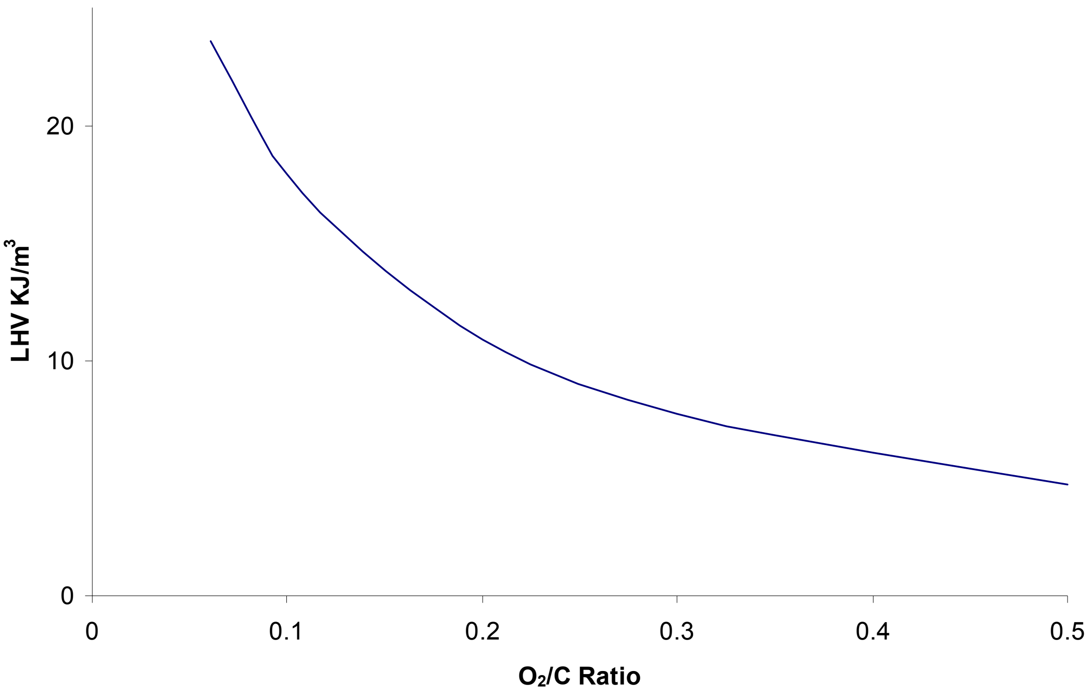

Figure 16. LHV of PO_x Reformed 85 Methane Number Natural Gas
400 C Reaction

