ARC GASIFICATION OF COAL

C. Sheer, S. Korman and T. J. Dougherty
Chemical Engineering Research Laboratory, Columbia
University, New York, NY, U. S. A., 10027

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ABSTRACT

Pre-treatment of coal entrained in steam in an arc plasma device stabilized by cathode nozzle injection and known as the "FCC", devolatilizes the coal and converts 80 - 90% of the residual carbon into a finely divided, highly reactive fume material. This is gasified and methanated in post arc reactors under relatively mild conditions. The gas output is autogenously desulfurized by the coal ash as a consequence of its passage through the arc.

INTRODUCTION

This paper is concerned with the results of an investigation into the feasibility of gasifying coal using an arc plasma as the energy source. Ordinarily the use of electrical energy for this purpose would be contra-indicated on economic grounds since the cost of electrical energy is about three times that of the equivalent amount of thermal energy generated, for example, by the combustion of fossil fuels, as is done in the case of conventional gasification processes. This is especially true when the electrical heating techniques involve an arc plasma device which generates temperatures an order of magnitude higher than required for coal gasification and which, therefore, is subject to greater losses than, say, an electrical resistance furnace.

The first step in most gasifiers is the well known water gas reaction:

$$C + H_2O \rightarrow H_2 + CO \qquad (1)$$

This reaction is quite endothermic. Thus, assuming the product gases issue at 1000^{o} K, a calculation of the heat input to supply reaction (1) and sensible heat totals 2710 K-cal per Kgm of coal fed. In electrical units this amounts to 3.15 KWH/Kgm of coal. To supply all of this energy electrically, would be very expensive, especially in consideration of the low efficiency of electrical power generation.

In what follows we shall describe a process in which the coal is pre-treated in an arc plasma and, thereby, largely converted into a highly reactive finely divided fume. This material is then treated with superheated steam in a post-arc reactor to carry out the gasification reaction under much milder conditions using only combustion energy input. The achievement of effective pre-treatment of the bulk of the coal feed is due mainly to the use of a particular kind of arc plasma device, especially adapted to the particular pre-treatment involved. This type of plasma device is described in detail in the next section, following which the overall gasification process is presented.

ARC PLASMA DEVICE

The development of arc plasma devices for chemical application has involved the problem of operating an electric arc when subject to a considerable amount of forced convection. Since the arc column generates temperatures considerably in excess of what is needed for most chemical reactions it follows that a rapid flow of gases, or gases with entrained solids, must pass through the arc column in order to achieve good energy transfer and a mass flow average temperature for the reactants much lower than the column temperature. A free-burning arc column is very sensitive to cross-flow convection and may be blown out by convection velocities of only a few feet per second directed transversely to the arc column. In order to operate stably in the presence of appreciable forced convection, some form of physical constraint must be applied to the arc column (1), which maintains its positional integrity and, therefore, stabilizes the arc. For example in the wall-stabilized arc the column is situated in a vigorously water cooled cylindrical channel, where it is constrained to stay regardless of the rate of gas convection through the channel, and the arc continues to burn so long as adequate power is fed to the electrodes. The water-cooled channel wall thus serves as a thermal constraint, stabilizing the arc column against the effects of forced convection.

One disadvantage of this type of arc stabilization, aside from the energy lost to the cooling circuit, is the steep radial temperature gradient which is set up near the wall boundary at which a relatively cool film of gas is formed. A study (2) of the mass flow through the channel of a wall stabilized arc unit reveals that the major part (70 - 90%) of the convected gas flows through this device within the thin relatively cool boundary layer and, therefore, does not come into direct contact with the hot core of the arc column. The rate of heat transfer to the convected mass is, therefore, not as rapid as desired for some purposes. Thus, when refractory powders are entrained in a carrier gas, and fed to a wall-stabilized arc, the solid particles can usually be melted, as occurs in plasma flame spraying, but little, if any, vaporization of the refractory solid occurs.

