DIRECT CONTACT PYROLYSIS OF METHANE USING NUCLEAR REACTOR HEAT

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ABSTRACT

An energy system based on fossil fuels is responsible for the generation of massive amounts of CO and CO_2, (from oxidation of about 6 gigatons C per year), which is recognized as a threat to our environment. An alternate energy system based on hydrogen would be more environmentally benign but significant developmental work is required for commercial acceptability. These greenhouse gas emissions are recognized as a threat to our environment. The U.S. safely uses about 4 trillion cubic feet of H_2, most of which is produced by the steam reforming of hydrocarbons, primarily methane (SMR). Two major disadvantages of the SMR technology are the concurrent generation of greenhouse gases and the energy costs. We are proposing to use direct contact pyrolysis (DCP) of methane/natural gas to minimize these disadvantages. In this process, methane is bubbled through a molten metal heated by the liquid metal coolant in Generation IV reactors to produce H_2 and carbon, which is collected on the liquid metal surface. Coking of active sites does not occur. Proof-of-principle experiments were recently completed and critical experimental parameters were identified. Methane was converted to H_2 and carbon when bubbled through lead at all temperatures studied, 600-900°C, without generating greenhouse gases. Conversion efficiency increased with temperature and residence time. The temperature dependence of the reaction was used to calculate the apparent energy of activation, 213 kJ/mol for temperatures between 750 and 900°C. This value is considerably lower than the bond dissociation energy of H-CH_3 at 431 kJ/mol, indicating an autocatalytic reaction. The maximum conversion at 900ºC was about 25%. Hydrogen is the only significant gaseous product in DCP, that is, the reaction, $CH_4 \rightarrow 2H_2 + C$ goes to completion. No heavier gaseous hydrocarbons were observed. Results of tests with a commercial grade of natural gas were similar to those with methane, although the ethane in the natural gas was preferentially pyrolyzed. Currently we are identifying methods to increase conversion efficiency at lower temperatures, such as longer residence times.

INTRODUCTION

The economic well-being of the world depends on reliable, affordable supplies of energy that are also environmentally benign. Fossil fuels provided about 80% of the total world energy needs in 1990 but at an environmental cost from emissions of CO, CO_2, NO_x, SO_2, unburned hydrocarbons, and particulates [1]. Hydrogen is an attractive energy source because it burns cleanly. Water is its only product of combustion. In addition, hydrogen's chemical properties make higher utilization efficiencies possible compared to fossil fuels. One example of a new technology based on hydrogen is the hydrogen fuel cell. Its advantages are that it produces electricity, has no moving parts, makes no noise, and is very efficient [2,3].

Efforts to change the energy mix from fossil fuels to hydrogen has given impetus to the reexamination of existing technologies to determine where synergies exist and where improvements can be made as well as to the development of new technologies. Currently, the

United States safely uses about 4 trillion cubic feet of hydrogen yearly, almost all of which is produced at oil refineries or by steam reforming of natural gas. Oil refineries produce and use 2.5 trillion standard cubic feet (scf) of hydrogen annually while the chemical industry uses 1.5 trillion scf. The need for hydrogen is growing at 5-10% per year [4-6]. Currently, steam reforming of methane (SMR) is the most efficient, economical, and widely used process for producing hydrogen and hydrogen-carbon monoxide mixtures [7]. Steam reforming is usually run at 700-925°C and is limited by the metallurgy of the tubes used in the reactor. The reaction is endothermic and the energy for the reaction is supplied by the combustion of the natural gas. Deep-sea and/or salt-mine sequestration have been proposed to handle the greenhouse gases generated by SMR. Greenhouse gases are produced, but they are sequestered in other developmental technologies, such as sorbent-enhanced reforming of natural gas [8].