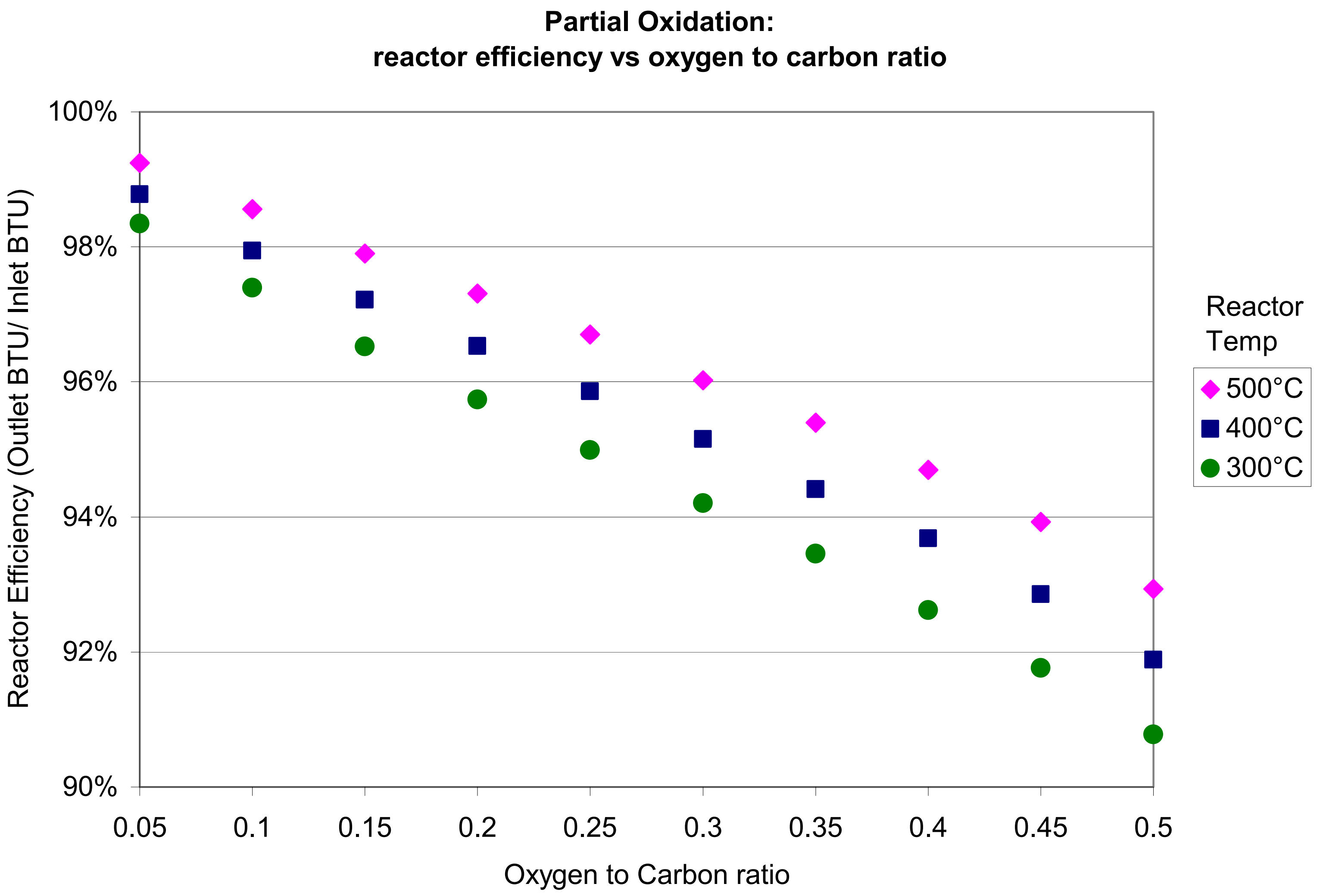

Figure 17. Effect of O_2/C Ratio on Reactor Efficiency of Partial Oxidation Reforming