Somewhat better heat transfer is achieved when a fluid mechanical constraint is used, as in the vortex-stabilized arc, or in some of the magnetically stabilized arc devices. However, these devices still fall short of the extremely rapid heat transfer rates desired for some purposes. What is needed is a device in which the convected materials can penetrate easily into the hot core of the arc column so that it can absorb heat very rapidly during its transit, permitting the achievement of high mass throughput rates per unit of electrical energy expended. A plasma device with this capability has been developed in this laboratory, based on injecting the working fluid into the arc column from the cathode end of the discharge. Since this device has been adequately described elsewhere (3), (4), (5) and (6) only a brief summary will be presented here. The device, which we have labelled the "fluid convection cathode" arc, or more briefly the "FCC", makes use of the Maecker effect at the cathode end of the column where a strong contraction of the column diameter exists, especially when a conically pointed tungsten cathode is used. Contraction ratios between the normal column diameter and its diameter as it contacts the cathode tip of 10 to 1 or higher produce a strong Maecker force propelling the column plasma along its axis away from the tip. This motion in turn causes the aspiration of ambient gas into the column through the column boundary in the contraction zone, as shown in Figure 1. This electro-magnetic pumping effect thus opens a "window" for the penetration of cold gas (including entrained solids) into the hot core of the column. The FCC merely replaces the ambient gas aspirated by the column with convected gas injected via an annular nozzle surrounding the cathode tip. The geometry is shown in Figure 2. Using the FCC nozzle we have found an exceptionally high order of arc stability with convection rates upwards of 20 or more times the natural aspiration rate. To achieve good arc stability under high throughput rates, it is necessary to use an axisymmetric nozzle so that a uniformly converging flow emerges from the annular orifice. In this case it is seen that a centrally directed force acting on the column in and near the contraction zone, is established by the radial component of the gas momentum, thus constraining the column to remain on the axis. In addition to stabilization, the radial compression of the column due to the convergent gas flow causes a local increase in current density as well as an increase in arc voltage gradient. The energy dissipated per unit volume ($\vec{J} \cdot \vec{E}$, where $\vec{J}$ = current density and $\vec{E}$ = voltage gradient) is, therefore, increased in the contraction zone, raising the local plasma temperature. This is made evident by the appearance of a large tear-drop shaped brilliant blue-white plasma bubble whose temperature (for a 300 ampere argon arc) has been determined as being in the range of 22000° to 24000° K. It should be pointed out that the occurrence of the hot plasma bubble in the contraction zone enhances the dissipation of electrical energy in the region where cold working gas is being continuously injected into the plasma. The high temperature bubble also serves as a copious source of ions which are driven along the column by the plasma motion within the column and which help maintain adequate electrical conductivity even for high flow rates, thereby enhancing operational stability.

The effectiveness of utilizing a FCC arc to heat reacting materials rapidly to a given temperature is determined by the degree to which the injected gas stream, along with any entrained solids penetrate into and flow within the arc column. Since the column is the zone of primary energy dissipation the maximum rate of heat transfer to the working gas (and any entrained powder) should occur inside the column. Accordingly, experiments were performed to measure the degree to which the convected gas penetrates and flows through the arc column. Penetration factors have been measured for argon, based on the current flow boundary yielding values ranging from 40% to above 90%, depending on the total mass flow rate and injection velocity. Using the same criterion for hydrogen results in significantly lower values. However, penetration to the 3000° K boundary yielded values ranging from 65% to 90+%. Similar results were observed for N_2, air, and steam. The measurements were carried out with the aid of transient probe diagnostics (7).

Penetration of the carrier gas was found to be a necessary but not always a sufficient condition for gases with entrained powders. Thus, for powders with too small a particle size and low thermal conductivity, the forces due to thermophoresis caused the particulate matter to be deflected out of the gas stream (8) such that only the carrier gas entered the column. This occurred for example in the case of silica particles of 7μ average diameter, entrained in argon. The effect was eliminated by using particles whose diameters were in the range 50μ to 85μ.

