PLASMA QUENCH TECHNOLOGY FOR NATURAL GAS CONVERSION APPLICATIONS

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ABSTRACT

This paper describes the experimental demonstration of a process for direct conversion of methane to acetylene in a thermal plasma. The process utilizes a thermal plasma to dissociate methane and form an equilibrium mixture of acetylene followed by a supersonic expansion of the hot gas to preserve the produced acetylene in high yield. The high translational velocities and rapid cooling result in an overpopulation of atomic hydrogen which persists throughout the expansion process. The presence of atomic hydrogen shifts the equilibrium composition by inhibiting complete pyrolysis of methane and acetylene to solid carbon. This process has the potential to reduce the cost of producing acetylene from natural gas. Acetylene and hydrogen produced by this process could be used directly as industrial gases, building blocks for synthesis of industrial chemicals, or oligomerized to long chain liquid hydrocarbons for use as fuels. This process produces hydrogen and ultrafine carbon black in addition to acetylene.

INTRODUCTION

Pyrolysis of natural gas at temperatures above 2100 K to produce activated hydrocarbons for subsequent conversion to chemicals and liquid hydrocarbon fuels has been practiced for many years in Germany and South Africa.[1,2] The application of pyrolysis technologies in the U.S. for conversion of remote natural gas to transportable liquid hydrocarbons has been limited due to the poor conversion rates and economics of known pyrolysis technologies. Development of an improved pyrolysis process at the Idaho National Engineering Laboratory (INEL)[3] has the potential for significant improvements in conversion rates and the accompanying economics of natural gas pyrolysis. The INEL process called the plasma fast quench process (PFQP) uses a thermal plasma arc to rapidly heat a argon/hydrogen gas mixture to >15,000 K. Methane (the major component of natural gas) is then injected into the hot plasma to convert the methane component to acetylene in high yields.

The PFQP technology overcomes many limitations of other pyrolysis processes by adiabatic isentropic expansion of product gases through a nozzle. Thermochemical modeling studies of the conversion of methane to acetylene were conducted to determine the equilibrium concentrations of acetylene and other reaction products

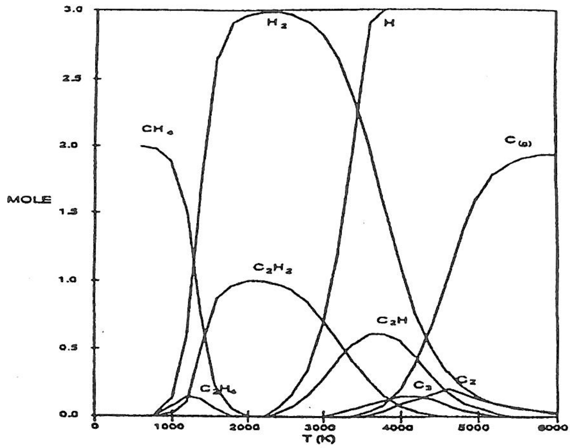

Figure 1: Simplified equilibrium diagram for CH_4.

between 500 to 3000 K. As shown in Figure 1, these studies determined that acetylene is a metastable compound that will decompose to carbon and other hydrocarbons if it is allowed to reach equilibrium at elevated temperatures (>800 K). The basic concept of the PFQP is that it will maximize the acetylene yield by "freezing" the product out of the reaction zone with extremely rapid decrease in temperature and pressure.

This paper describes the formation of acetylene from methane in a rapidly quenched thermal plasma process. In this process rapid quenching is accomplished by the expansion of a partially ionized and totally dissociated mixture of $Ar/H_2/CH_4$ through a converging/diverging supersonic nozzle. The nozzle is essentially an adiabatic device and when the upstream to downstream pressure ratio is sufficiently high the velocity of the gas reaches sonic velocity at the throat, and becomes supersonic in the diverging section. The increase in velocity is accompanied by the conversion of random translational energy to translational energy in the z-axis of the bulk flow, resulting in an effective decrease in the kinetic temperature of the gas. Cooling rates achieved are on the order of 10^7 K/s.[4] Higher cooling rates of up to 10^9 K/s can be achieved with improved expansion designs.[5,6]. The rapid quench results in large departures from equilibrium and "freezing" of chemical reactions that would normally pyrolyze the produced acetylene to solid carbon and hydrogen under slower cooling rates. Reheating of the gas by standing shock waves is avoided by concurrent velocity reduction and enthalpy removal from the hot gas stream. Chemical reactions in this chemical system are essentially halted at gas temperatures below 800 K.