We propose that methane be pyrolyzed using the heat contained in the liquid metal coolant in Generation IV nuclear reactors and that the pyrolysis reaction be run to produce only hydrogen and carbon, the latter being collected on a liquid metal surface. This direct contact pyrolysis (DCP) of methane or natural gas, therefore, couples the synergies between nuclear power generation and hydrogen generation from methane. No greenhouse gases are generated because there is no oxygen source and air and water are not involved in the process. This process provides all of the advantages of the more typical SMR process without the disadvantage of CO and CO_2 formation and with lower energy costs. The reaction of steam with methane is twice as endothermic as the pyrolysis per unit volume of methane [9]. The carbon is easily removable from the liquid-metal surface because of the density differences. The recovered carbon can be burnt for fuel, sequestered, or used to power the direct carbon conversion cell, a promising new fuel cell application whose thermodynamic efficiency exceeds 70% [10].

We recently completed proof-of-principle experiments that led to identification of critical experimental parameters. Methane and natural gas were converted to hydrogen and carbon at all temperatures studied, 600-900°C. We are currently refining our experimental procedures to obtain more quantitative information. We are also investigating various methods to increase the efficiency of hydrogen production, especially at the lower end of the temperature range.

EXPERIMENTAL

Experiments have been conducted with both a horizontal and a vertical microreactor. The two designs differ primarily in the path length the methane bubbles traverse in the molten lead. The gas handling systems are nearly the same for both reactors. Mass-flow controllers (labeled FIC in Figs. 1 and 2) are used to control the flow rate of the gases entering the system. Pressure relief valves, check valves and pressure gauges are safety features. Heating is accomplished with either a single-zone or four-zone furnace. Thermocouples, labeled TIC and TSS in Figs. 1 and 2, are used for temperature control and over temperature protection, respectively. Gases enter and exit the reactor via Swage-Lok® fittings, which are attached on the flanges at either end of the reactor and are not shown.

The horizontal reactor is a 61-cm quartz tube with a 2.5-cm. OD. Stainless steel flanges are welded onto both ends of the reactor tube via metal-to-glass graded seals. A sketch of the reactor and the gas handling equipment is given in Fig. 1. The gas delivery tube inside the reactor contains four open-bore 0.32 cm diameter tubes. The delivery tube in situated in the reactor so that the tubes extend into the molten lead to a depth of about 0.32-cm. The lead is contained in nickel boats (10-cm x 1.6-cm x 0.95-cm). A single-zone furnace was used.

The vertical reactor in Fig. 2 is a 2.5-cm OD 304 stainless steel (SS) tube, closed at the bottom, with a stainless steel flange welded at the top. The lead is contained in a 1.3-cm OD-304 SS cup to which a thermocouple well is attached. The methane is bubbled through an open-bore 0.64-cm OD feed tube extending to the bottom of the cup, which allows the methane to travel through approximately 5.1-cm of lead. In some experiments, a by-pass line was used to measure the partial pressure of the inlet gas before each change in flow rate or temperature. The furnace shown in Fig. 2 is a four-zone furnace, which provides a longer heated zone and smaller temperature gradients than the single zone furnace, which was used in some experiments.
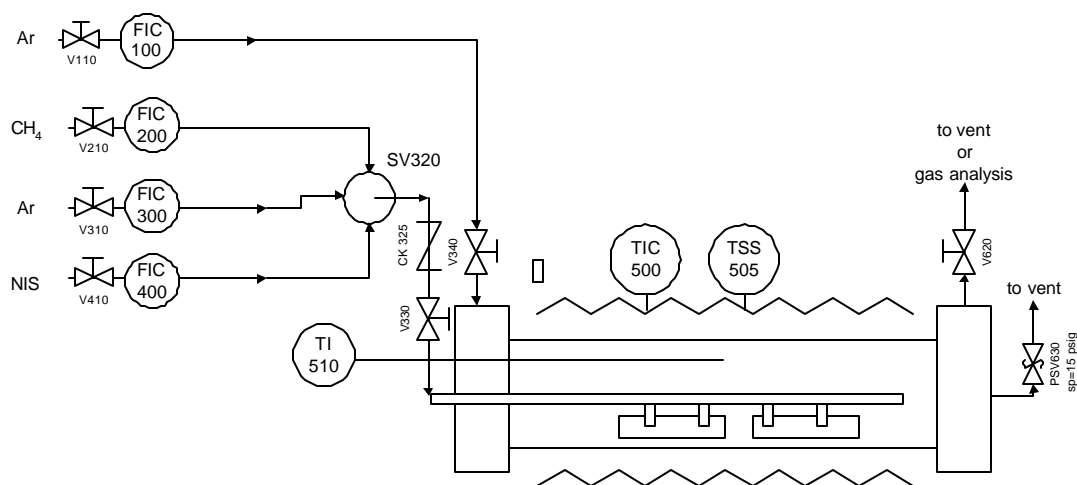

