

## A NEW ROTATING-ARC HEATER FOR CHEMICAL PROCESSING

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A number of hot cathode plasma processes of the Gerdien type have been proposed for chemical synthesis on the basis of laboratory experiments.<sup>1</sup> Most of these processes, however, are generally limited in their application since the hydrocarbon or air cannot be directly heated by the arc because of their deleterious effects on the electrode. The reactant gases are generally introduced into the plasma downstream from the electrode. Although excellent yields of acetylene, for example, have been obtained, the commercial application appears impractical because of scale-up problems, and the necessity to utilize either inert or reducing-gas plasmas.

The commercial application of electric-arc gas heaters have been realized, however, in the Hüels type of arc by Chemische Werke Hüels AG, in Germany<sup>2</sup>, and by DuPont in the United States.<sup>3</sup> Both of these processes are of the long-arc, direct-current type. Although the details of the DuPont process have not been disclosed, it is known from the patents issued that electrical rotation of the arc is utilized. The arc rotation in the Hüels process is obtained by introducing the gas into the arc-chamber in a swirl.

Some of the important technical details of both these processes are that 1) 4.5-6.0 kilowatt-hour of electrical energy are required to produce one pound of acetylene from methane; 2) that the residence time of the gas at ~1500°C in the plenum chamber is 1-3 milliseconds; 3) the product acetylene concentration is about 15 and 20 volume per cent, respectively, in the Hüels and the DuPont processes.

This paper describes the design and application of a rotating arc device of the short arc type which has recently been developed for gas heating. The short arc necessitates high current application, at relatively low voltage. The electrodes, therefore, must be capable of carrying this high current (and heat flux) without failure. Some of the advantages which may be expected from this device are: 1) relatively more uniform temperature profile as compared to the long arc device; 2) better control of arc with both direct and alternating current power; 3) longer electrode life; 4) improved mixing of the reactant gases in the heater.

### Thermodynamics

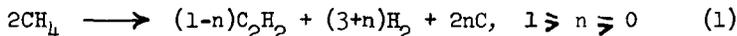
In the application of any high temperature device to a particular chemical reaction, the thermodynamics of the system is first considered. If the reaction is carried out under equilibrium conditions, the products are then clearly defined. The  $C + 2H_2$  system, for example, has been studied by a number of workers under equilibrium conditions, and the products agree quite well with the equilibrium calculations based on available thermodynamic data.<sup>4</sup> Similar studies with methane, as it will be shown, also apply in the arc heater under certain conditions. Some of the economically practical reactions, however, will require high flow conditions at which non-equilibrium conditions prevail. In such instances one needs detailed kinetic information to predict the path of the reactions, and the product compositions thereof. Unfortunately, dependable high-temperature kinetic data for the

cracking of methane are sparse; in particular, such data for flow-reaction conditions approaching those in the arc-heater are practically non-existent.

When the methane passes through the electrode gap of the heater, that volume which sees the arc is perhaps heated to temperatures in excess of 7000°K. This volume of gas is therefore completely dissociated. Part of the gas will not be arced, the proportion depending on the rate of arc rotation and on the gas flow velocity, but will mix with the hot arced-gas in the plenum chamber. Herein lies the critical period of the chemical process. At low gas velocities and high rotation, the gas mixture may easily attain equilibrium conditions. At high gas velocities the residence time of the mixture in the hot zone may be too short to reach equilibrium. The average temperature of the mixture at high flow will also be lower at a given power input. It will be shown that these latter conditions prevail in methane processing, and may be important economical factors.

Figure 1 shows the equilibrium for the  $C + 2H_2$  system at a total pressure of one atmosphere. Since our studies are at approximately one atmosphere, this consideration applies. The computation is based on data reported in the JANAF Tables<sup>5</sup> and programmed by Chambers and Tuba.<sup>6</sup> Note that solid carbon is an important constituent up to 3400°K, but disappears at 3700°K. At the latter temperature the gaseous species of carbon become important. The maximum acetylene concentration of  $x = 9$  appears at 3600°K, and decreases rapidly above 3700° and below 3400°K. Also note that  $CH_4$  and  $C_2H_4$  are quite unstable at these high temperatures. If the gas at 3600° is quenched at a rate of about  $10^5$  degrees/sec, the acetylene will be essentially frozen, and there will be precipitation of carbon and recombination of H and the other radicals. The composition of the gas phase, then, may contain ~15 mole %  $C_2H_2$ ; the remainder being  $H_2$ ,  $C_2H_4$  and  $C_4H_2$ . It is noteworthy that the kinetics of formation of acetylene is much faster than its decomposition, so that essentially all of the acetylene may be quenched. Earlier work<sup>4</sup> has shown that agreement between theory and experiment is excellent. The amount of solid carbon frozen from an equilibrium mixture, therefore, is about 40% of the total carbon.