In practice the FCC device features a double shroud with a small thin layer of argon flowing from the inner shroud to protect the hot tungsten tip from contact with either accumulated solids or reactive gases which may be fed into the outer shroud. The geometry of the doubly shrouded FCC nozzle is shown in Figure 3. The use of reactive gases (e.g. steam) fed through the outer shroud or any carrier gas with entrained solids also caused some problems at the anode contact surface; this consisted either of chemical erosion at the arc crater surface or a build-up of solid material in the vicinity of the anode spot, which ultimately interfered with termination of the arc. These difficulties were overcome for laboratory experiments by using anodes consisting of porous graphite plugs mounted in water-cooled copper holders, and through which a slight flow of argon was maintained. This protected the arc anode terminus from chemical erosion and kept the surface free of accumulated solids. The porous anode holders were mounted laterally a short distance away from the column axis. Electrical contact to the main discharge was established via the short auxiliary column extending from the anode surface to its junction with the main column issuing from the FCC. By utilizing three such anodes spaced laterally 120° apart around the cathode axis, the main effluent could be caused to issue in a straight path along the cathode axis. Figure 4 shows the geometry of the triple-anode assembly.

THE ARC GASIFICATION PROCESS

Two major problems confronting the use of electric arcs to gasify coal are the cost of electric power and the need for a high conversion of carbon to gas. Early experiments in this laboratory indicated that coal (-100 mesh) could be fed at high rates into an open arc through an FCC using steam as a carrier gas. Feed rates up to 2.3 Kg coal/min. in 0.68 Kg steam/min. are easily achieved with arc power as low as 92 KW (475 Amps, 193 Volts) for a power/feed rate ratio of 0.66 KWH/Kg coal, with 112 KW (600 Amps, 187 Volts) and 0.81 KWH/Kg coal being more typical. Samples were withdrawn from the center of the arc, just beyond the anodes, using probes. The gas analysis is typically 60% H_2, 30% CO, 10% CO_2 (dry basis) with virtually no sulfur compounds. Frequently small concentrations of hydrocarbons are observed. The coal "fume" collected in this way has a high surface area (> $80m^2/g$) and reacts rapidly with steam in a tubular, fixed-bed reactor yielding several liters/min./g charged at 850° C. The gas composition depends on temperature but is similar to the arc effluent composition.

Attempts to duplicate these results in a small enclosed arc encountered many difficulties but eventually the coal feed rate was increased from 10 - 30 g/min. to 250 g/min. at 80 KW (5.3 KWH/Kg with carrier steam up to 100 g/min. The gas composition was similar to that obtained from the open arc and the fume was highly reactive with high surface area when steam was used as the carrier gas. This was not the case however, for runs made with nitrogen or argon as carrier gas and for runs with a modified cathode which produced poor penetration of solids into the arc column. The arc effluent was quenched with a water spray which provided additional steam for the gasification reaction and which also served to improve arc stability and to cool the arc chamber.

On the basis of these results, a new cathode and new arc chamber were designed. The new cathode was larger with larger feed slots and provided good penetration. Residence time in this chamber is approximately one second and secondary steam is injected to increase the amount of coal gasified and to cool the arc chamber. At the present time, feed rates of 0.61 Kg coal/min. and 0.45 Kg steam/min. have been achieved at a power level of 120 KW (3.3 KWH/Kg coal). Approximately 40 - 50% of the coal feed is gasified in the arc chamber, the remainder appearing as fume with a surface area of 20 - $25m^2/g$ ($\sim$ 0.1 micron diameter). The gas produced is approximately 62% H_2, 26% CO, 12% CO_2 over a wide range of feed rates.