Fig. 1. Schematic of Methane Pyrolysis Unit. (Four delivery ports and two nickel boats are shown.) FIC units are mass-flow controllers. FIC 100 and FIC 400 were not used in most experiments.

A residual gas analyzer (RGA) mass spectrometer is attached to the outlet to allow for continual on-line analysis of the effluent gases. The RGA is connected to a computer interface, which allows for continual readout and data logging. Data are collected in two modes: (1) partial pressure versus time (p-t) for selected atomic mass units (amu) and (2) analog scans from 1 to 100 amu. The mass spectrometer samples only a small fraction of the outlet gas. The pressure is reduced from the initial value of about 1000 mbar to 10^{-6} mbar at the inlet of the mass spectrometer.

Most experiments were conducted with research grade (99.995%) methane. Some experiments were conducted with natural gas. The composition of the natural gas was measured by gas chromatography as 95.4% methane and 4.5% ethane, with no measurable amounts of CO_2 or H_2S.
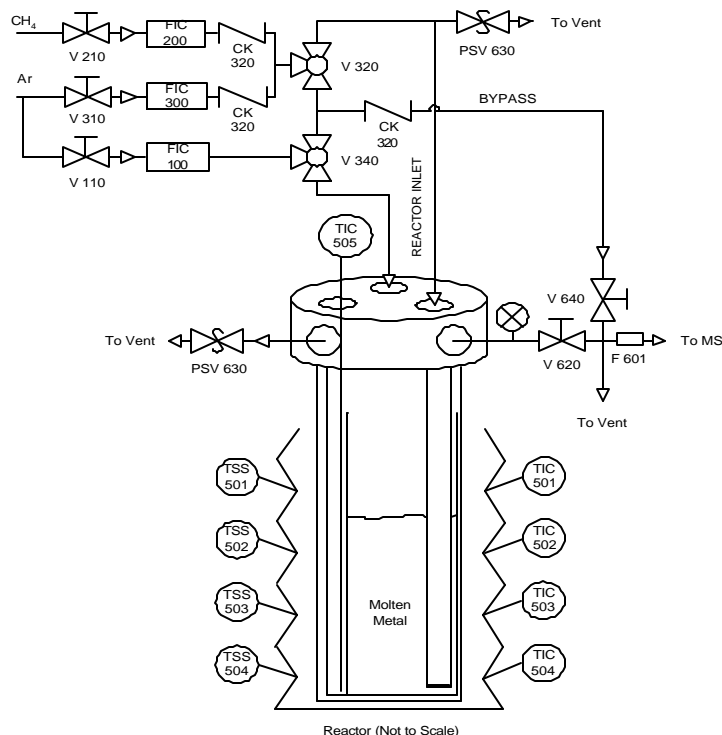
Fig. 2. A Sketch of the Vertical Reactor Heated in a Four-Zone Furnace. The abbreviations have the same meaning as in Fig. 1.

RESULTS

The results of the preliminary experiments are the following: (1) H_2 yields increase as the flow rate decreases; (2) H_2 yields increase with temperature; (3) H_2 yields are small but measurable between 600-700°C; (4) no other gaseous products are observed; (5) carbon is segregated on the lead surface, and (6) the pyrolysis products of methane and natural gas are H_2 and C, but H_2 yields are greater with natural gas than with methane under identical conditions. Each of these results is explained in more detail below.

