

The Autogenous Hydrogen Automobile

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ABSTRACT

The first phase of a feasibility study for the incorporation of catalytic steam reforming reactors into mobile power plant fuel systems has been completed. Two laboratory prototype reformers were used to steam reform hexane feedstock to fuel gas mixtures consisting of H_2 , CH_4 , CO , and CO_2 . Above $485^\circ C$ conversion was found to be equilibrium (rather than kinetically) controlled by the methane reforming and water gas shift reactions. Reactors used were 1) a 9" long section of 2" stainless steel pipe, and 2) a 5" long section of 3-1/4" stainless steel pipe. In both cases the reactors were filled with Girdler 5/8" raschig ring nickel reforming catalyst. Reactor residence times near .01 seconds allowed complete conversion of hexane to theoretically predicted equilibrium product distributions. Experimental hydrogen composition in the fuel gas generated at 2.5 atm with a steam to carbon ratio of 2.56 ranged from .38 to .68 mole per cent (dry basis) at temperatures of $485^\circ C$ and $695^\circ C$ respectively. The equivalent reactor volume required to provide fuel gas at a rate sufficient to power a medium sized car at 60 mph is estimated to be on the order of 0.2 cubic feet. Additional size reduction may be realized with more active reforming catalysts especially considering that operation was not found to be kinetically controlled.

Introduction

Hydrogen has been shown to be a superior engine fuel or fuel additive from an emission standpoint (1, 2, 3, 4, 5, 6). Lee and Wimmer [1] compared engine operation using simulated reformer fuel gas, methane, propane, and gasoline. Their comparison was made with regard to fuel consumption and CO , hydrocarbon (HC), and NO_x emissions. They found simulated fuel gas to be extremely advantageous from fuel economy and emission standpoints, as

compared to other fuels, when care is taken in using proper mixture control. Murray and Schoepfel [2-4] found that the hydrogen engine is not only capable of operating over a wider range of conditions and with lower NO_x emissions than its gasoline counterpart, but it is also capable of exceeding the manufacturer's maximum engine power rating. Eccleston and Fleming [5] compared engine operation using synthetic coal gas, natural gas, and hydrogen enriched natural gas to obtain comparative data on emissions and performance. They found that coal gas and hydrogen-enriched natural gas have lean limits extended significantly beyond the lean limit of natural gas. For lean operation the presence of hydrogen can reduce emissions even for natural gas and at the same time vehicle performance is enhanced due to improved flame propagation with hydrogen present. Swain and Adt [6] have converted a 1970 Toyota to run on hydrogen and obtained a 50% increase in engine efficiency over that of the gasoline fueled engine. NO_x emissions are expected to meet the 1975 and later standards with minor modifications. A more extensive review of hydrogen fueled engines is given by Billings and Lynch [7, 8].

The improvement in emission characteristics with hydrogen is due primarily to the lower flame temperature resulting from lean combustion. An allied factor is the high rate of combustion of hydrogen resulting in decreased residence time necessary in the flame zone to obtain complete combustion. Both these factors tend to reduce NO_x formation since it is the result of slower, high temperature reactions.

The concept being tested in this study is the autogenous catalytic steam reforming of liquid hydrocarbons to produce a hydrogen rich fuel gas for automotive use. The principal advantages to the concept are diminished emissions of HC, CO, and NO_x and the possible enhancement of fuel economy because of more efficient combustion and through the utilization of waste engine heat to provide process heat for the reforming reactor. Similar, but not identical concepts are currently under development by International Materials Corporation of Boston, Mass.; Siemens of Munich, Germany; and the National Aeronautics and Space Administration-Jet Propulsion Laboratory in Pasadena, California. The University of Arizona concept is discussed in more detail elsewhere [9].

This report will present the results of the initial phase of the development program. The initial phase was intended to answer the question of whether a fuel gas generator (reformer) supplying sufficient fuel gas to sustain engine operation, could be made small enough to be reasonably incorporated into an automobile. The study was conducted in two parts: 1) the theoretical prediction of equilibrium fuel gas composition for various reformer temperatures, pressures, and water to carbon ratios, and 2) the experimental operation of a reformer to determine the approach to equilibrium achieved in actual practice for reasonably sized reformers. Specific details of the study are contained elsewhere [10]. What

follows in this report is a description of the experimental results and their comparison with theoretical equilibrium predictions.