The coal fume produced in this arc has a lower surface area and reacts somewhat less rapidly than material produced in the smaller arc and the open arc, possibly because of the increased residence time in the hotter, better insulated, larger chamber (temperature over 1000° C) and the use of secondary steam instead of a water spray. Most of the highly reactive fume has probably already reacted to form gas and only less reactive materials survive as solids. The other possibility is that penetration was poorer but the high catalytic activity described below makes this explanation unlikely.

The gasification reaction was carried out in a 1" ID steel pipe with a 6 - 7" bed containing 15 - 30 g of coal fume depending on the degree of compression of the bed. Four thermocouples were spaced 1.5" apart in the bed. Steam flow was monitored with a small orifice and D. P. cell (differential pressure measurement) and the condensate was collected and measured. Gas analysis was performed on line using Barnes Engineering Multispec analyzers for CH_4, C_2H_2, CO, CO_2, and MSA thermatron analyzer for H_2. Samples were taken at intervals for analysis on a Beckman Process Chromatograph Model 6700, a Perkin-Elmer 283 IR Spectrophotometer and a Hewlett-Packard 5830 Gas Chromatograph which has recently been acquired.

Gasification rate as a function of temperature at 80 psig is shown in Figure 5. The composition of the product gas is shown in Figure 6. Considering the much higher surface area, it is surprising that these samples behave much like devolatilized coal (9), which data are also plotted in Figures 5 and 6 for comparison. The data for devolatilized coal were obtained at higher pressures (300 psig compared to 80 psig) and somewhat different conditions (2000 cc N_2/Hr to transport steam). Conversion efficiencies of 84 - 92% (based on ignition losses of charge and residue) are typical. Ignition losses (at 1000° C) of the fume samples vary from 66 - 76% while the coal feed LOI is 85%.

At lower temperatures (500° - 600° C) high concentrations of methane are produced; the gas is principally CO_2 and methane. More precisely, a mixture of hydrocarbons is produced with methane the major constituent. Heating above 700° C in the presence of steam causes an irreversible loss in methane producing activity. At temperatures above 700° C, H_2S can be liberated from the solid, the effect being more pronounced the higher temperature. Since these materials have already been exposed to steam at high temperatures in the arc chamber, it appears recombination of H_2S, probably with iron, occurs rapidly as the arc effluent cools. It is evident that the coal fume contains an active methanation catalyst which is destroyed by steam at elevated temperatures. A separate investigation was initiated to determine the nature of this catalytic activity. The results, described in the next section, strongly indicated that the iron deposited on a high surface area silica is the active agent and, incidentially, that iron is the desulfurization agent in the fume. It should also be pointed out that finely divided iron liberates H_2 from steam at temperatures of 700° C or higher at

80 psig.

CATALYTIC METHANATION

One gram of high surface area silica (fumed SiO_2 or Cabosil) was placed in a 3/8" tubular steel reactor with a source of iron (powdered iron, iron oxide, steel wool). Passing pure CO through the bed at 500° C and 60 psig yields an active catalyst in about one hour. The mechanism is dependent on a temperature gradient in the reactor and the iron source need not be mixed with the silica. A plug of steel wool at the inlet (low temperature zone) will suffice. Iron is deposited from the vapor phase (probably by decomposition of a carbonyl) onto the silica surface. To confirm this mechanism, iron filings were placed in a separate reactor followed by a second reactor containing silica. Passing CO over the iron at 150° - 200° C and 60 psig and the effluent from this reactor over the silica at 500° C and 10 psig produces an active catalyst. Care must be exercised to prevent plugging due to carbon deposition which is more pronounced at high temperatures and pressure. However, if plugging occurs, it can be eliminated by passing H_2 over the catalyst at 500° C and 60 psig, producing methane (> 50%).

A number of runs were made using Cabosil in copper tubes and in steel tubes with no other source of iron to demonstrate that the steel tubes themselves had no significant effect and that iron was necessary for catalytic activity. Further tests were performed with different materials and substrates (fumed ash, fumed alumina, quartz sand). Fumed ash, by itself, is a reasonably good catalyst after suitable activation. Fumed alumina proved a poorer substrate than silica and quartz sand proved as good as an equal volume of fumed silica (30 g sand, 1 g silica fume) but took substantially longer to activate.