Dependence on Flow Rate. A typical mass spectrum in the pressure versus time mode for a run conducted at 850°C is shown in Fig. 3. This figure illustrates the experimental procedure. During the first 10 minutes of the run, the system is flushed with argon and the temperature is increased from room temperature to 500°C to remove any residual water or air. When oxygen and water partial pressures are at background, the argon flow is terminated; the methane flow is started at 15 standard cubic centimeters per minute (sccm), and the temperature is increased to 700ºC. When the temperature has stabilized and the methane partial pressure reaches steady state (t = 75 m) the temperature is increased to the run temperature, 850°C. The flow rate was maintained at 15 sccm. After the H_2 partial pressure reaches a steady-state value (t = 128 m), the flow rate is lowered to 3 sccm and then to 1 sccm at t = 190 m. The vertical lines in Fig. 3 represent the times at which the flow rate was changed. The most notable feature in Fig. 3 is that the hydrogen partial pressure increases as the flow rate decreases, i.e., the longer the methane resides in the reactor, the greater the conversion. Residence time is calculated by dividing the

reactor volume by the flow rate. For experiments in a constant volume reactor where the volume (lead versus heated zone) is uncertain, we can say that the increase in the H_2 yield is proportional to residence time. Note that the vertical axis is given in units of torr and that the measured pressure is a small fraction of the total pressure of the hydrogen. For clarity, we have not shown the time dependence of any of the other gases.
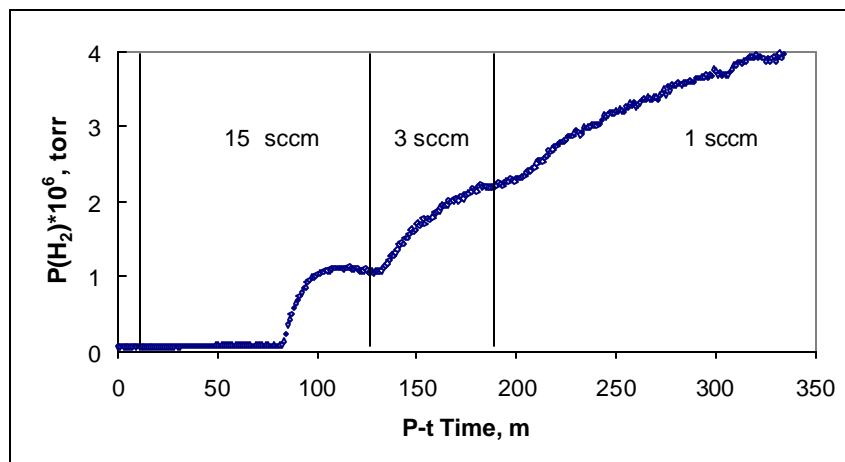

Fig. 3. Partial Pressure vs. Time for Methane Pyrolysis at 850°C. See text for details on experimental procedure.

Fig. 4 is a plot of the steady state H_2 partial pressure for each of the three flow rates for the run conducted at 850°C, showing that the H_2 partial pressure is linearly related to the inverse of the flow rate. Similar graphs were obtained for experiments conducted from 750 to 900°C. Three flow rates, 15, 3, and 1 sccm were used in each of these experiments.
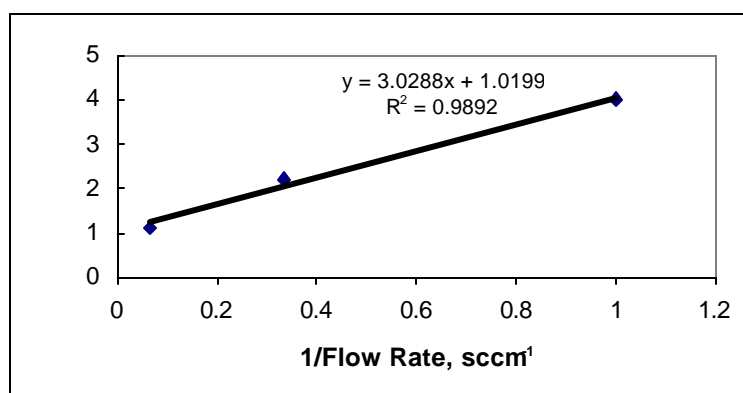