Experimental Apparatus

A schematic of the experimental apparatus used is shown in Figure 1. In operation the steam generator was used in conjunction with the radiant heating units to bring the reactor temperature to the desired level. Once this temperature was obtained a mixture of hexane and water with the desired H_2O/C ratio was injected into the vaporizer septum. The system pressure was monitored during the run as was the composition of the gas generated (water was condensed out). The pressure was observed to rise to about 2.5 atm rapidly and to stay at that level for the time required for reaction. After this, the pressure rapidly decreased to atmospheric. Composition data was collected on this pressure wave. No significant gas composition differences were noted at various times into the run indicating a steady state situation on the pressure wave.

Gas composition was measured using a Perkin-Elmer, 154D Vapor Fractometer with thermal conductivity detector. The G. C. column was a $10' \times 1/4''$ tube packed with Porapak Q. Helium carrier gas was fed at a rate of 27 cc/min at 12 psig and the oven temperature was $70^\circ C$.

Catalysts used were Girdler G-56B and G-90A nickel reforming catalysts in the form of $5/8''$ raschig rings.

Results

Figure 2 represents the experimental and theoretical equilibrium compositions of H_2 , CO, CH_4 , and CO_2 as functions of temperature for a pressure of 2.5 atm and a H_2O/C ratio of 2.56 with hexane as the hydrocarbon feed. Figure 3 represents the composition of fuel gas as a function of the H_2O/C ratio at a temperature of $560^\circ C$ and a pressure of 2.5 atm. As can be seen, the agreement between theoretical equilibrium values and experimental values is good, indicating that the reaction was equilibrium controlled by the methane reforming and water gas shift reactions.

Carbon formation was a common occurrence particularly at high temperatures and low steam ratios. For the G-56B catalyst, up to 12.3% of the hexane carbon was cracked to elemental carbon under such conditions, as is shown in Table 1. Carbon deposited in the reactor was easily removed by injecting steam in order to gasify it. Using this procedure to quantify the amount of carbon formed, a material balance about the reformer could be reasonably well closed. A sample material balance is shown in Table 2.

At $485^\circ C$ with a H_2O/C ratio of 2.56, heavier gases appeared in the gas generator product. In particular acetylene, ethylene, and propane were observed