The gas analyses were performed on line with the same system used in the steam-coal fume gasification tests, with occasional samples taken for mass spectrometry and gas chromatography. Inlet and outlet flows were measured with flow meters. The effect of temperature and feed composition are shown in Figures 7 and 8. These data were obtained using one gram of Cabosil and steel wool at the reactor inlet. At least two processes are occurring:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (2)$$

$$2CO + 2H_2 \rightarrow CH_4 + CO_2 \qquad (3)$$

In some cases (higher temperatures, lower H_2/CO ratio in feed) there is also evidence of carbon deposition:

$$2CO \rightarrow C(S) + CO_2 \qquad (4)$$

These equations, of course, have no implication regarding mechanism. The rate of methane production is comparable to that obtained with a good nickel catalyst (10). It is not uncommon for the "methane" meter (IR absorption - CH stretching band) to move offscale (pure methane reads full scale) because of the presence of other hydrocarbons. The catalyst is not affected by high temperatures (700° - 800° C) but can be deactivated at low temperatures (< 300° C) by loss of iron through carbonyl formation.

The catalyst is poisoned by H_2S. Using H_2 containing 2% H_2S, the activity declines essentially to zero in 10 - 20 minutes. If iron (or iron oxide) is placed in the catalyst bed, the catalyst life is extended to several hours and the iron removes the H_2S from the gas. The catalyst can be regenerated by raising the temperature to 700° C even in the presence of H_2S. Upon cooling, methane reappears but the catalyst is soon poisoned by the H_2S.

CONCLUSION

Considerably more work is needed to determine the effects of arc operating conditions and gasification conditions on the course of the coal-steam gasification reaction but the rough outlines appear. Among arc operating conditions, cathode design, residence time and temperature in the arc chamber appear particularly significant. Of course, the nature of the carrier gas (steam) is of major importance. The effect of power/feed rate ratio at values less than 3 KWH/Kg coal feed is an open but critically important question which is under intense investigation at the present time. Among the gasification conditions, temperature and steam flow are particularly significant, the reaction rate increasing with increasing steam flow and temperature with very high reaction rates at temperatures of 1000° C or more.

The possibility of a complete flow process is intriguing, especially if a sulfur free gas can be produced with a properly chosen temperature profile. Direct production of methane appears possible but difficult because of the temperature and pressure dependence of the reaction rates and equilibrium involved. Coal fume behaves in many ways like a fluid and is easily transported in pipes and tubes raising the possibility of transport in pipelines. This is especially interesting in view of the fact that coal fume because of its treatment in the arc contains its own SO_2 absorption system. This is more fully described in a collateral paper which is presented in this Round Table (11). Figure 9 shows a process flow sheet.