In the production of acetylene from methane, we may consider the reaction



Ideally, the reaction should proceed with  $n = 0$ , with a heat of reaction of approximately 90 kcals. The free energy change for this reaction is approximately  $\Delta F_T = 95.4 - 0.0680T$ . In engineering units, the heat requirement is equivalent to 5000 Btu/lb  $CH_4$  just for the heat of reaction. Additional sensible heat needs to be added to heat the methane to the reaction temperature. For instance, 2100 Btu/lb are required to heat the gas to 1500°K. The free energy for the reaction also becomes negative at ~1500°K. For the reaction as shown in equation (1), the heat of reaction is  $\Delta H_T = \Delta(\Delta E_0)_i + \Delta(H_T - E_0)_i$ , where the symbols have their usual thermodynamic designations. Note that the last term is the sensible heat at T. As carbon precipitates, therefore, the heat of reaction decreases at 1500° since it's  $\Delta E_0 = 0$ .

From the equilibrium computation, the enthalpy-temperature relationship is obtained as shown in Figure 2. This curve conveniently allows the average temperature determination for equilibrium systems since the enthalpy is usually known in an experiment. This does not apply, however, to non-equilibrium systems.

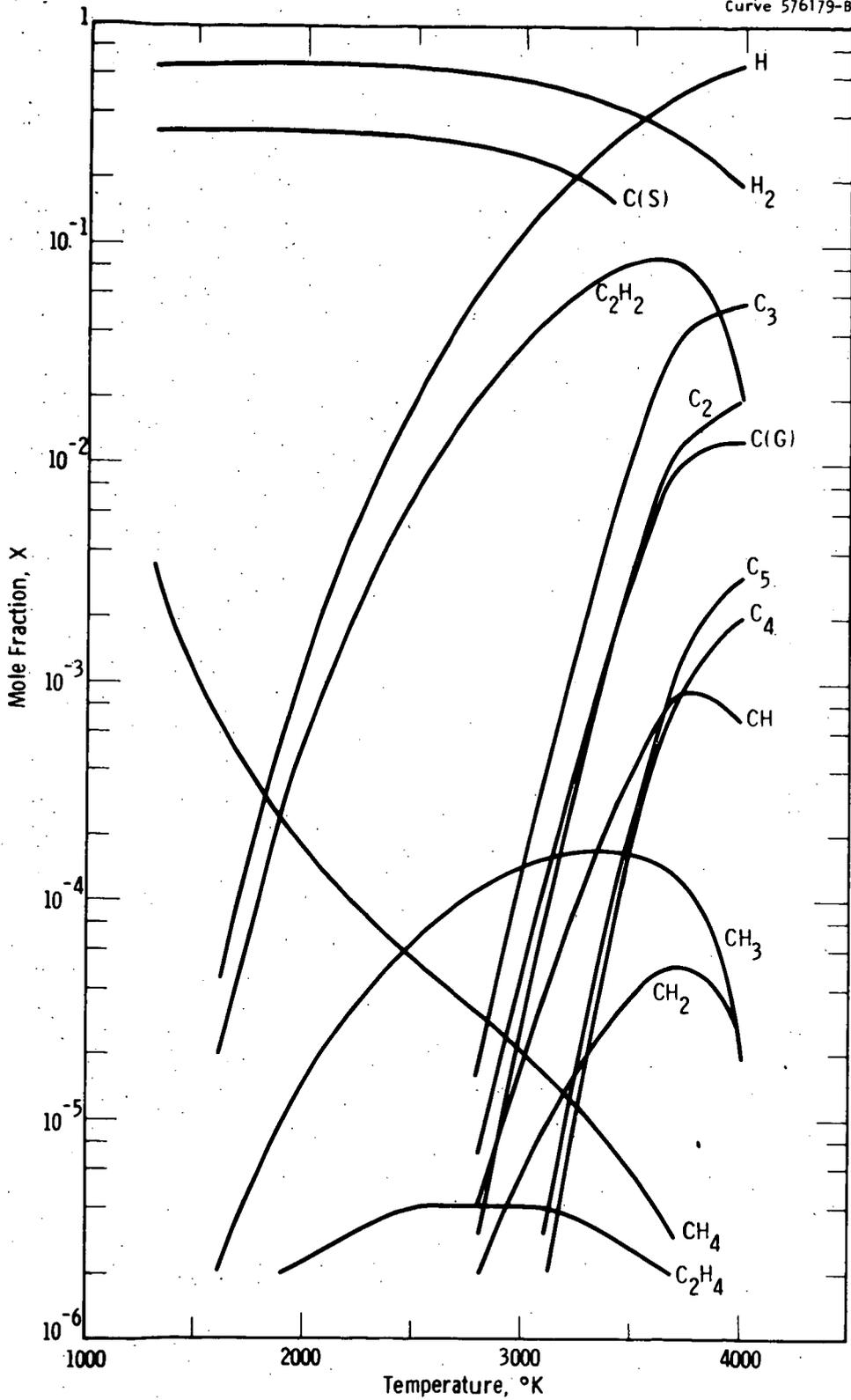


Fig. 1—Calculated  $C + 2H_2$  as a function of temperature (Total P = 1 atm)