EXPERIMENTAL

A schematic of the PFQP apparatus is shown in Figure 2. The thermal plasma is generated by a conventional plasma torch. Typical operating conditions for 918 amps at 136 volts on a mixture of Ar/H_2 (60.8:39.2) for a total flow rate of 240 slm. The torch exit, and nozzle inlet pressure, was 1 atm. Operating at 1 atm. the torch had a thermal efficiency of 69%.

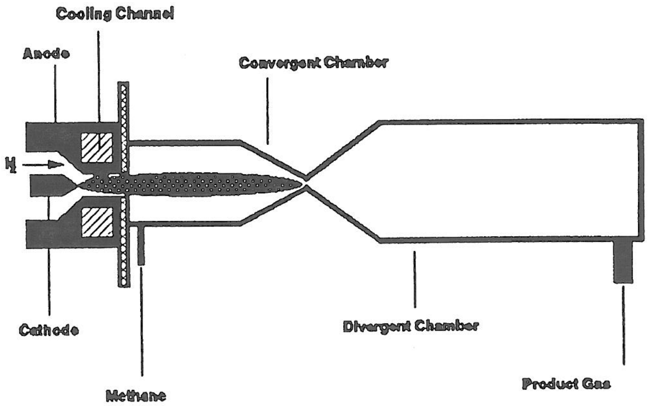

Figure 2: Schematic of experimental apparatus.

Methane gas was injected normal to the axis of the reactor at a velocity of approximately 100 m/s through a stainless steel tube. Pressure downstream of the nozzle throat was maintained at 75 torr (0.1 atm) by a vacuum pump. The gas temperature of the expanded gas was 650 K and the estimated temperature at the throat entrance was 2100 K. Ultrafine solid carbon particles were collected in a cyclone and gas composition measured by mass spectroscopy using a dedicated residual gas analyzer. Gas compositions were also confirmed by taking periodic gas samples for analysis using combined gas chromatography/mass spectroscopy techniques.

RESULTS AND DISCUSSION

Work to date has concentrated on large bench scale experiments to confirm conversion rates and development of an economic model of PFQP. Additional studies are being conducted on the catalytic conversion of acetylene to higher hydrocarbons, equilibrium thermodynamic calculations of equilibrium compositions for the CH_4-H_2 system, and computational modeling of the fluid dynamics of the PFQP chemical system.

Mass spectral analysis of the product gas showed acetylene with traces of methane as the only hydrocarbon product. The major product gas constituents were H_2, and C_2H_2. An argon peak was also present when argon/hydrogen plasma gas mixtures were used. The hydrogen peak was a combination of hydrogen from the plasma gas and hydrogen produced by the pyrolysis of methane. The ratios between H_2, Ar, CH_4, and C_2H_2 have been confirmed by gas chromatography. In addition to the gaseous products a small amount (less than 5%) of ultra fine high surface area solid carbon is also produced by this process. Results of two experimental runs using the PFQP for pyrolysis of methane are shown in Table 1.

Table 1: PFQP methane pyrolysis test results.

Test	Process Gas Input (slm)	Electric Power kWhr/kg C_2H_2	PRODUCT (kg/hour)			
			Acetylene	Hydrogen	Methane	Carbon
Run 1	Argon-148 Hydrogen-67 Methane-489	8.0	15.1	3.5	0.0048	0.21
Run 2	Argon-148 Hydrogen-67 Methane-530	7.2	17.0	4.0	0.0110	0.13

Process economic analysis of the process has shown that this process may be economically competitive with other natural gas conversion technologies. This analysis has demonstrated that although this process requires a high energy input, its high yield and product specificity result in economical production of acetylene. Acetylene produced in this process can be catalytically upgraded to high value liquid hydrocarbons.

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