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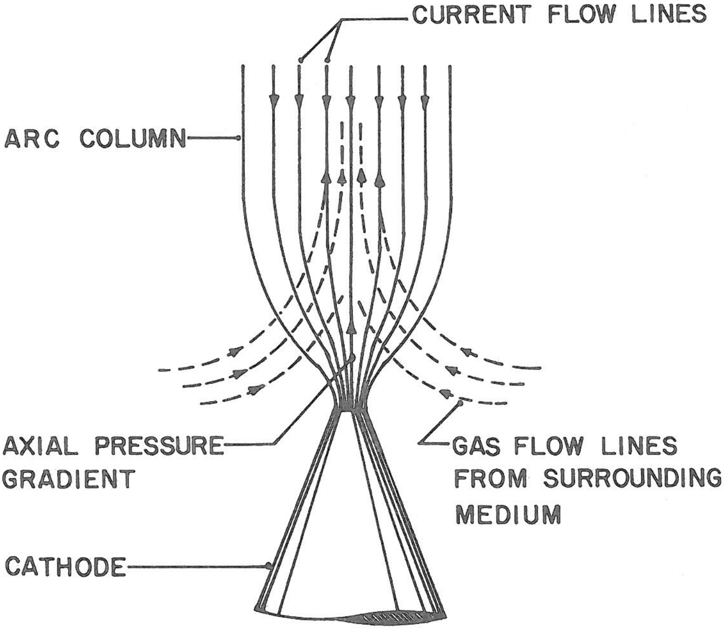
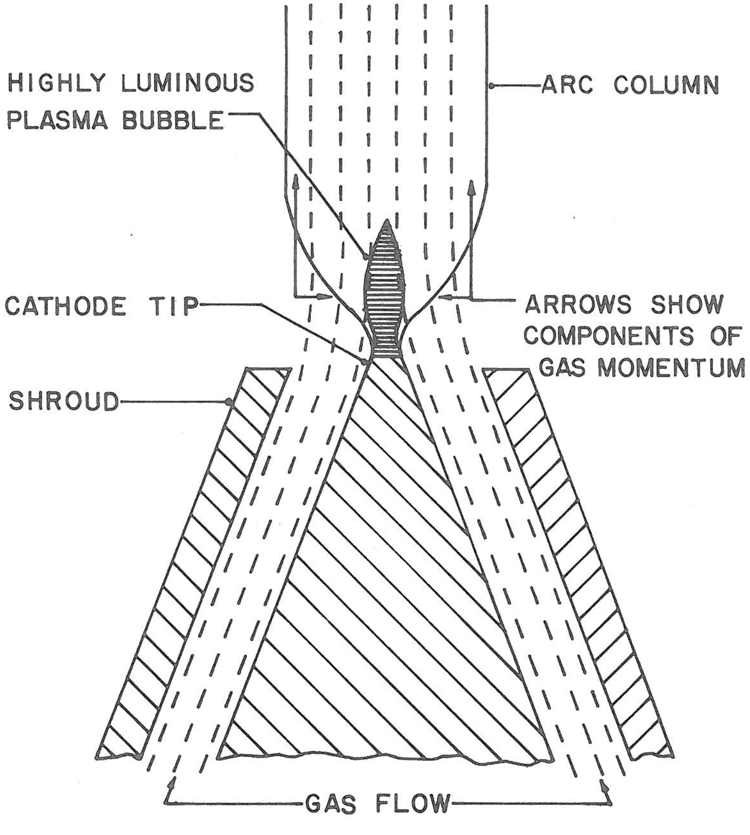
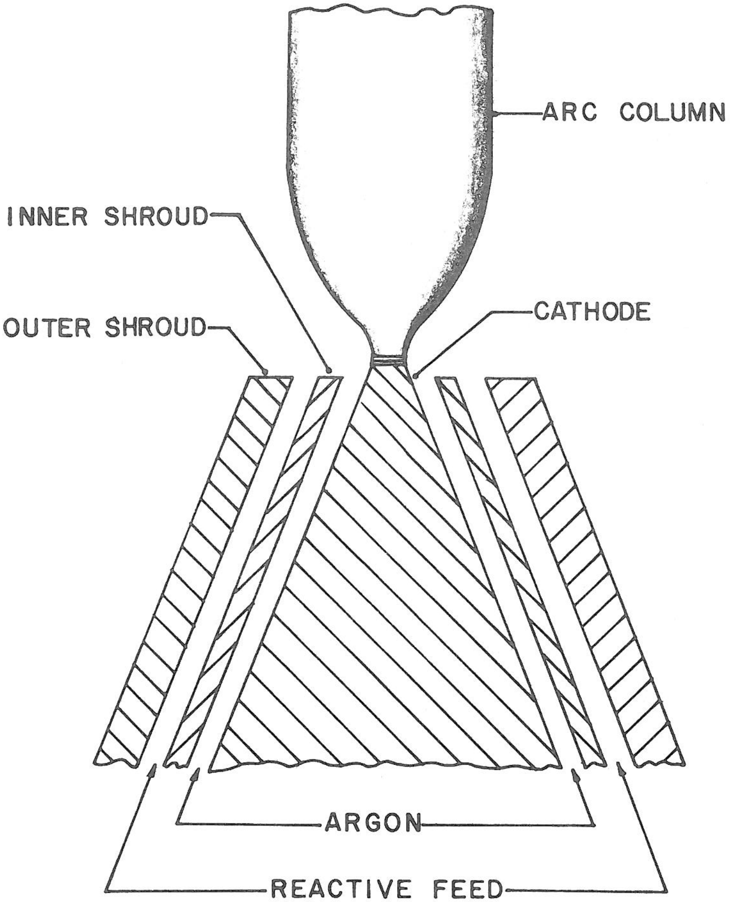