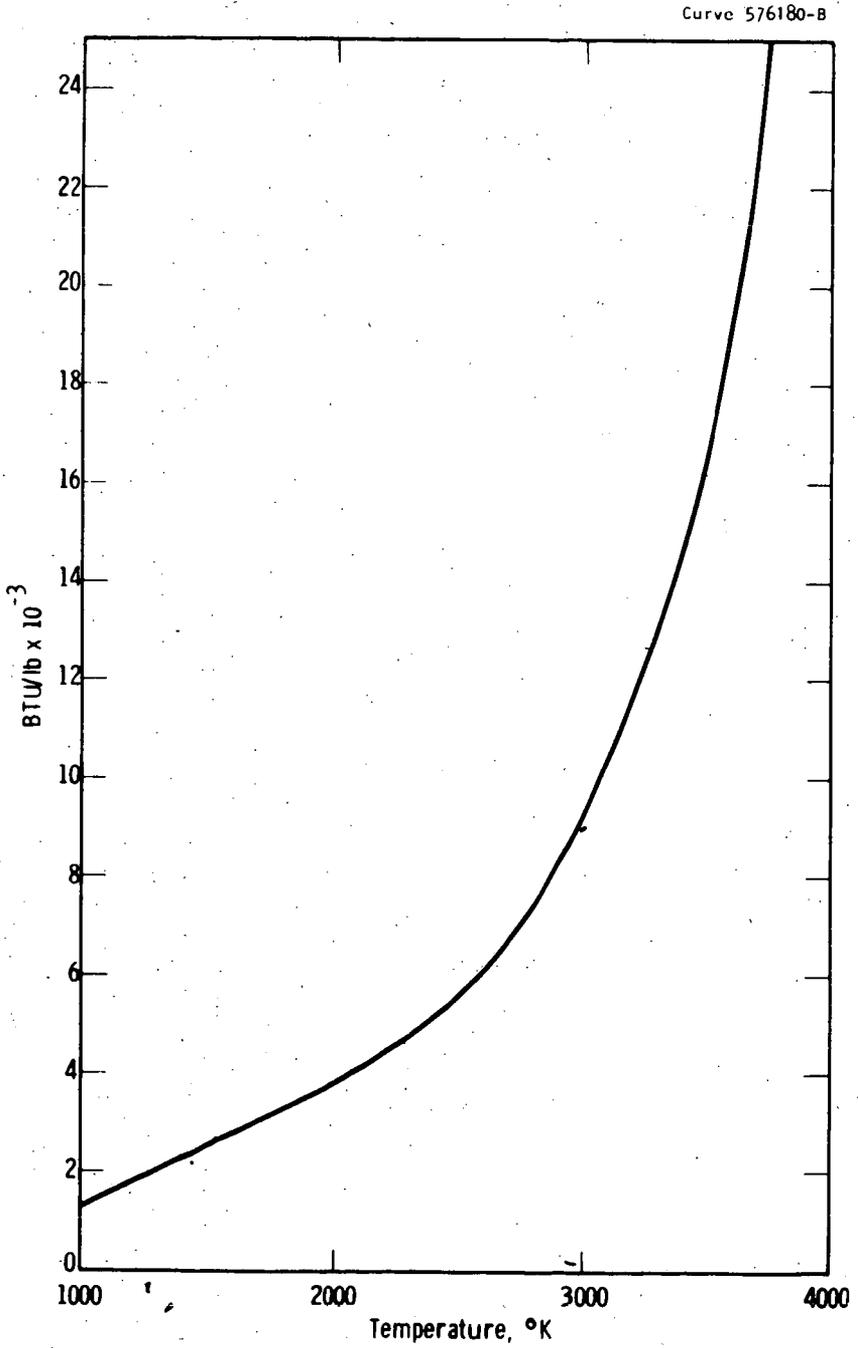


Fig. 2—Enthalpy vs temperature for  $C + 2H_2$  at total pressure of 1 atm

## Kinetics

It is apparent from the rapid flow reactions, such as the Hüels and the DuPont processes, that equilibrium is not obtained in the cracking of methane. This reaction, under optimum conditions, shows low carbon yields of about 5%. Also, there is present about 1% of ethylene among other minor hydrocarbon constituents. The kinetics of thermal decomposition of methane has been studied by many workers. The exact mechanism, however, remains unresolved. It is generally believed<sup>7</sup> that two primary steps may take place near 2000°C:



The  $\Delta H_{298}^\circ$  for the reactions are 102 and 103 kcal, respectively. The overall monomolecular decomposition of methane is  $k = 10^{14.88} \text{Exp}(-103 \text{kcal}/\text{RT})$ , and the free radical reaction chain is apparently very short. The following chain is often postulated:  $\text{CH}_4 \xrightarrow{k_1} \text{C}_2\text{H}_6 \xrightarrow{k_2} \text{C}_2\text{H}_4 \xrightarrow{k_3} \text{C}_2\text{H}_2 \xrightarrow{k_4} \text{polymeric products}$ .

The ethane is presumably formed by the reaction  $\text{CH}_3 + \text{CH}_4 \longrightarrow \text{C}_2\text{H}_6 + \text{H}$ , with the ethane dehydrogenating rapidly. At isothermal conditions it is shown that  $[\text{C}_2\text{H}_6] / [\text{CH}_4] = 10^{-5}$  at 1800°K, thus  $\text{C}_2\text{H}_6$  is not detected in the cracked products. The polymerization of acetylene to diacetylene is a second order reaction whose rate constant is relatively slow compared to the other monomolecular rates. Hydrogen is known to retard the decomposition of ethane, thus the formation of acetylene. Also, increasing the temperature in the neighborhood of 1100°C increases the rate of  $\text{C}_2\text{H}_2$  formation. It appears, then, that maximum acetylene is obtained at temperatures higher than 1100°C and at short residence times at the high temperatures. In a rapid flow system there will be no hydrogen accumulation to decrease the acetylene formation.