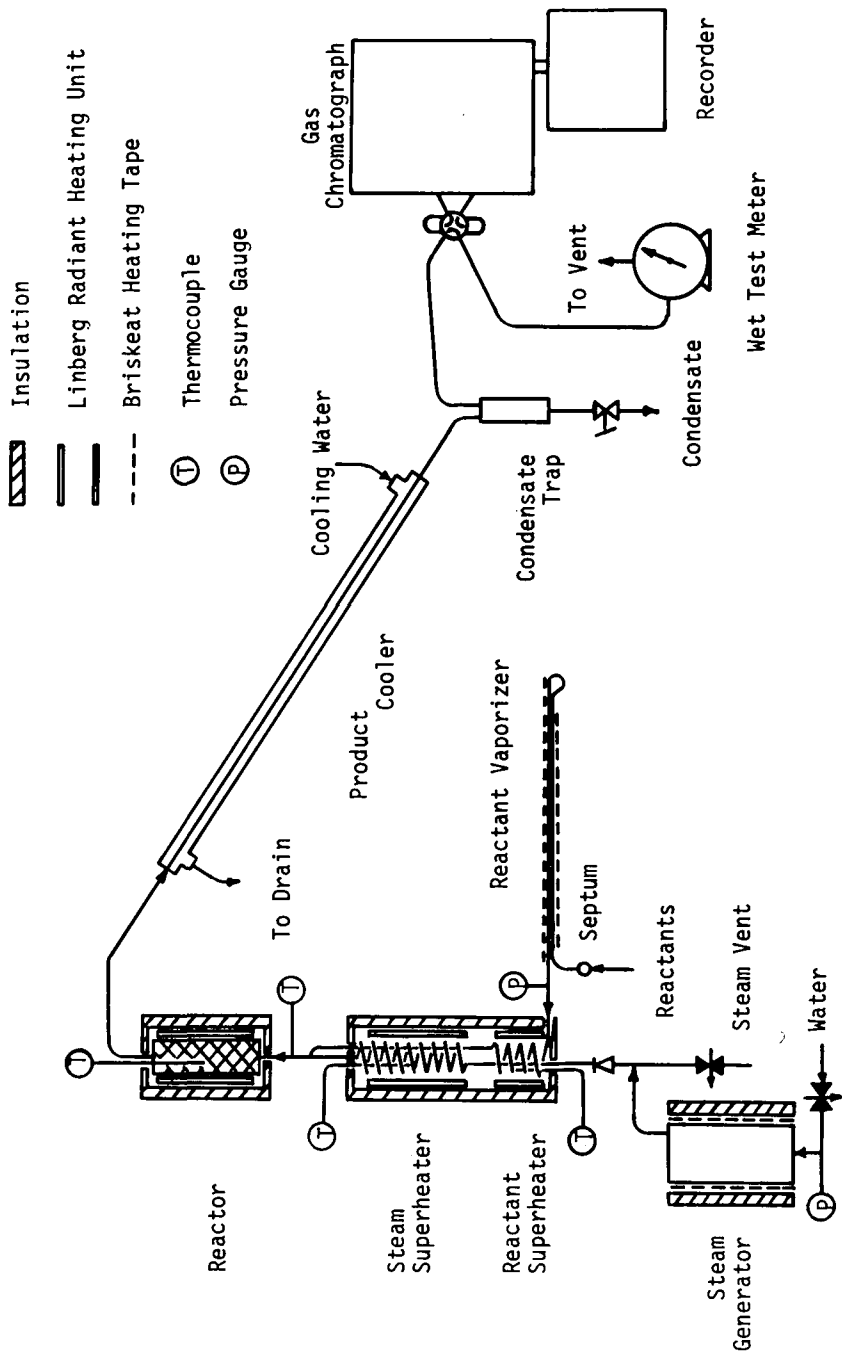


Figure 1. General experimental flow scheme.

