

THE EFFECT OF CORONA ON THE REACTION OF CARBON MONOXIDE AND STEAM

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SUMMARY

The water-gas shift reaction was chosen for study in a corona discharge with the aim of establishing the important variables associated with the production of hydrogen.

The reaction was carried out in a quartz Siemen's type ozonizer having an electrode length of 12 inches and an electrode separation of 8 mm. The electrodes consisted of fired-silver paint--one electrode coating the inside of the inner (high voltage) tube, and the other coating the outside of the outer (ground) tube.

The reaction was studied by means of a four-factor, two-level, factorially designed set of experiments. This consisted of input power levels of 60 and 90 watts, pressures of $\frac{1}{2}$ and 1 atmosphere, hourly space velocities of 200 and 800, and reactor temperatures of 127 and 527°C (400 and 800°K). Although voltage was not a factor, the voltage ranged from 3100 to 11,000 rms volts.

The prediction equation resulting from the statistical analysis of the data indicates that more hydrogen is produced at higher pressures, temperatures, and power inputs, and lower space velocities. Practically no hydrogen is produced in the absence of a discharge, regardless of the values of space velocity, temperature, pressure, or power dissipated.

The highest yield of hydrogen within the factorial region studied was 4.5 percent. An extra-factorial region, which was indicated by the prediction equation to be fruitful, was explored and 11.5 percent hydrogen was obtained.

It was found that the water-gas shift reaction in a corona discharge is kinetically, rather than thermodynamically controlled.

INTRODUCTION

Novel techniques are being investigated at the Bureau of Mines to introduce energy into coal and coal products in an effort to find new uses for coal. One technique under study involves chemical reactions in a corona discharge. Initially the gas-phase reaction of carbon monoxide and steam to produce carbon dioxide and hydrogen will be investigated.

The immediate aim of this study is to establish the important variables associated with the production of hydrogen in the water-gas shift reaction in the presence of a corona discharge. A more general goal is to determine the dependence of product yield on the important variables in a corona discharge for several gas-phase reactions. As knowledge is gained on the effect of corona discharge in chemical reactions, more complex reactions involving coal and its products will be studied.

The water-gas shift reaction, which is usually carried out industrially over an $\text{Fe}_2\text{O}_3\text{-Cr}_2\text{O}_3$ catalyst at 300-500°C and 100-300 psig, has been discussed at great length in the literature. Summary articles are available.¹⁻⁴ It is almost certainly a surface reaction⁵ as opposed to the apparent homogeneous nature of the reaction in the corona discharge. Experiments with the quartz Siemen's type ozonizer to be described have shown that no reaction occurs between water and carbon monoxide at

600°C and 1 atmosphere pressure in the absence of a corona. This suggests that the reaction is homogeneous when it does occur with a corona. That is, the reactor walls probably do not enter into the reaction by acting as a catalyst or as a third body.

The physics⁶⁻⁸ and chemistry⁹⁻¹¹ of corona discharge have been surveyed by several authors. A bibliography of chemical reactions in electrical discharges over a thirty-year period, 1920-1950, has been compiled.¹²

PROCEDURE

The corona discharge unit is shown in figure 1. The operational scheme can be seen in the flow diagram, figure 2. Carbon monoxide from a compressed gas cylinder (1) is passed through an activated carbon adsorption trap (5). The metered flow (7) passes through a flow control valve (9); a second stream of gas may be blended here if desired. The carbon monoxide at the pressure of the system passes through a steam generator (11). The thermocouple immediately above the reflux condenser (17) controls the steam flow rate via a time-proportionating temperature controller (not shown). The carbon monoxide and water flow rates may be individually varied between 0.2 and 3 ft.³/hr. by adjusting the flow controller (9) and temperature controller settings. The carbon monoxide-steam mixture then enters the Siemen's-type reactor through preheaters (18) and (21). The reactor is enclosed in a tube furnace (23). The product gases pass through a series of three cold traps (25, one shown) at -80°C. Bypass cold traps (26) are available if required. The non-condensable gases pass through a sample train (28,29) and then through a flow meter (30) which is at system pressure. On leaving the flow meter the non-condensable gases pass through the system-pressure regulator (32), vacuum pump (34), and finally a wet test meter (35). The system is designed to operate from 0.5 to 2.0 atmospheres.

The Siemen's type reactor, shown in figures 3 and 4, consists of two concentric quartz tubes, 45 and 33 mm. OD, having a 4 mm. annular space. The electrode length is 12 inches and there is an 8 mm. electrode-to-electrode separation. The electrodes consist of fired-silver paint--one electrode coating the inside of the inner (high voltage) quartz tube, and the other coating the outside of the outer (ground) tube. Tungsten (or optionally copper) wires are attached to the outside and inside of the reactor with two or three coatings of fired-silver paint. The capacitance of the reactor was measured as 86-89 pfd using an impedance bridge.