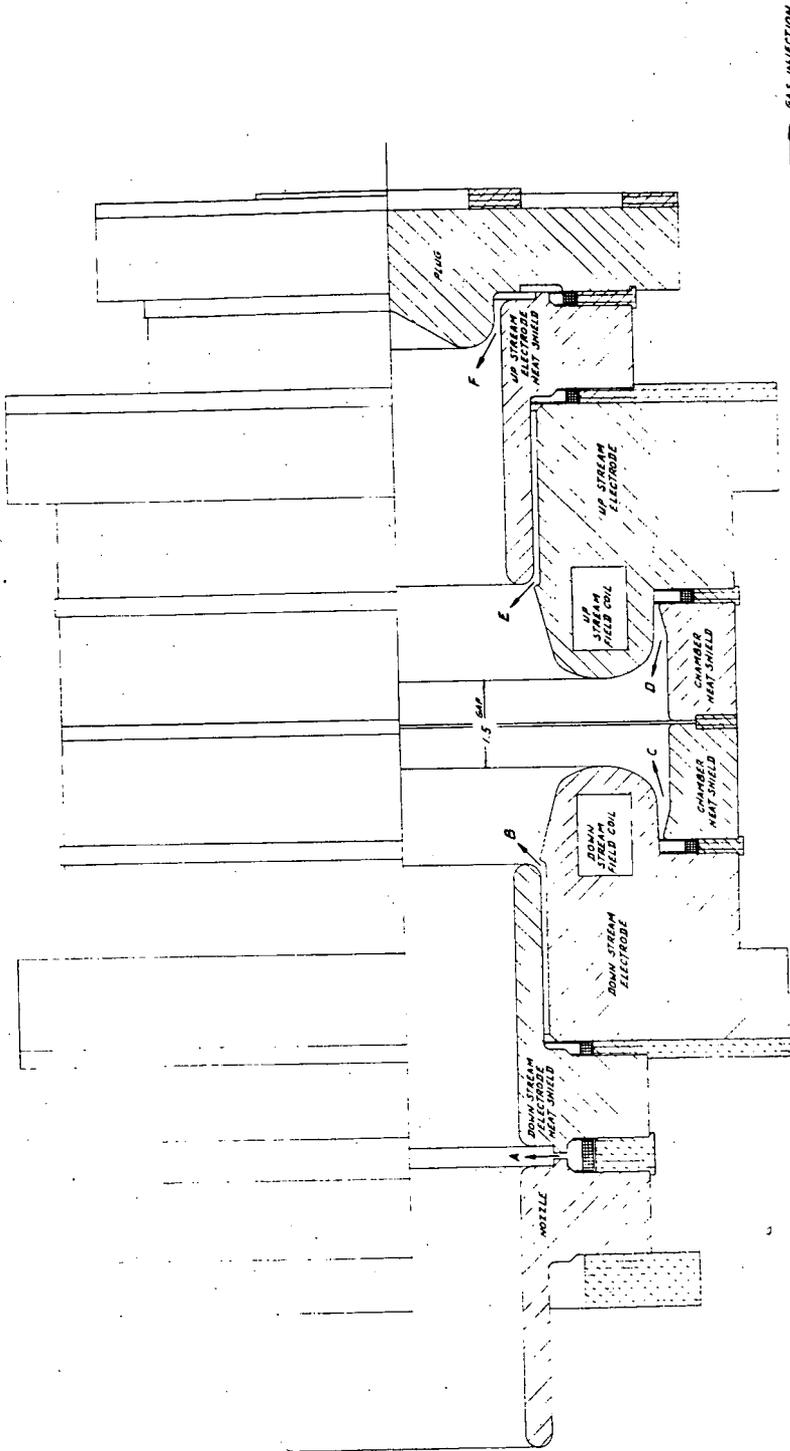
It is generally believed in methane cracking that the gas should be heated to at least 1500°C, at residence times in the neighborhood of one millisecond. It should be remembered in reactions in an arc-heater that the temperature gradient may be much greater than those obtained in the above kinetic studies.

### Description of Rotating-Arc Heater

A cross-section of the heater used in this program is shown in Figure 3. One or more process gases can be added at the six locations designated "A" thru "F". With the arc established between the two toroidal electrodes, only the gas added at locations "C" and "D" will actually pass thru the arc zone. Some small amount (2 to 5% of total flow) must be added at the other four locations to keep the gaps clear of debris and prevent short circuiting of the electrodes.

All internal parts of the heater exposed to the gas are fabricated from copper or copper alloys. These parts are all water cooled. To prevent vaporization of metal from the electrode surface at the point of arc attachment, the arc is rotated around the gap at high speed. This is accomplished by the field coils which establish a magnetic field perpendicular to the arc column. The resulting force acts on the arc column causing it to rotate at speeds on the order of 2000 feet per second.

To start the heater, a thin metallic wire is inserted between the electrodes. Application of power causes a high current to flow and rapidly



← GAS INJECTION

MARC 30  
ARC HEATER  
DB 08165

Figure 3. Cross-section of Heater

vaporize the wire. The explosion of the wire provides an initial ionized path to establish the arc. In testing with hydrocarbons, the heater is usually started with an inert gas such as nitrogen. This allows the arc to stabilize without any solid by-products being formed in the heater. After several seconds, the nitrogen flow is stopped and hydrocarbon feed started.

The heater configuration shown in Figure 3 has been operated on both single phase A.C. and D.C. power. For A.C. arc operation, the field coils are separately powered from a D.C. power supply. When operated as a D.C. device, the field coils are connected in series with the arc and do not require a separate power supply.