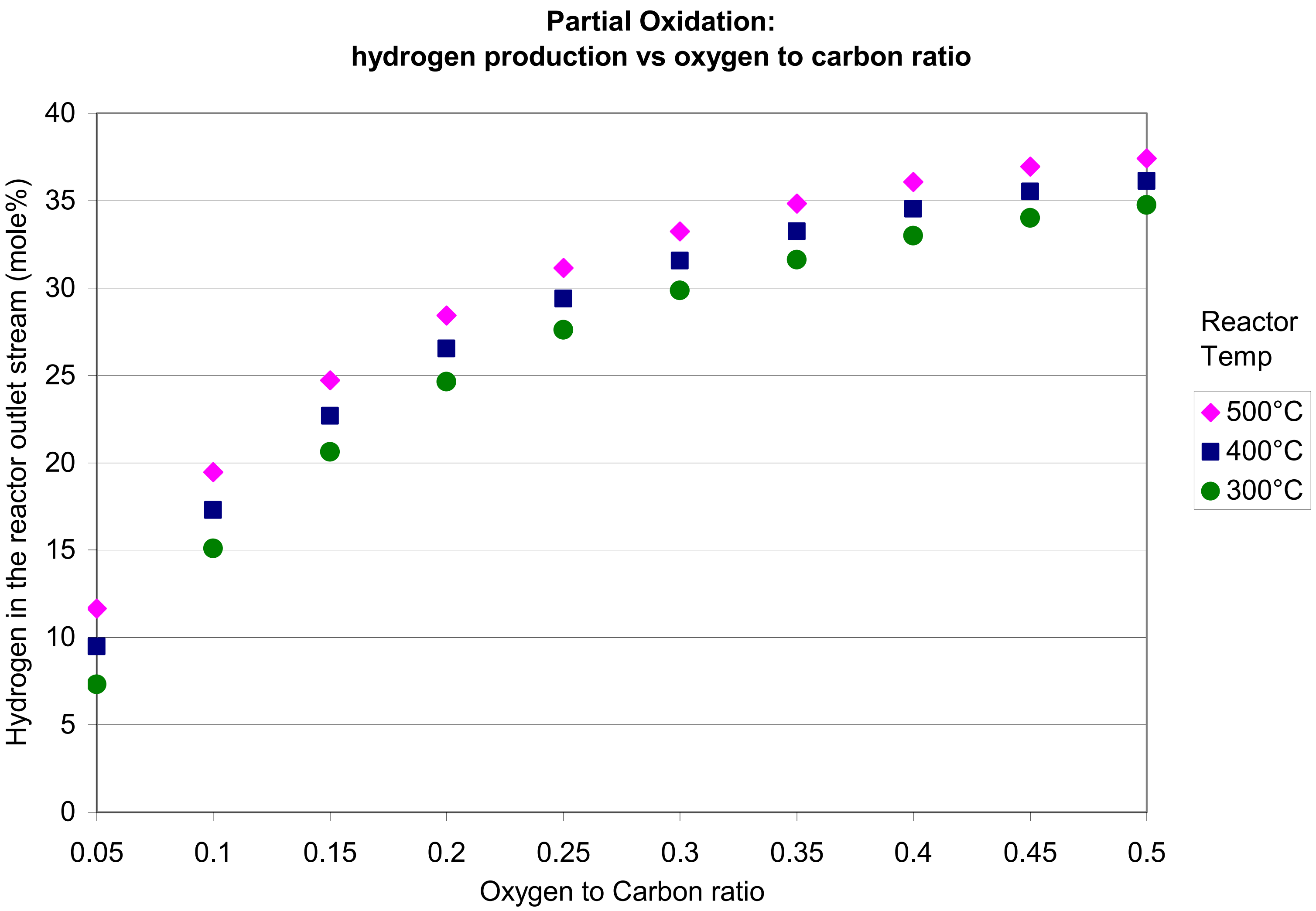

Figure 18. Effect of O_2/C Ratio on Hydrogen Produced by Partial Oxidation

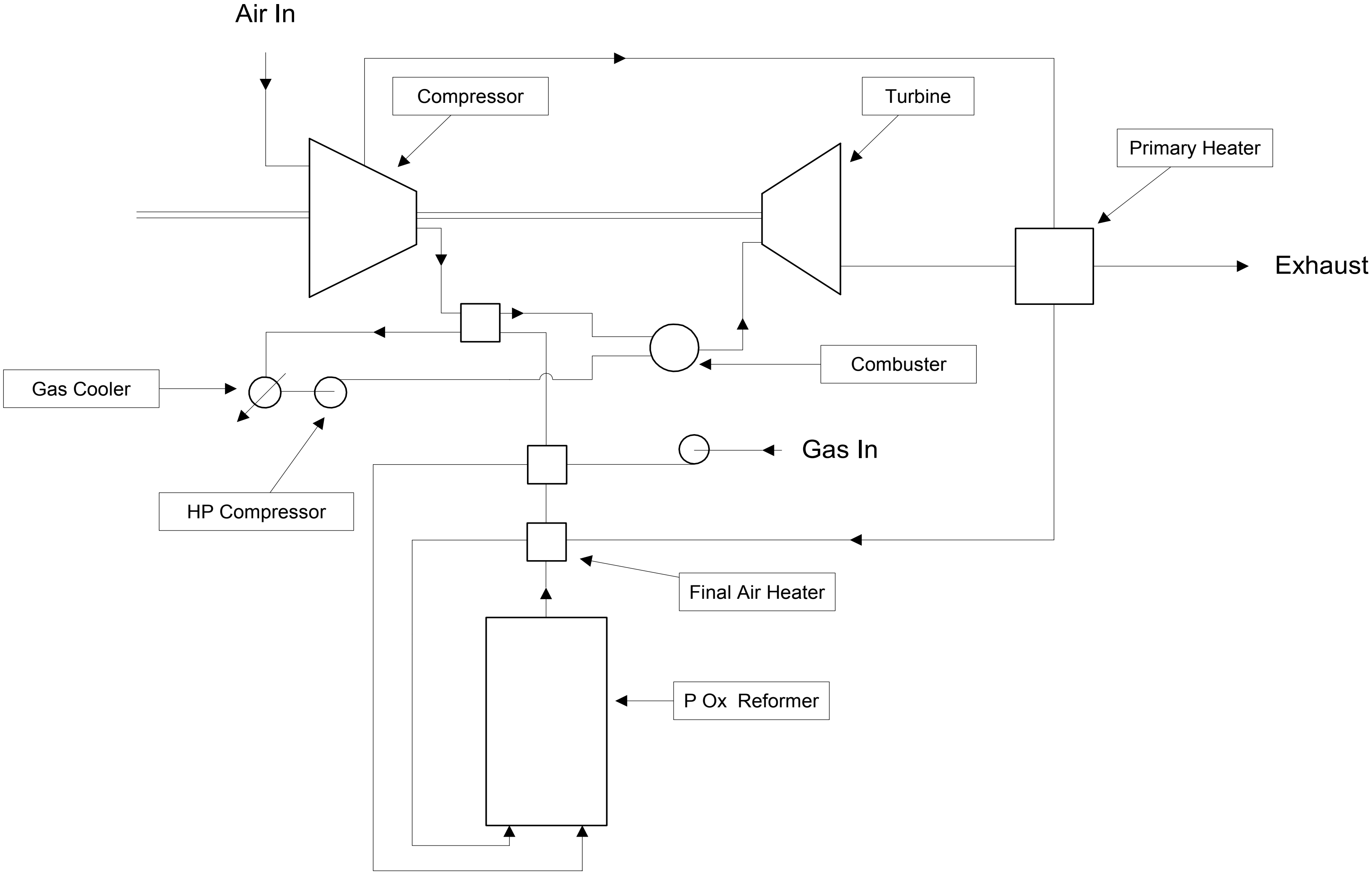

Figure 19. Flow Schematic Integrating Partial Oxidation Reformer and Gas Turbine

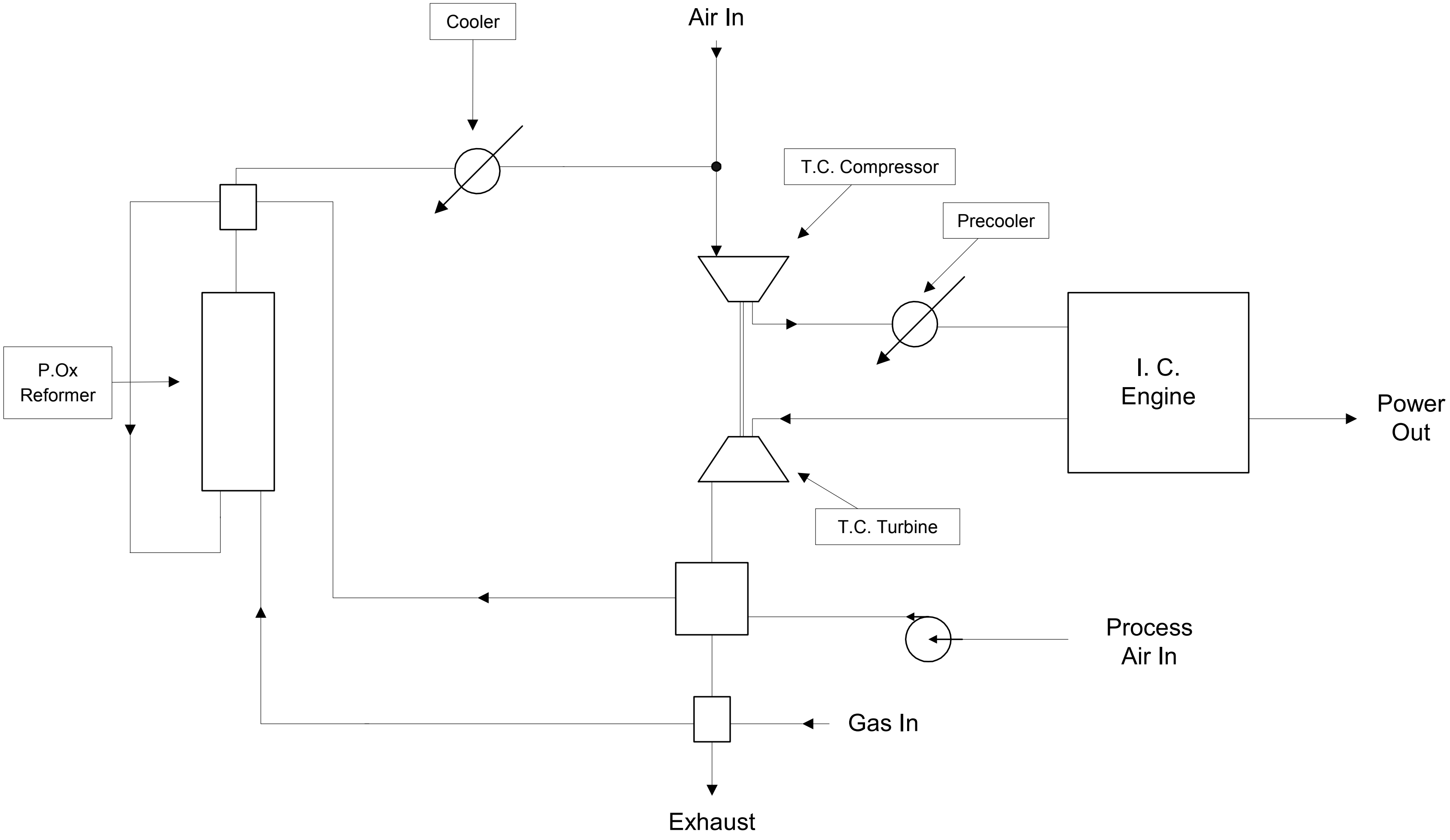

Figure 20. Flow Schematic Integrating Partial Oxidation Reforming and Reciprocating Engine

mildly affected by the inclusion of steam and at reactor inlet temperatures there is a significant gain in the hydrogen yield over that obtained by the use of air alone. The improvement in reactor efficiency is significant if considered from the viewpoint of reduction in thermal losses. Under conditions of higher O_2/C ratios, the reduction in losses would be expected to be more significant, with a possibility of some gains due to the recuperative effects of the steam/carbon reactions.

Assessment of Reformed Natural Gases Applied to Engines