The average wall temperature was used as a measure of the temperature of the system. Three thermocouples were equally spaced vertically along the inside wall of the reactor (fig. 2) and three along the outside wall. The inside wall thermocouples were at the corona potential and thus were isolated from ground. A millivoltmeter was connected in series to each of the inside wall couples, and thus was similarly "floated". To simplify the electrically hot thermocouple circuits, no compensating ice junction was included; the room temperature correction was added to each millivoltmeter reading. The corona potential had a positive effect on the millivoltmeter readings in the hot circuit. Therefore the millivolts were read before the corona potential was impressed on the system. The system temperature was taken as the average of all six thermocouple measurements.

The study was made according to a factorially designed set of experiments to determine the effect of pressure, space velocity, temperature, and input electrical power on the yield of hydrogen.

This was a four factor, two level set of experiments as shown in Table 1.

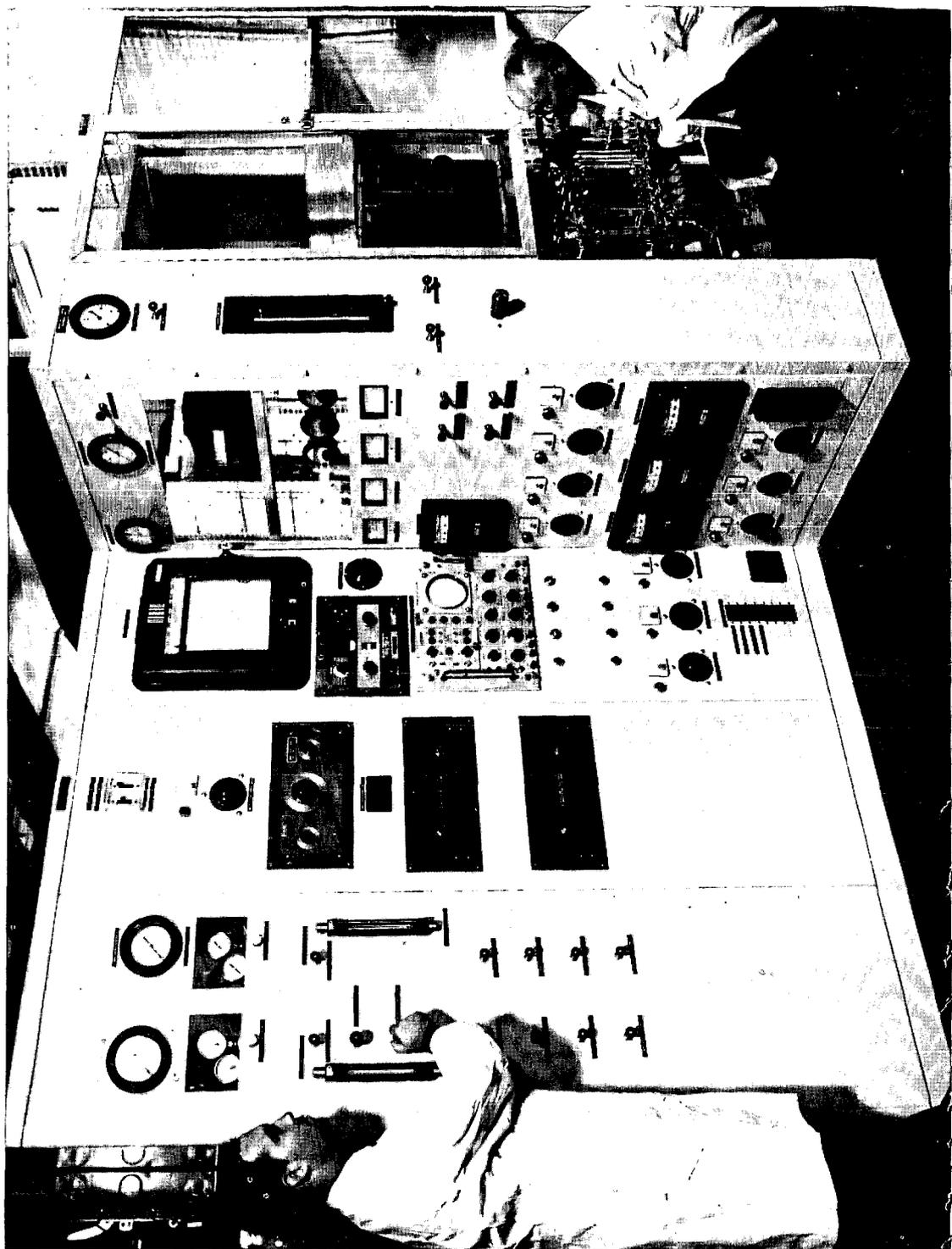
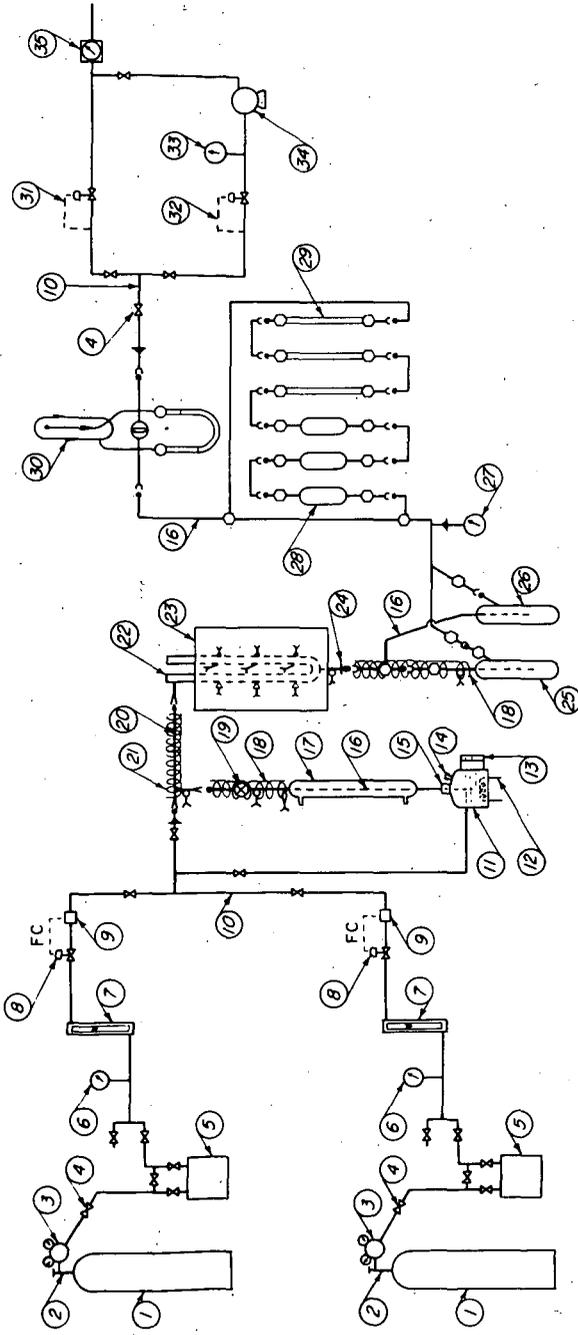