CONTRACTION ZONE OF THE ARC COLUMN
AT THE CATHODE END OF AN ARC DISCHARGE
FIG. 1



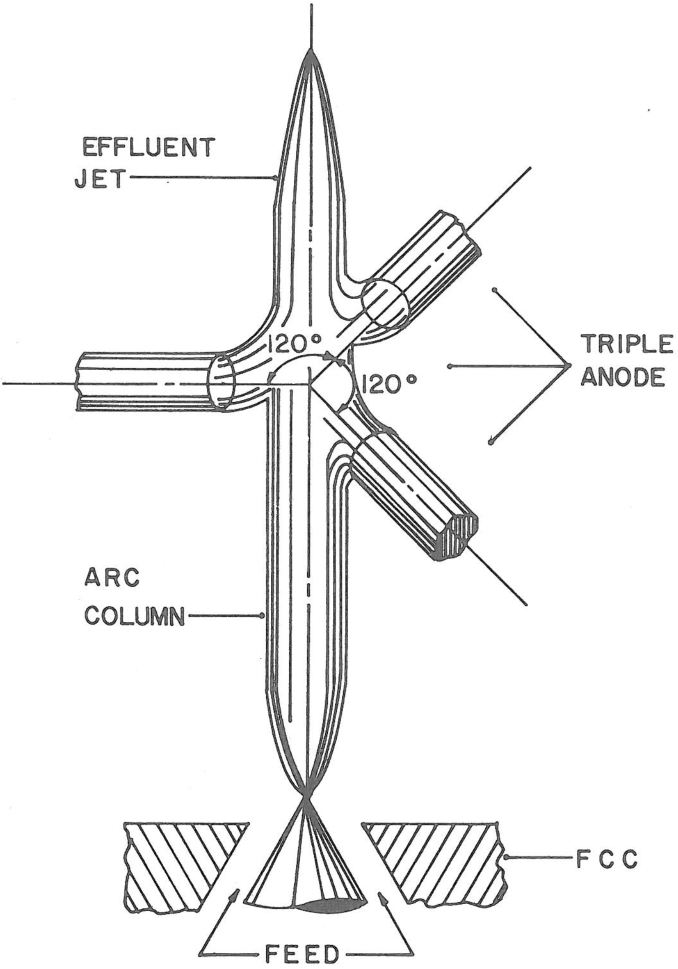
FCC NOZZLE SHOWING COMPRESSIVE EFFECT OF GAS FLOW ON ARC COLUMN

FIG. 2