As already noted, reforming serves a valuable purpose in delivering a fuel gas of relatively constant composition and properties from natural gas feedstocks, including field gas, with widely varying contents of ethane, propane, butane and higher order hydrocarbons. Table 7 sets out the more important combustion related properties of selected products, together with those of a high methane natural gas, a hypothetical methane/methane reformate mix used as a datum case, and the biomass derived gases and blends considered earlier.

To compare the merits of these gases for use as reciprocating engine fuels, Table 8 has been prepared. In this table, the maximum air/fuel ratio has been calculated at which the engine power output could be maintained equal to that with the base case fuel. This is listed in the first column and is divided by the stoichiometric air/fuel ratio in the second column to provide the maximum value of the parameter λ. This parameter is a measure of the ability to operate in lean burn mode to control NO_x emissions. In the case of the natural gas fuel, the ability to do so is knock limited rather than capacity limited, and the value of $\lambda = 1.67$ has been assumed. For the other fuels, the knock limit is unknown and subject to experimentation. However, in every case, the adiabatic flame temperature is lower than that for the datum case fuel which reduces the need for excess air as a diluent. The fuels with higher contents of inert gases have lower adiabatic flame temperatures. Thus, the 50/50 mixture of natural gas and air blown partial oxidation biomass gas, (#9) and the reformate from the combined partial oxidation and steam reaction may prove to be low NO_x fuels, although #9 has a low flame speed. However, peak flame temperature is only one factor to be considered and it is impossible to select the better fuels without testing. The amount of C2 and heavier hydrocarbons in fuel gases is of special concern for high compression ratio engines, and full stream reforming, even at very mild conditions, can effectively eliminate them.