Figure 1.- Unit for studying chemical reactions in a corona discharge.



- (1) FED GAS (2)
- (2) VALVES (2)
- (3) REDUCING REGULATORS (2)
- (4) VALVES, 1/8 IN. BALLS, ALLOY STEEL TIPPED STEEL, MAKE NO. 2611538 (24)
- (5) ACTIVATED CARBON TRAP, FOR HYDROGEN GAS USE ONLY (2)
- (6) GAGES, 0-30 PSIG, AIRCRAFT DISBURGANCE (2)
- (7) FLOWMETER, 0.1-1.5 SCFM, WITH INTERCHANGIBLE TUBES, FISCOR & PONTRE NO. 104333A (2)
- (8) VALVES, 1/8 IN. BALLS, BRASS, MAKE NO. 262266 (2)
- (9) FLOW CONTROLLERS, 0.015-11 SCFM, MODEL NO. 6380-L (2)
- (10) TUBING, SOFT COPPER, 1/4 IN.
- (11) STEAM GENERATOR
- (12) INTERNAL WATER HEATER
- (13) DISTILLED WATER LEVEL SIGHT GLASS
- (14) WATER FILLER CAP
- (15) O-RING COMPRESSION SEAL
- (16) TUBING, PEXEL, 7 MM.
- (17) REFLECT CONDENSER, FOR CONDENSAT TEMPERATURE OIL CIRCULATOR
- (18) HEATING TAPS, ELECTRICAL (2)
- (19) STYROFOAM, PEXEL, TETRAFLUORO-ETHYLENE, 3 MM. MAKE, ACE NO. 8176-T
- (20) TUBING, VITON, 7 MM.
- (21) PERMATERIAL, CERAMIC TUBE TYPE
- (22) CORONA CELL, QUARTZ, QUANT SCIENTIFIC CO., LANSING, MICH
- (23) FURNACE, CONDUCTION TUBE TYPE, WILCOX, 2 ELEMENT, 25-1000°C. ELECTRO-APPLICATIONS, INC., WASHINGTON, PA.
- (24) SEAL, BRASS, QUARTZ-PEXEL
- (25) OIL TRAP
- (26) BYPASS OIL TRAP
- (27) GAGE, 30 IN. HG VACUUM TO 15 PSIG, AIRCRAFT DISBURGANCE
- (28) GAS SAMPLING TUBES, 250 CC, FLEXIBLE NO. 10-935 (1)
- (29) GAS SAMPLING TUBES, 10 CC, 3 MM I.D. PEXEL TUBING (3)
- (30) FLOWMETER, PEXEL, CAPILLARY-TYPE, FOR 0.1-5 CFM AT 15 IN. HG VACUUM
- (31) REGULATORS, PRESSURE, 0-15 PSIG, MODIFIED CONROL
- (32) REGULATORS, VACUUM, 1-30 IN. HG CONSOLE NO. V10
- (33) GAGE, 0-30 IN. HG VACUUM, AIRCRAFT DISBURGANCE
- (34) PUMP, VACUUM, 0-25 IN. HG, EXPUSION PUMP MOTOR, ALIGHT CHURCH, UNCOMPENSATED GAUGE
- (35) METER, NET TEST, 0.1 CU.FT. PER REVOLUTION, 0.1-20 SCFM, AMERICAN METER CO.
- (36) JOINTS, BALL, PEXEL, WITH TETRAFLO-ETHYLENE, SIZE 1/75, WEST NO. W-1531-T (20)
- (37) JOINTS, BALL, VITON, SIZE 1/75, CONSOLE NO. 16762
- (38) JOINTS, SOCKET, PEXEL, SIZE 1/75, WEST NO. W-1540 (18)
- (39) JOINTS, SOCKET, VITON, SIZE 1/75, CONSOLE NO. 16764 (1)
- (40) SEALS, PEXEL-SEAL (3)
- (41) STYROFOAM, MONOLITHIC GLASS, 3 MM MAKE, 3 WAY, EXCEL-CELLO NO. 3035 (3)
- (42) STYROFOAM, MONOLITHIC GLASS, 3 MM MAKE, 3 WAY, EXCEL-CELLO NO. 3000 (16)
- (43) THERMOCOUPLES, TO FLOWING MILLIVOLTMETER NO. 1 (3)
- (44) THERMOCOUPLES, TO FLOWING MILLIVOLTMETER NO. 2 (2)
- (45) THERMOCOUPLES, FOR INTERNAL WATER HEATER CONTROL (2)
- (46) THERMOCOUPLES, FOR MULTIPORT RECORDER (5)