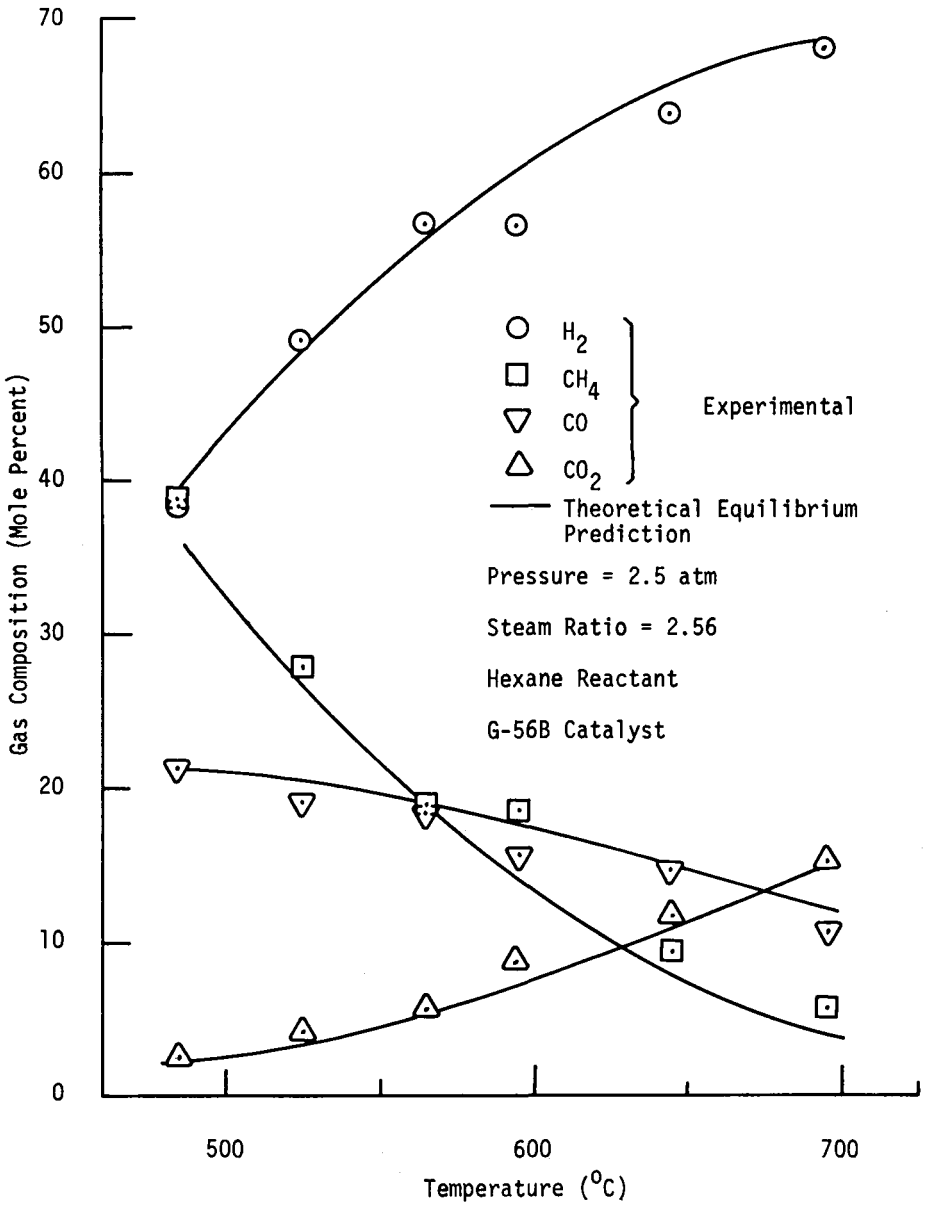


Figure 2. Dry gas composition versus temperature.

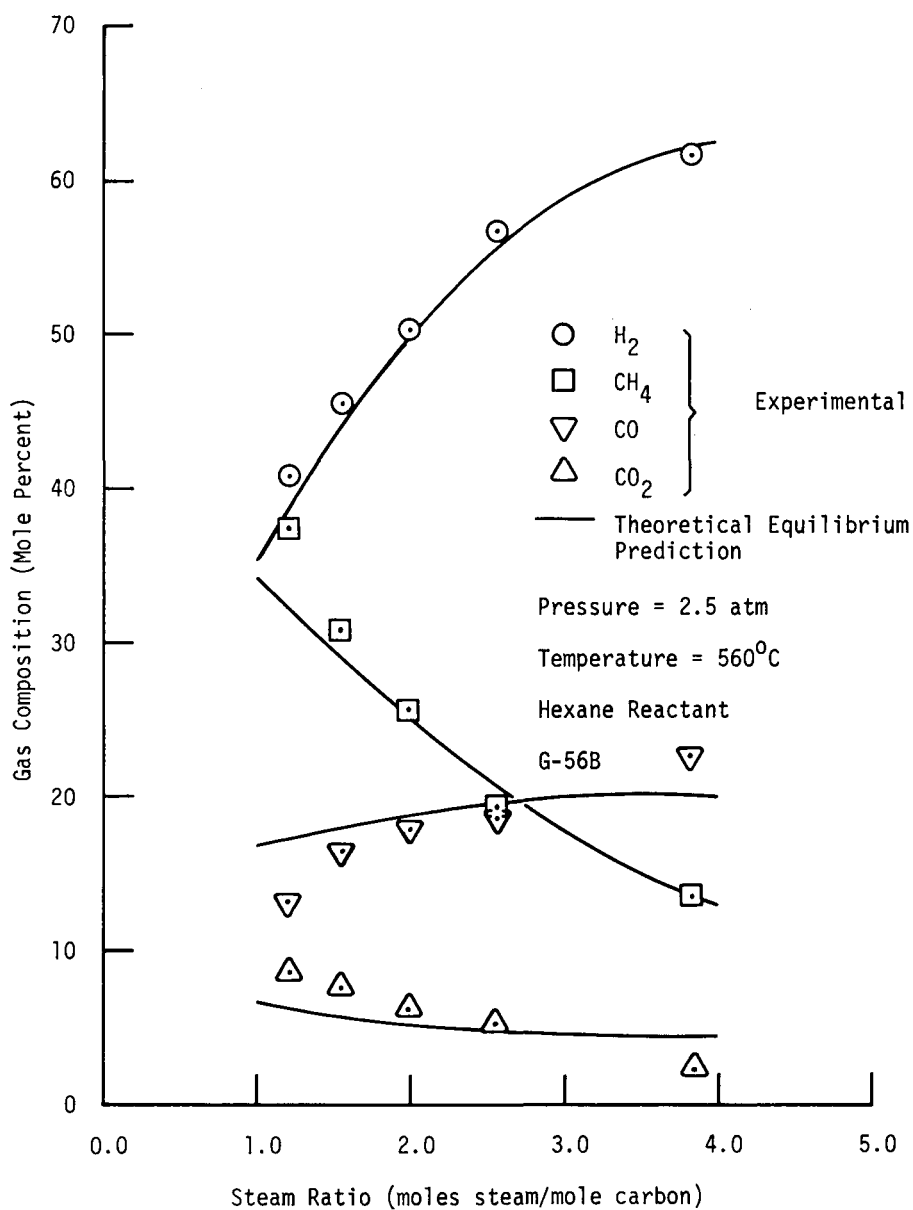


Figure 3. Dry gas composition versus steam ratio.