In the case of gas turbines, all of the listed fuels could probably be used successfully provided that flashback could be avoided in lean premix combustion systems. The blended biomass derived fuels appear to be fully competitive with both commercial natural gas and reformed natural gas. For gas turbines, the capacity limited values of λ are irrelevant and the main concerns are the lean extinction limit at combustor inlet conditions, the adiabatic flame temperature, and flashback at the stoichiometry of the combustor inlet mixture conditions.

Table 6. Input/Output Data for Partial Oxidation Reformer with Added Steam

	Inlet	Outlet		
Oxygen to carbon ratio		0.1	0.15	0.3
Molar flow kmol/min	0.0285	0.0568	0.0676	0.1002
Mass flow kg/min	0.4829	0.987	1.1867	1.7857
Temp C	49.3872	533.1012	567.4475	632.6307
Heating values (60 F)				
Gross kJ/kmol	9.01E+05	4.47E+05	3.73E+05	2.47E+05
Net kJ/kmol	8.12E+05	3.98E+05	3.32E+05	2.19E+05
Std vap 0 C m3/h	38.3273	76.3783	90.9144	134.7434
Component mole %				
Methane	95.136	41.016	30.508	12.507
Ethane	2.675	0.001	0.001	0.000
Propane	0.288	0	0	0
I-Butane	0.030	0	0	0
N-Butane	0.049	0	0	0
I-Pentane	0.014	0	0	0
N-Pentane	0.013	0	0	0
N-Hexane	0.013	0	0	0
N-Heptane	0.010	0	0	0
N-Octane	0.006	0	0	0
Hydrogen	0	23.098	27.200	34.006
Water	0	5.580	4.794	3.737
Carbon Monoxide	0	5.435	8.273	13.537
Carbon Dioxide	1.014	5.238	4.644	3.256
Nitrogen	0.752	19.632	24.581	32.957
Oxygen	0	0	0	0
kJ/min				
gross	25664	25390	25228	24759
net	23131	22601	22430	21964
Efficiency				
gross		**98.9%**	**98.3%**	**96.5%**
net		**97.7%**	**97.0%**	**95.0%**
kJ/m3				
gross	40176	19945	16650	11025
net	36210	17754	14803	9780

Partial Oxidation with steam
0.2 steam/carbon, 400C inlet, 85 methane number gas

Table 7.