Tests were conducted using both A.C. and D.C. power. Electrode gaps of 0.38, 0.75, and 1.5 inches were required to cover the power range from 90 to 2360 kilowatts into the arc. Stable arcs were maintained with currents as low as 780 amps. Currents of 3830 amps with methane and 9200 amps with nitrogen have been carried by the heater electrodes without damage.

The efficiency of the heater, calculated on the basis of electrical power and heat lost to the cooling water, has gone as high as 79%. Heat addition to the process gas has been as high as 19,900 Btu/lb. of  $\text{CH}_4$ . The maximum methane flow in the heater is about 30 lbs/minute.

#### Chemical Tests

Tests have been run with methane of technical and C. P. grades. Propylene has also been cracked in the heater. The range of methane flow was from 0.04 to 0.275 lbs/sec. at arc power levels up to 2360 kilowatts. The gas was introduced into the heater at room temperature, and the flow was controlled by metering through a sonic orifice. At least three cylinders (15 lbs. methane when full) were opened to the manifold during a run. The pressure of the gas thus feeding into the heater was approximately 40 psig, and the total pressure in the heater chamber was 18 psia.

During a test the product gas was sampled by inserting a probe just inside of the heater nozzle. The probe was a water-cooled, concentric copper tube, with a 1/8 inch bore which was connected to the sampling manifold. The latter held 5 sample bottles, with a solenoid valve connected in parallel at each end of the bottle. The valves were remotely controlled from the instrument operating room. During a run the valves were all opened a few seconds after the nitrogen was turned on into the heater, and the system pumped continuously. At appropriate time intervals after the methane flame was started, the product gas was sampled by closing off the set of solenoid valves on any bottle. Thus, for any given run it was possible to obtain one or more samples at different periods. Since the quench rate is high in the probe, the gas samples should be representative of the composition at the nozzle. The chemical analyses of the product gas in all cases was made mass spectroscopically.

The power levels during any given run were varied after one to two minute intervals, usually by altering the current. The gas samples were taken at the end of a given power period. Simultaneously with the sampling, the electrical and flow data were recorded on the strip chart; subsequently, the current was stepped up or down. It should be noted that the arc reached stable equilibrium during any power level in the matter of a few seconds. The length of a given run varied from a few minutes to about 12 minutes.

The proprietary nature of this work prevents the authors from presenting the detailed data at the present time. However, the specific data presented will suffice to illustrate some of the important operating characteristics of the arc heater when used as a chemical processing tool.

TABLE I. Product Gas Analysis From Methane Run (Mole %)

<u>H<sub>2</sub></u>	<u>CH<sub>4</sub></u>	<u>C<sub>2</sub>H<sub>2</sub></u>	<u>C<sub>2</sub>H<sub>4</sub></u>	<u>C<sub>4</sub>H<sub>2</sub></u>	<u>Other HC</u>
50.98	38.17	9.52	0.88	0.21	0.25

TABLE II. Composition of Products in Mole %

<u>H<sub>2</sub></u>	<u>CH<sub>4</sub></u>	<u>C<sub>2</sub>H<sub>2</sub></u>	<u>C<sub>2</sub>H<sub>4</sub></u>	<u>C<sub>4</sub>H<sub>2</sub></u>	<u>Other HC</u>	<u>C</u>
46.3	34.7	8.7	0.8	0.2	0.2	9.1

TABLE III. Conversion of Reacted Methane to Products

<u>C<sub>2</sub>H<sub>2</sub></u>	<u>C</u>	<u>C<sub>2</sub>H<sub>4</sub></u>	<u>C<sub>4</sub>H<sub>2</sub></u>	<u>Other</u>	<u>% CH<sub>4</sub> Reacted</u>
57.0	32.3	5.2	2.5	3.0	46.7

Table I shows the product gas analysis of a methane run. The material balance is then shown in Table II. This particular run corresponds to a methane conversion of 46.7%, as shown in Table III. The energy conversion for this run was 6.8 kwh/lb C<sub>2</sub>H<sub>2</sub>. Depending on operating conditions, the acetylene concentration in the gas has ranged from 7-12 mole %, the other major constituents always being hydrogen and the unreacted methane. The energy conversion obtained was as low as 2.64 kwh/lb C<sub>2</sub>H<sub>2</sub>. The methane conversion was increased appreciably when the arc-rotation was increased by increasing the field current. Although not yet optimized, methane conversions of 80% have been obtained in this way, where previously the conversion was only about 50%. The increased conversion obviously results from the better mixing and greater proportion of gas which passes through the arc.