Figure 2.- Flow diagram for corona discharge.

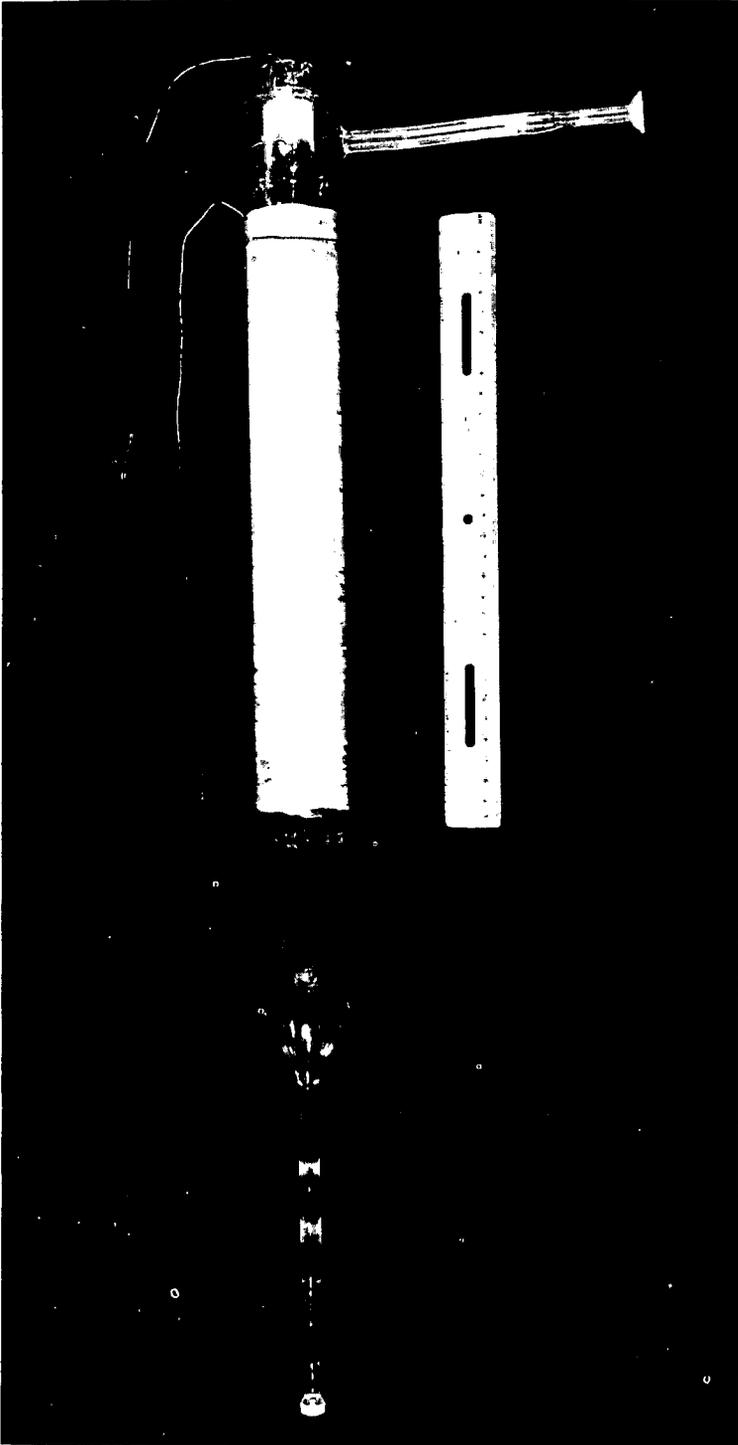


Figure 3.- Siemen's type reactor.

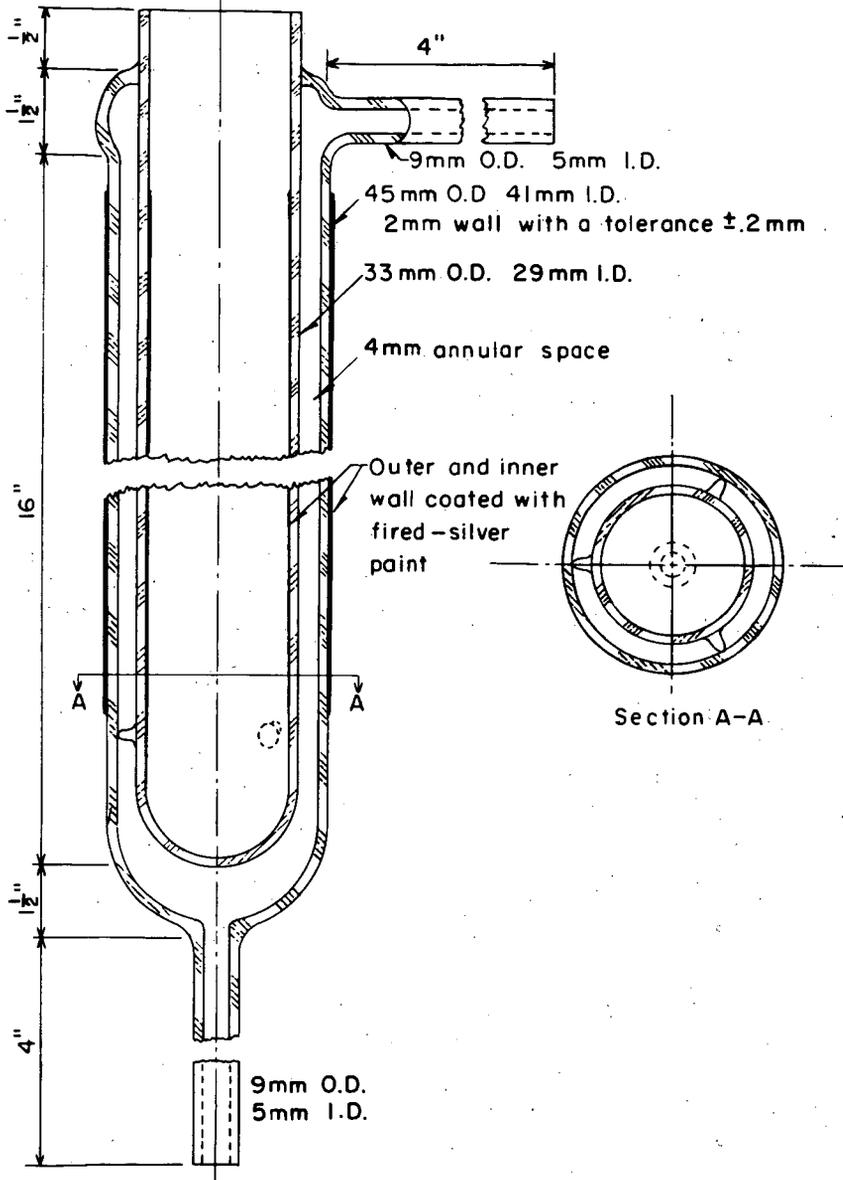


Figure 4. Siemen's type reactor.

Table 1.- Factorial design of the experiments

2 level, 4 factor, full factorial

 $2^4 = 16$ experiments1:1 molar mixture, $H_2:CO$

Factor	Level	
	Low	High
Pressure, atm.	0.5	1.0
Space velocity, $hr.^{-1}$	200	800
Temperature, $^{\circ}K$	400	800
Input power, watts	60	90

It was found that no hydrogen was produced in the absence of a discharge, no matter what the potential impressed on the high voltage electrode. Thus Paschen's law curves, discharge-initiating potential vs. the product of pressure and electrode separation, were developed for the reactor. These are shown in figure 5. A second reactor with 12 mm. electrode separation was also used to obtain these curves.