Fig. 4. Equilibrium Partial Pressure of Hydrogen at Three Flow Rates and 850°C

In Table 1, the slope, intercept, and square of the correlation coefficient are given for the linear dependence of H_2 partial pressure on the inverse of the flow rate at five temperatures. Both the

slope and the intercept increase with temperature, indicating that H_2 production increases with temperature as the flow rate becomes smaller, or as the time spent at temperature becomes longer. The intercept, which provides an estimate of the H_2 produced at very short residence times, is not zero and also increases slightly with run temperature.

Table 1. Values of the Slope, Intercept, and Square of the Correlation Coefficient for Hydrogen Generation from Methane Pyrolysis Runs at 750-900°C

Run Temperature, °C	Slope, torr·min/cc	Intercept, torr	R^2
750	4.26 E-07	0.764 E-07	0.999
800	1.10 E-06	1.56 E-07	0.985
820	2.45E-06	1.55E-07	0.998
850	3.03 E-06	1.02 E-06	0.989
900	1.12 E-05	3.00 E-06	0.962

The results from experiments with pure argon and with an argon-methane mixture also show that hydrogen yields from methane pyrolysis depend on residence time. Pyrolysis runs were conducted at 800°C with pure methane (1 sccm), and with an argon (9 sccm)-methane (1 sccm) mixture. The H_2 partial pressure was about 11 times smaller in the experiment with the argon-methane mixture than with pure methane, even though the methane flow rate was identical in the two experiments. The higher argon flow rate controlled the residence time.

Temperature Dependence. An apparent activation energy was calculated using the slopes given in Table 1 for the five temperatures studied. The slopes rather than a single point were used for each temperature to account for the variation in flow rate. The apparent activation energy was calculated with the Arrhenius equation, $k = Ae^{-Ea/RT}$. The value of $-E_a/R$ is given by the slope of the line in Fig. 5 and E_a, the apparent activation energy, is about 213 kJ/mol. The square of the correlation coefficient is 0.98, indicating a good fit with the data. The data were insufficient to determine a mechanism and an order for the reaction.
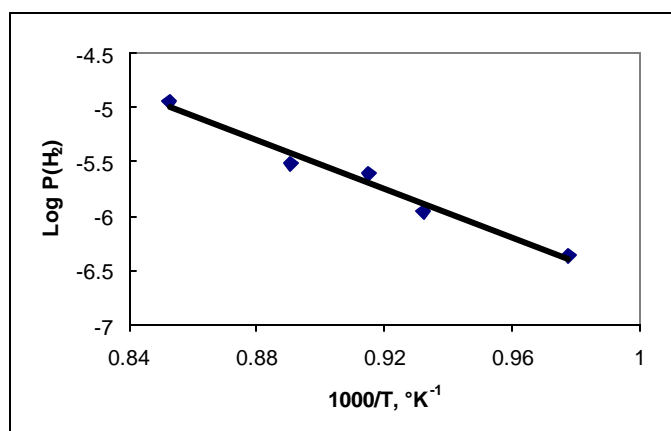

Fig. 5. Log of the Partial Pressure of H_2 vs. 1000/T(K).

Hydrogen Production at Lower Temperatures. We measured the partial pressure of H_2 at 600 and 700°C for methane flow rates of 1 and 3 sccm. The slopes for the two-point lines are 0.173 E-07 and 0.765 E-07, respectively. Hydrogen production increases with temperature and residence time; but it is about 5-6 times lower at 700 than at 750ºC. The mechanism at 600 and 700°C is probably different than that at =750°C because the 1/T dependence is different.