Table 1. Carbon Formation*

<i>Catalyst</i>	<i>Reactor Temperatures °C</i>	<i>Steam Ratio</i>	<i>Carbon in Reforming Condensate</i>	<i>Carbon in Decoking Condensate</i>	<i>Carbon reacted by Decoking</i>	<i>Total Carbon</i>
G-56B	485	2.56	0.0193	0.0045	0.0260	0.0401
G-56B	520	2.56	0.0238	0.0188	0.0520	0.0946
G-56B	565	2.56	0.0347	Decoking step not done		
G-56B	595	2.56	0.0317	Decoking step not done		
G-56B	645	2.56	0.0310	Decoking step not done		
G-56B	695	2.56	0.0300	0.0092	0.0601	0.0993
G-56B	565	1.21	0.0283	0.0164	0.0687	0.1134
G-56B	565	1.54	0.0271	0.0150	0.0598	0.1019
G-56B	555	1.97	0.0353	0.0124	0.0755	0.1232
G-56B	565	3.83	0.0257	0.0070	0.0342	0.0669
G-90A	565	1.97	0.0033	0	0.0201	0.0234
G-90A	600	1.97	0.0047	0.0023	0.0212	0.0282

* Based on the number of moles of elemental carbon formed per mole of fixed carbon in the hexane.

at a total of .33% by volume of the mixture. None of the runs at higher temperatures resulted in these heavier gases. From this it may be concluded that with the catalyst used, 485°C is a lower operating temperature limit, below which reaction rate becomes the controlling factor.

Conclusion

A 5cc hexane-water mixture at a H₂O/C ratio of 2 would pass through the gas generator operating at 560°C in about 10 seconds. This is equivalent to a continuous flow rate of .125 gm/sec of hexane and .310 gm/sec of water. The gas generator residence time (reactor void volume per volumetric flow rate at S.C.) was about 0.016 seconds. The reactor void fraction was 0.59 (reactor no. 1). Using this information and assuming a 3 gm/sec reformer feed rate requirement to sustain a medium size car at 60 mph, it is estimated that a gas generator with an internal volume of about 0.2 cubic feet should suffice for this application. This is well within the range of reasonability.

The continuing effort of this study is to integrate a continuous reformer gas generator into a test stand engine on a hydraulic dynamometer. Engineering problems of startup, heat exchange, variable engine power demand, and pollution levels will determine the ultimate system configuration.

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Table 2. Material Balance

Stream	1		2		3		4		5		6	
	moles	grams	moles	grams	moles	grams	moles	grams	moles	grams	moles	grams
Component												
Hexane	0.230	19.77	0	0	0	0	—	—	0	0	0	0
H ₂ O	1.667	30.00	0	0	0.813	14.60	2.667	50.00	0	0	2.440	44.00
H ₂	—	—	0.843	1.69	—	—	—	—	0.187	0.37	—	—
CO	—	—	0.178	4.98	—	—	—	—	trace	trace	—	—
CH ₄	—	—	0.774	12.38	—	—	—	—	0	0	—	—
CO ₂	—	—	0.274	12.06	—	—	—	—	0.088	3.87	—	—
C	—	—	—	—	0.039	0.46	—	—	—	—	0.023	0.27
Total	1.897	49.77	2.069	31.11	0.852	15.16	2.667	50.00	0.275	4.24	2.463	44.27
Moles C	1.379		1.226		0.039		—		0.088		0.023	
Moles H	6.552		4.782		1.626		5.333		0.374		4.880	
Moles O	1.667		0.726		0.813		2.667		0.176		2.440	

Total grams in = 99.77
 Total grams out = 94.78
 Stream #1 = Reforming Reactants
 #2 = Product Gases (51.93 liters = 2.069 moles)
 #3 = Condensate
 #4 = Decoking Water
 #5 = Decoking Gases (6.90 liters = 0.275 moles)
 #6 = Decoking Condensate
 Moles C in = 1.379
 Moles C out = 1.376
 Moles H in = 11.885
 Moles H out = 11.670
 Moles O in = 4.334
 Moles O out = 4.155

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