The carbon content and its properties have varied with the operating conditions. The conversion to carbon varied from a few per cent to about 40% of the total carbon input. With A.C. power the carbon was generally of an amorphous nature, whereas at D.C. power at high enthalpy levels, the properties approached those of pyrolytic graphite. Thus, surface areas varied over almost one order of magnitude from about 20 to over 100 m<sup>2</sup>/g. The purity of some samples, determined by a spark-source mass spectrometer, showed extremely low metal contamination (at least an order of magnitude less metal contamination than in spectroscopic carbon).

There are certain basic differences in uniformity of heating between A.C. and D.C. excitation. This arises from the alternating 60 cycle power cycle of the

A.C. excitation as opposed to the steady D.C. system. The latter allows a more uniform heating, with less temperature fluctuations; whereas the former shows the alternating pulses of relatively hot and cold volumes of gas as observed by high speed photography.<sup>9</sup>

The rotating arc heater has been in intermittent operation for a period of over a year. There have been many start-ups, with runs of duration up to approximately 12 minutes. The length of a run has been limited by the available power supply and cooling water. The heater has performed dependably with the original set of electrodes. Only difficulties encountered were under certain conditions in which excessive carbon deposited between the electrodes. However, a surprisingly large deposition of carbon may be tolerated in the heater, and still allow safe start-ups without removal of this carbon. It should be emphasized that start-up conditions are the most severe since large power surges are involved. It is felt that the heater is capable of continuous operation for periods up to 1000 hours, based on electrode and heater examination after repeated tests.

### Discussion

From the equilibrium shown in Figure 1, the maximum acetylene concentration of about 15 mole % should be in the gas quenched from 3600°K. The  $C_2H_2$  concentration decreases rapidly above and below the latter temperature. When the product gas analyses in this work are normalized by subtracting out the unreacted methane, the acetylene concentration remains at around 15 mole % over the wide range of enthalpy levels. It is apparent then that thermodynamic equilibrium is not attained, particularly at low enthalpies. At high enthalpies, however, the gas probably attains equilibrium and the average temperature is in the region of 3600°K. Since temperature measurements have not been made at low enthalpy levels, we can only conjecture that the average gas temperature is around 1500°K.

The low energy conversion of 2.64 kwh/lb.  $C_2H_2$  is significantly lower than the 4.5 to 6.0 kwh/lb.  $C_2H_2$  reported for the other arc processes. On examining the enthalpy requirements for this low conversion, it was found that 2.4 kwh is required just for the heat of reaction. Since sensible heat must be supplied, our value of 2.64 kwh/lb. appears too low. This determination obviously needs re-confirmation by further tests. It may be of interest, however, that a recently publicized electro-thermic process<sup>8</sup> reports an energy conversion of 2-3 kwh/lb.  $C_2H_2$  in the cracking of methane at around 2000°K.

From the dimensions of the rotating-arc heater, a plenum chamber of 80 in.<sup>3</sup> is obtained. The average residence times of the gas, then, varied from 4 to 0.7 milliseconds in our tests.

The relative stability of acetylene during quench was qualitatively demonstrated by sampling the product gas with the 1/8-inch and a 2-inch sample probes. The gas analyses from both systems were very similar, in spite of the difference in quench rates.

### Conclusion

A versatile rotating-arc heater, and some of its operating ranges, has been described. The device is of a short-arc type in which the gas is introduced in five positions. Thus two or more different gases may be easily heated together, and finely divided solids are not excluded. Methane flows up to about 30 lbs/min.

is possible at either A.C. or D.C. power inputs up to 2.4 megawatts into the arc. Thermal efficiencies as high as 79% have been obtained. The design of the heater is amenable to the direct heating of reducing inert and oxidizing gases.

Methane and propylene have been processed through the heater with some results for the former reported herein. Energy conversions at least comparable to other arc processes have been obtained. An added advantage is the relatively small physical dimensions of the heater. This feature allows higher thermal efficiencies.

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