Carbon Segregation. In all of the experiments completed with the horizontal reactor in which lead was present, carbon was observed only on the surface of the lead. The quartz tube remained clear and free of carbon deposits. Visual inspection of a cross section of the lead after the experiments with the horizontal reactor showed no carbon entrainment. However, when lead was absent, the quartz tube quickly blackened. In the vertical reactor, carbon was found deposited on the walls of the stainless steel regardless of whether lead was present or not. The exposed surface area of the molten lead in the horizontal reactor was about 25 times larger than that in the vertical reactor. We expect that the smaller surface area of the lead in the vertical reactor may be at least partially responsible for carbon being found throughout the reactor. Examination of the carbon product by x-ray diffraction showed only amorphous carbon.

Reactor Design. The data obtained from experiments with the horizontal reactor led us to believe that increasing the residence time in the molten lead might result in more efficient methane pyrolysis. The vertical reactor was designed so that the distance the methane bubbles traveled through the molten lead was increased from ~ 0.3-cm (in the horizontal reactor) to ~ 5-cm. The volume of lead in the two reactors was about the same, about 5 cm^3.

In both the horizontal and vertical reactors, hydrogen production increased with temperature and decreased with flow rate, but there was no significant increase in methane conversion efficiency. In Table 2, we compare the maximum methane conversion in the two reactors. The conversion fraction was calculated from this expression: $(P(CH_4(i) - P(CH_4(f))/P(CH_4(i))$, where i and f represent the initial and final methane partial pressures. Data are given for two temperatures. We obtained the maximum conversion of methane with flow rates of 0.2 and 2 sccm in the horizontal and vertical reactors, respectively. The minimum flow rate depended on the pressure drop. If the flow rate on the methane mass flow controller was set too low, methane flow stopped and air was detected by the mass spectrometer. (The exit gas tube is open to the atmosphere.) These data indicate that an increase in path length in the molten metal does not necessarily lead to longer residence times and greater conversion efficiency. However, this technique may be useful in systems with less dense metals. We also tested the effect of using an open-bore delivery tube to which a 325 SS mesh screen was attached. The purpose of the screen was to deliver smaller bubbles to the molten lead, thereby providing a greater surface area for reaction. The results of tests with the screened delivery tube were essentially the same as those for the open bore tube.

Table 2. Fraction of Methane Conversion in Two Reactors

Temperature, °C	$(P(CH_4(i) - P(CH_4(f))/P(CH_4(i))$	
	Horizontal Reactor	Vertical Reactor
750	0.070	0.096
900	0.24	0.26

Other Design Improvements. Mass balance between hydrogen and methane partial pressures was not obtained in the proof-of-principal experiments with the horizontal reactor. It was necessary to determine the sensitivity of the mass spectrometer to various gases by calibrating the mass

spectrometer's response using either pure gases or gas mixtures whose composition was known or determined from gas chromatography. It was also necessary to measure the methane partial pressure before each change in temperature or flow rate, which was done by adding a bypass to the inlet line. These experiments were conducted with the vertical reactor after the bypass line was installed.

Results with Natural Gas. Pyrolysis experiments were also conducted with natural gas as well as methane. These experiments were run in the SS vertical reactor. The results of the experiments with natural gas were similar to those experiments with research grade methane. Hydrogen generation increased with temperature and decreased with flow rate. With the improvements in the experimental set-up, it was possible to calculate hydrogen yields based on mass balance from this equation: $(P(H_2)/(P(CH_4(i)) - P(CH_4(f)))$, where i and f represent the initial and final partial pressures, respectively. The data in Table 3 show that the hydrogen yield was higher with natural gas than it was with methane. Subsequent experiments show that ethane in the natural gas was preferentially pyrolyzed compared to methane. For example, at 750°C and 2 sccm, about 5% of the methane is reacted but over 30% of the ethane. The C-H bond dissociation energy is lower for ethane (410 kJ/mol) than for methane (431 kJ/mol). Preferential pyrolysis of the small amount of ethane in the natural gas results from the difference in bond dissociation energy and accounts for the nearly twofold increase in H_2 yield.

