THE CONVERSION OF METHANE IN AN ARC REACTOR

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The conversion of hydrocarbons into other products, namely acetylene, has been of considerable commercial and academic interest during the past few decades. Several types of arc devices have been reported for carrying out the pyrolysis of methane.

Thermodynamic calculations show that if the acetylene is to be recovered from an equilibrium chemical mixture, high temperatures in the range of 2000 to 3500°K are required, depending on the carbon-hydrogen ratio and the pressure of the system. Furthermore, kinetic considerations indicate that the pyrolysis of methane is fast relative to the decomposition of acetylene, and that there is an optimum reaction time to maximum both the conversion of the methane and the yield of acetylene.

The most desireable accomplishment of high temperature methane pyrolysis would be to effect the endothermic reaction.

$$2CH_4 \; = \; C_2H_2 + 3\,H_2$$

High temperature chemical equilibria for the carbon-hydrogen system have been computed by Blanchet[1] and Bauer and Duff[2]. Assuming that chemical equilibrium is achieved in an electric arc reactor, the data indicate that the temperature at which the acetylene concentration is a maximum. The kinetics of methane pyrolysis and acetylene decomposition during heating and cooling ultimately determine the yield of acetylene.

Anderson and Case[3] developed a kinetic model to describe the reactions between arc heated hydrogen and methane. Calculations provided information on conditions, such as H_2/CH_4 ratio, and reaction time, to achieve optimum conversion of methane to acetylene. The analyses indicated that conversion is not sensitive to contact time, within 0.1 and 1.3 milliseconds, and that speed of mixing is the most important parameter.

Reactions of methane and hydrogen with carbon vapor produced by an electric arc were reported by Baddour and Blanchet[1]. In their experiments, high acetylene concentrations of 20 to 40 percent in the product gas were found.

In an arc process, the reactions which determine the success of the process occur during the heating step and also during the cooling step. Heating of the reactant may proceed either as it passes through the discharge, or when it mixed with arc-heated gases. Cooling of the high temperature gases is usually carried out quickly, either by contact with cold surfaces, or mixing with cold fluids. This paper describes an experimental study on the conversion of methane which either (1) passed through a confined arc discharge, or (2) was mixed with an arc-heated gas. In this investigation, an attempt was made to understand the factors which affect the extent of methane pyrolysis and the yield of acetylene.

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In experiments on the direct conversion of methane, the reactant was passed through a confined arc discharge and quenched by mixing hydrogen or helium at several different quench to methane flow ratios. The net enthalpy of the gas from the arc discharge varied between 78 and 150 kcal per gram mole which correspond to equilibrium temperatures of 2500 to 3300°K. The conversion of methane, that was observed, varied from 65 percent at the low enthalpy to 85-100 percent at the high enthalpy. With a helium quench, the methane conversion varied between 90 and 98 percent, but at low He/CH_4 ratios, a large fraction of the methane went to carbon black, due principally to lower quenching rates and greater acetylene decomposition. Methane conversion was slightly lower with a hydrogen quench and the latter probably affected the kinetics of methane decomposition.

The conversion of methane by mixing with arc-heated hydrogen was studied in a plug-flow type reactor. Hydrogen was passed through a confined arc discharge. Methane was mixed with the hydrogen leaving the arc zone, and heated and reacted as the gases flowed co-currently through a cooled pipe. The conversion of the methane was correlated with the enthalpy of the hydrogen arc gas. Conversions were low (15-20 percent) at low enthalpies, and were nearly complete at high enthalpies (90-100 percent). These energies corresponded to 50-60 kcal per mole of methane at the low enthalpies to 220 kcal at high values, and were very large for the degree of methane reaction. Two effects were important. The arc gas lost energy to the cool reactor walls and the rate of energy transfer decreased with time due to a decrease in the energy driving force. By allowing for energy losses, the conversion was correlated and fair agreement was obtained between the data from (1) cracking methane in the arc discharge, (2) cracking methane in an arc-heated hydrogen stream, and (3) the experiments of Anderson and Case[1]. The yield of acetylene was also observed to be a function of the available energy, and under some conditions, acetylene yields of 90 to 100 percent of theoretical were achieved.

References

1. Blanchet, J. L.,"Reactions of Carbon Vapor with Hydrogen and with Methane in a High Intensity Arc," Sc. D. Thesis, M.I.T., June, 1963.

2. Bauer, S. H., and Duff, R. E., The Equilibrium Composition of the C/H System At Elevated Temperatures, LA-2556, Los Alamos Scientific Laboratory, Los Alamos, N. M., September 18, 1961.

3. Anderson, J. E., and L. K. Case, An Analytical Approach to Plasma Torch Chemistry, 1, 3, 161-165 (1962).