Initially it was intended to factorize secondary voltage, rather than input power. However, it was not possible to factorize voltage (set a high and low level) without losing the discharge at low temperatures or drawing too high a current at high temperatures. At high currents the arc would puncture the quartz reactor. Maintaining a discharge in some cases and not others would introduce a very significant unfactorized (uncontrolled) qualitative variable, discharge vs. no discharge, into the design. While it might be possible to factorize discharge vs. no discharge, it was known that no hydrogen would be produced with no discharge, regardless of the power level.

Input power was factorized since the voltage and amperage required for a chosen power level are determined by the discharge and therefore need not meet set requirements of a factorial design.

Although the voltage was not a factor, the voltage ranged from 3100 to 11,000 rms volts.

The above factors were chosen intuitively. Other factors, such as AC frequency, distance between reactor electrodes, and electrical current, may also have an effect. Future experiments using a frequency of 10,000 cps are planned to detect any frequency effect on hydrogen production.

The factorial design form of experimentation has the advantages of 1) obtaining an empirical regression equation with minimum effort, 2) isolating the magnitudes of the effects of each variable and its interaction with other variables (synergism) on the dependent variable, 3) allowing optimization of the dependent variable within the levels of the factors studied, and 4) suggesting the direction to be taken outside the region studied for further optimization.

After the desired carbon monoxide and steam flow rates were obtained and stabilized at $\frac{1}{2}$ or 1 atmosphere, the discharge was initiated. It was monitored with an oscilloscope (Tektronix Model RM 35A), typical oscillographs of which are shown in figure 6. The waveforms on the left show the voltage trace above the current trace. The area enclosed by the Lissajous figure on the right is a measure of the true power used by the discharge.

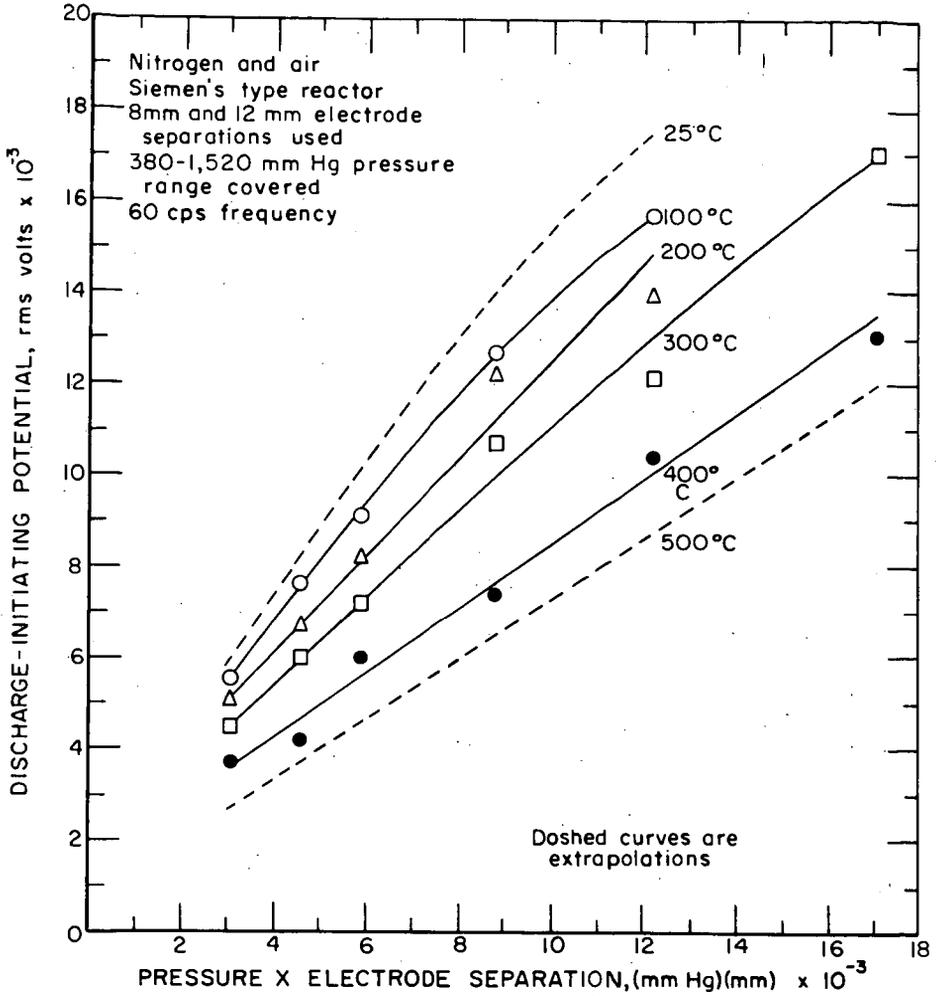
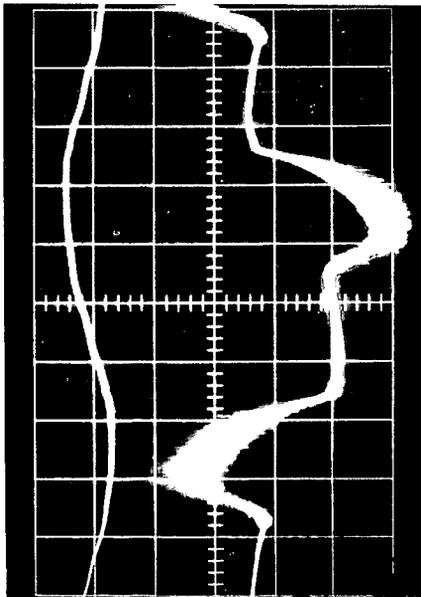
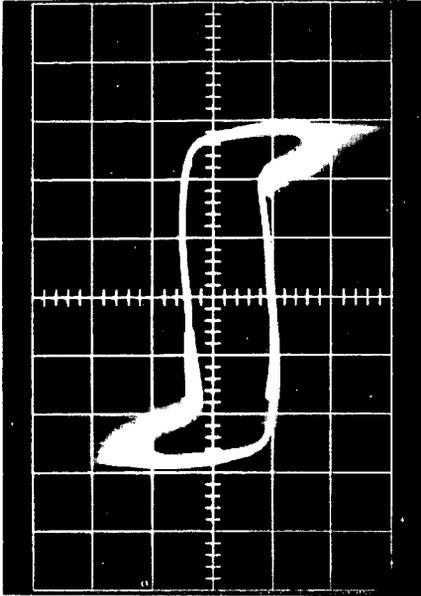