Table 3. Hydrogen Yield from CH_4 and Natural Gas (mol)

Flow Rate, sccm	H_2 Yield at 750°C from		H_2 Yield at 850°C from	
	CH_4	Natural Gas	CH_4	Natural Gas
9	0.53	1.17	0.94	1.56
5	0.56	1.41	1.00	1.82
3	0.61	1.66	1.25	2.06
2	0.67	1.82	1.32	2.08

Other Pyrolysis Products. Analog scans from 1 to 100 amu were routinely obtained for the various experiments. Measurable amounts of other gaseous hydrocarbons were never detected. In Fig. 6, scans are shown for 700 and 900°C. Scans from runs at other temperatures were essentially the same. Only hydrogen and methane are present in Fig. 6a. Note that the ratios of hydrogen and methane vary with temperature. Scans are also shown on an expanded scale in Fig. 6b for trace gaseous constituents. Very small partial peaks are observed at 28, 32, and 44 amu, which are due to air leaks. We considered the possibility that the peak at 28 amu was due to ethane, ethene, and/or CO_2. However, comparison with the library fragmentation patterns for air, ethane, ethene, CO, and CO_2 showed that the peak at 28 amu was more likely due to air than to ethane.
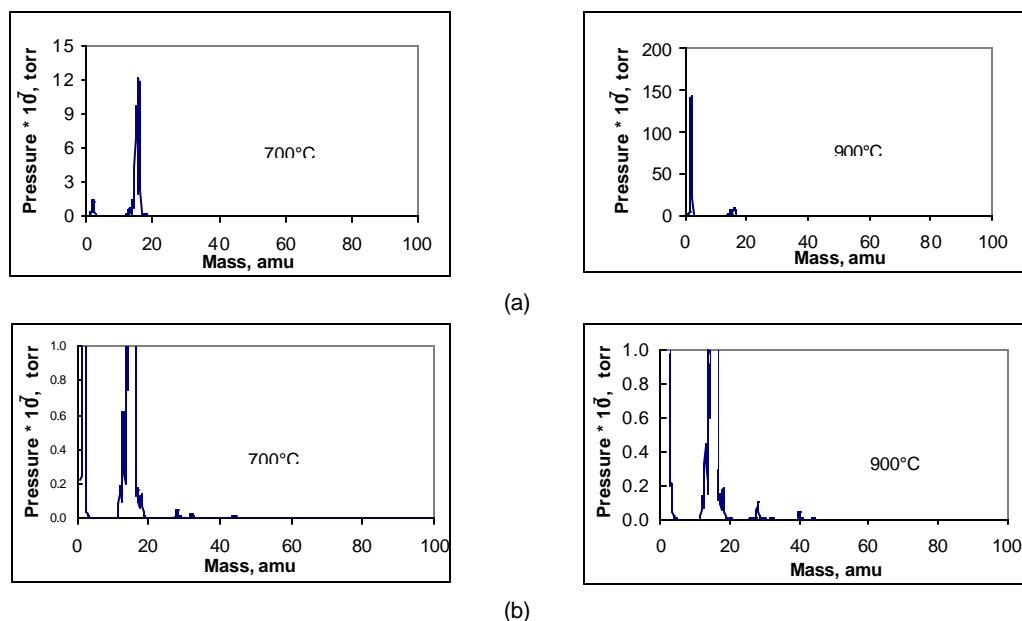
Fig. 6. Analog Scans Taken during Methane Pyrolysis at Two Temperatures. The peak at 2 amu is assigned to hydrogen. The cluster of peaks near 16 amu is assigned to methane. Figs. 6b are expanded graphs of Figs. 6a to show that there are essentially no other pyrolysis products other than hydrogen. The very small peaks at 28, 32, and 44 amu are assigned to air.

Furnace Design

Preliminary experiments with a 38-cm long four-zone furnace rather than a30 cm long single-zone furnace showed some improvement in hydrogen yield at 600°C. Slightly less than 3% of the natural gas was converted to hydrogen in the four-zone furnace. This compares with <1% in the one-zone furnace. The increased yield is due to the longer residence time at temperature.