DOE FUEL-QUALITY CHARACTERISTICS FOR LEAN-BURN ENGINES Reuther

		Species	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO	H_2	CO_2	N_2	H_2O	Inert	Sum	A/F	LHV	LHV	MW	FS
															Btu/ft3	mJ/m3	g/mole	cm/s
	Neat Air/Fuel Ratio		9.5	16.7	23.8	31.0	2.4	2.4										
	Neat Lower Heating Value	Btu/ft3	911	1622	2322	3018	321	275										
	Neat Molecular Weight	g/mole	16	30	44	58	28	2	44	28	18							
	Neat Maximum Flame Speed	cm/s	45	47.5	45.5	46	52	326										
	Neat Adiabatic Flame Temperature	C	1927	1922	1967	2007	2032	2072										
	Neat Adiabatic Flame Temperature	F	3501	3492	3573	3645	3690	3762										
1	Natural Gas, 85 Methane Number		95.1	2.7	0.3	0.1	0.0	0.0	1.0	0.8	0.0	1.8	100.0	9.8	920	34.3	16.9	43
2	Methane 20% Steam Reformate		57.1	0.0	0.0	0.0	14.3	28.6	0.0	0.0	0.0	0.0	100.0	6.5	645	24.0	13.7	126
3	500C Steam Reformate, 93% dry		63.1	0.0	0.0	0.0	0.1	22.6	6.9	0.5	7.0	14.4	100.2	7.7	640	23.9	15.0	75
4	400C Steam Reformate, 93% dry		72.1	0.0	0.0	0.0	0.0	15.1	5.2	0.6	7.0	12.8	100.0	8.3	698	26.0	15.6	63
5	400C POx Reformate 0.15 O_2/C		33.8	0.0	0.0	0.0	13.4	24.7	0.6	27.1	0.6	28.3	100.2	6.1	419	15.6	17.6	50
6	400C POx Reformate 0.45 O_2/C + 40% NG		40.2	1.1	0.1	0.0	11.5	22.2	0.8	23.7	0.5	25.0	100.1	6.8	484	18.1	17.5	53
7	400C POx Reformate 0.45 O_2/C + 50% NG		49.3	1.4	0.1	0.0	9.1	18.5	0.8	19.9	0.5	21.2	99.6	7.4	554	20.7	17.3	54
8	400C POx Reformated 0.1 O_2/C		46.5	0.0	0.0	0.0	11.0	19.5	0.6	22.1	0.4	23.1	100.1	7.0	513	19.1	17.4	52
9	NG + 50% AB POx Biogas		47.5	1.3	0.3	0.0	11.5	10.0	4.0	22.0	3.5	29.5	100.0	7.8	523	19.5	20.1	28
10	NG + 50% Pyro Biogas		54.5	2.8	0.3	0.0	19.0	11.0	8.0	1.0	3.5	12.5	100.1	7.4	640	23.9	19.7	56
11	Pyrolytic Biogas		14.0	3.0	0.0	0.0	38.0	22.0	15.0	1.0	7.0	23.0	100.0	4.3	359	13.4	22.4	59
12	400 POx 0.1 O_2/C + 0.2 Steam/C		41.0	0.0	0.0	0.0	5.4	23.1	5.2	19.6	5.6	30.4	99.9	6.9	454	16.9	17.3	45

Table 8. Combustion Related Values and Reciprocating Engine Operating Parameters at Base Case Load

	Actual A/F	Stoich A/F	λ	Flame Speed Cm/S	Adi Temp C	LHV MJ/m^3	Inerts %	H_2 %
Natural Gas, 85 Methane Rating	16.3	9.8	1.67*	43	1859	34.3	1.8	0
Methane 20% Steam Reformed	13.7	6.5	2.11	126	1912	24.0	0	28.6
500 C Steam Reformate 93% Dry	13.7	7.7	1.78	75	1829	23.9	14.4	22.6
400 C Steam Reformate 93% Dry	15	8.3	1.80	63	1831	26.0	12.8	15.1
400 C PO_x Reformate 0.15 O_2/C	8.5	0.1	1.40	50	1815	15.6	28.3	24.7
400 C PO_x Reformate 0.45 O_2/C + 40% NG	10.1	6.8	1.49	53	1827	18.1	25.0	22.2
400 C PO_x Reformate 0.45 O_2/C + 50% NG	11.7	7.4	1.58	54	1834	20.7	21.2	18.5
400 PO_x Reformate 0.1 O_2/C	10.7	7.0	1.52	52	1829	19.1	23.1	19.5
50/50 NG/7% m AB PO_x	10.9	7.8	1.40	28	1796	19.5	29.5	10.0
50/50 NG/7% m Biopyro	13.7	7.4	1.85	56	1861	23.9	12.5	11.0
Pyrolytic Biomass 7% Moist	7.2	4.3	1.69	59	1867	13.4	23.0	22.0
400 C PO_x 0.1 O_2/C + 0.2 Steam/C	9.4	6.9	1.35	45	1778	16.9	30.4	23.1

Note: Steam reformats are based on 1:1 steam/carbon ratio
m – moisture content (molar)

Conclusions

Biogas from pyrolysis of biogas, and blends of this gas with natural gas, appear suitable for use in both reciprocating gas engines and gas turbines. Mild reforming is an effective way of eliminating C2 + hydrocarbons from natural gases, and possibly from biogas.

Partial reforming of natural gas using either partial oxidation or steam reforming routes is feasible using only heat extracted from the engine exhausts.

Combining partial oxidation and steam reforming appears to involve the least thermal losses and makes good use of low grade exhaust heat.