Figure 5.— Paschen's law curves.

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Voltage (above) and current waveforms



Lissajous figure

Figure 6.- Typical oscillographs of same corona discharge.

The water-free product gases were analyzed by gas chromatography. However the hydrogen yields are reported with water present.

RESULTS AND DISCUSSION

The data were analyzed according to the linear hypothesis statistical model resulting in the following empirical prediction equation for the percent hydrogen (water included):

$$\begin{aligned} \text{Pct. H}_2 = & -1.885 \pm 0.762 - (1.946 \pm 0.499)P + (0.00402 \pm 0.00042)SV \\ & + (0.00486 \pm 0.00121)T - (0.0106 \pm 0.00830)W \\ & + (0.00470 \pm 0.000791)(P \cdot T) - (0.0000103 \pm 0.0000006)(T \cdot SV) \\ & + (0.0000288 \pm 0.0000132)(T \cdot W) \end{aligned}$$

where P = pressure, atmospheres
 SV = space velocity, hr.⁻¹
 T = temperature, °K
 W = input power, watts.

An inspection of the terms in the equation, after numerical values are inserted, shows that temperature has the largest effect on the production of hydrogen, with space velocity being the least important.

The coefficient with the largest error associated with it is in the input power term. Since the factorial levels were maintained quite closely, the inference which can be drawn is that the yield of hydrogen tends to be least correlatable with input power. The reverse is also true, that hydrogen production tends to correlate best with the interaction term T·SV.

The coefficients were determined with an IBM 7090 digital computer available at the University of Pittsburgh, using a program for a regression equation previously developed by Bureau personnel.

According to the equation, maximum production of hydrogen, within the range studied, was found to be at 1 atmosphere, 200 hourly space velocity, 800°K, and 90 watts input. At these levels the percentage of hydrogen was 4.5, compared with the figure 4.1 calculated by the equation. The extra-factorial region of interest suggested by the equation would be higher pressures, temperatures, and inputs, and lower space velocities. Within the limitations of our equipment, and operating on a flow basis, this was P=2, SV=100, T=800, and W=100. The hydrogen percentage increased to 8.6. By stopping the gas flow, 11.6% H₂ was obtained in the product.

Extrapolating an empirical equation is always dangerous. There is no guarantee that an indicated extra-factorial region will yield good results. In the present case, the extra-factorial region proved to be more fruitful than predicted. The advantage of an empirical equation is the ease in which it is obtained while representing the data well in a compact form within the region in which the data were taken.

If one could define the reaction temperature in a corona discharge, it would be possible to discuss the thermodynamics of the system. However it is difficult, if not impossible, to define an equilibrium with respect to the corona reaction. While there are methods available for obtaining measurements of the average (translational) temperature of the gas or plasma, there is a valid question as to the "local temperature" at the reaction site of the activated species. However it was attempted in this study to correlate the average wall temperature of the system with hydrogen production and thus to define the system sufficiently for design purposes. The prediction equation strongly indicates that this approach is satisfactory.