DISCUSSION

The results of the proof-of-principle experiments show that direct contact pyrolysis is a promising new technology for obtaining H_2 without greenhouse gases and offers significant advantages over conventional steam methane reforming. Steam reforming consists of three steps: (1) synthesis gas generation ($CH_4 + H_2O \rightarrow CO + 3H_2$, accompanied by minor reactions: $CO + H_2O \rightarrow CO_2 + H_2$, and $CO + 3H_2 \rightarrow CH_4 + H_2O$); (2) the water-gas shift (WGS)($CO + H_2O \rightarrow CO_2 + H_2$); and (3) gas purification [6, 7]. The synthesis gas generation is highly endothermic requiring indirect heating. Typical process conditions for the reforming reaction are temperatures of 800-900°C, pressures varying between 1.5 and 3.0 MPa, and a Ni catalyst supported on alumina, which must be periodically reactivated. A large excess of steam is used to obtain maximum hydrogen yields. The composition of a typical synthesis gas (feed gas to the WGS) is a blend of H_2 (74 vol%), CO (18 vol%), CO_2 (6 vol%) and CH_4(2 vol%). The WGS reaction is generally run at 300-400°C and also involves a catalyst, Fe or Cu on alumina, which must be reactivated. Technologies such as pressure swing absorption have been developed to separate the gases. Gas purification generally involves a multicolumn pressure swing absorption process containing 4-12 absorption beds. Direct contact pyrolysis is a simpler process, which uses heat energy available in the liquid-metal coolants of Generation IV nuclear reactors as the energy source. Neither CO nor CO_2 is generated. No catalysts with active sites are used, so coking is not a problem. Temperature

requirements are similar to those in SMR, but no steam is used. In full-scale operation, any unreacted CH_4 will be recycled. Separation of the exit gases, consisting only of CH_4 and H_2, might be accomplished simply by filtering hydrogen from the exit gas using gas permeation membranes. Alternately, it should be possible to piggyback on the conventional technologies for gas separations developed for SMR, such as pressure swing absorption. The DCP system will have to be designed to monitor the carbon build-up on the metal surface, but subsequent removal of the carbon should be relatively easy based on the density differences between the carbon and the metal. The collected carbon could be sequestered or used for fuel. Currently, residual soot and hydrocarbons with very high C/H ratios produced in the petroleum industry are used for fuel [9]. Another possible market for the carbon is the carbon fuel cell, which requires disordered carbon, typically produced at temperatures <1200ºC [10].

Another objective of our research is to increase the hydrogen yield at lower temperatures, 500-700ºC. The advantages to this temperature region are lower energy consumption, less severe requirements on materials, and greater applicability to current nuclear reactors. The proof-of-principle experiments suggest two possible methods that should yield improved conversion efficiency: (1) longer path lengths in less dense molten metals and (2) mixing to maintain smaller bubbles.

CONCLUSIONS

The proof-of-principle experiments demonstrated that methane is pyrolyzed and yields only hydrogen and carbon at temperatures between 600-900ºC. No greenhouse gases are generated. Conversion efficiencies depend on temperature and residence time. In the microreactors tested, about 25% of the methane was converted at 900ºC and up to 10% at 750ºC. For a given temperature, residence time was identified as a critical parameter, and hydrogen yields increased with decreasing flow rates at all temperatures. The pyrolysis products of methane and natural gas were the same, carbon and hydrogen only. The hydrogen yield was higher for natural gas than for methane because of the preferential pyrolysis of ethane.

FUTURE WORK

Different methods for increasing yields, especially at 500-700ºC are now being investigated. We plan to test the effect of larger reactors, with varying surface areas and volumes of molten metal and mixed reactors. We are also planning to test different metals, such as tin, which is less dense and has a lower vapor pressure than lead. We also plan to investigate the effect of sulfur-containing gases and CO_2 on the DCP process, since raw natural gas usually contains mercaptans and CO_2.

ACKNOWLEDGEMENTS

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