The decrease in equilibrium constant of the water-gas-shift reaction with temperature is shown in figure 7. As the prediction equation indicates a positive temperature effect on the production of hydrogen, the water-gas-shift reaction in an electrical discharge must be kinetically rather than thermodynamically controlled.

The yields of hydrogen shown here are less than the yields achieved industrially¹³ by catalytic means. What is of more interest to us is the empirical determination, for several reactions, of the functional dependence of the yield of a given product on the several independent variables in a corona discharge. This information is a prelude to future experiments where powdered coal or coal volatiles will be treated with certain gases in a corona discharge.

CONCLUSIONS

The conclusions that can be drawn from this study are:

- (1) No hydrogen is produced in the absence of a discharge, regardless of the values of space velocity, pressure, temperature, or power dissipated.
- (2) The prediction equation arising from the statistical analysis of the data indicates that more hydrogen is produced at higher pressures, temperatures, and power inputs, and lower space velocities.
- (3) Within the range of variables studied, temperature has the largest relative effect on the production of hydrogen, while space velocity has the least relative effect.
- (4) Of the four factors chosen, input power is the least correlatable with the production of hydrogen, while the first order interaction: (temperature) X (space velocity) is the most correlatable.
- (5) The water-gas-shift reaction in a corona discharge is kinetically, rather than thermodynamically controlled.

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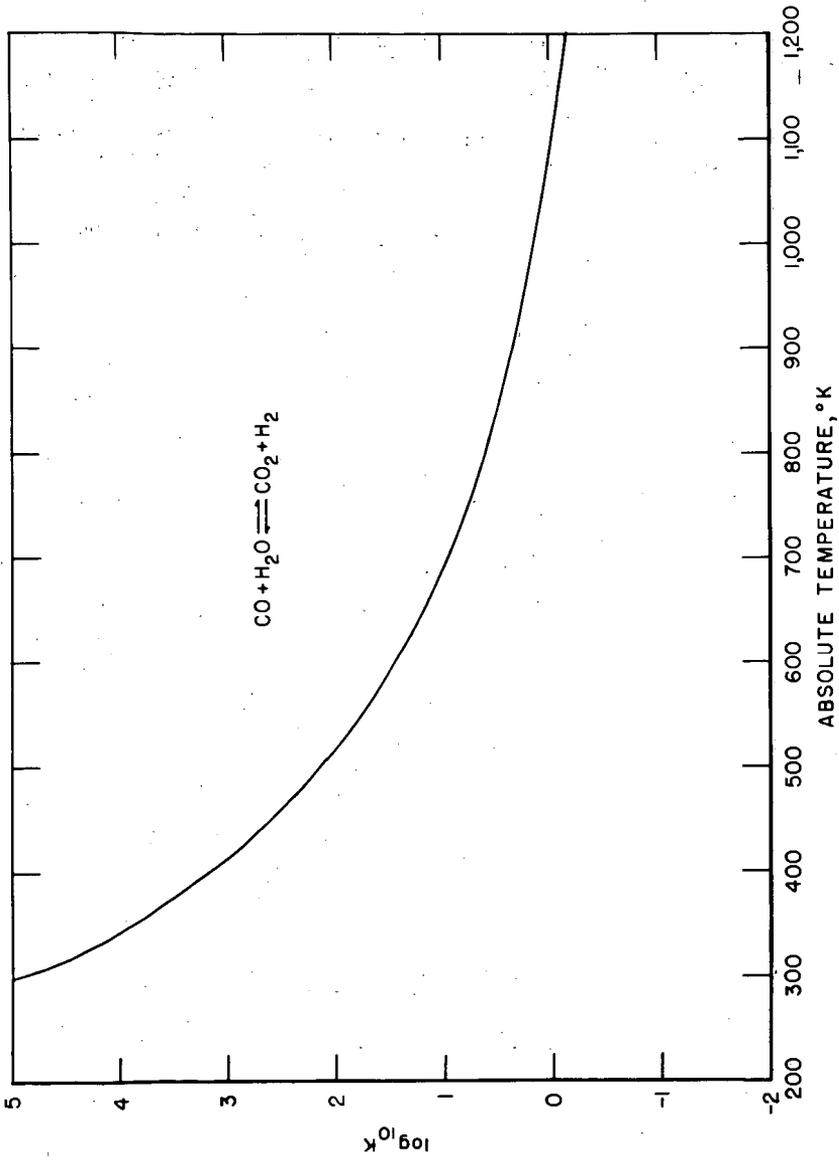


Figure 7. Change in equilibrium constant of the water-gas shift reaction with temperature.

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