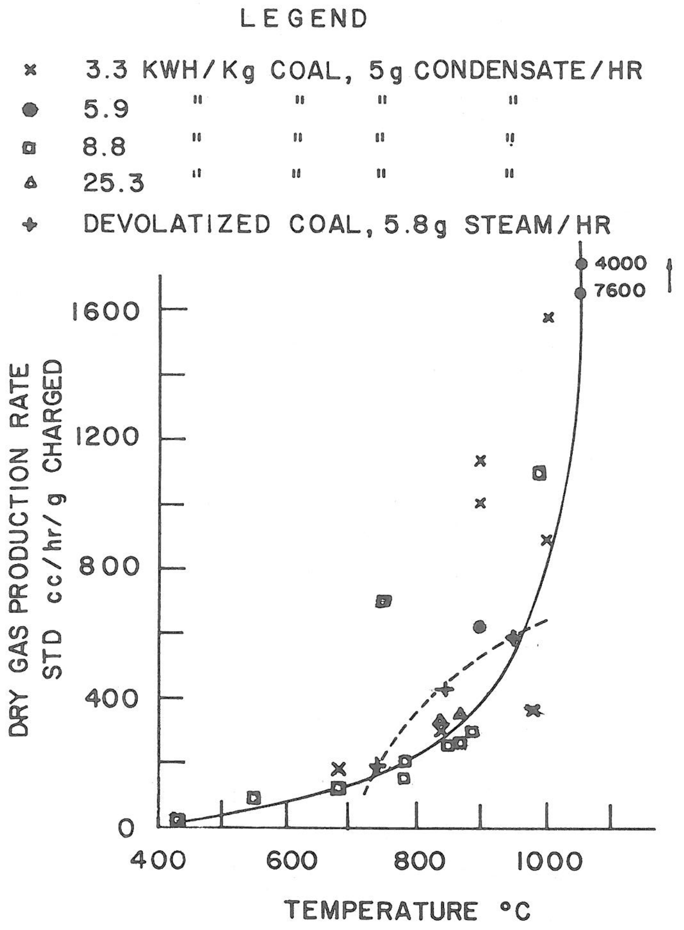
DOUBLE SHROUD FCC

FIG. 3



PLASMA GENERATOR CONSISTING OF FCC WITH TRIPLE ANODE CONFIGURATION

FIG. 4

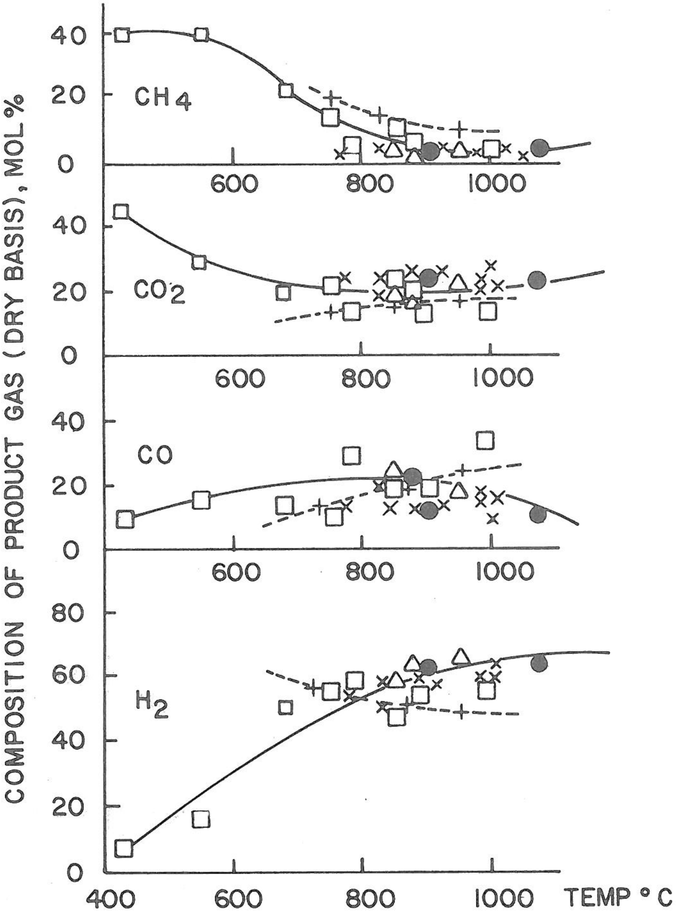


GASIFICATION RATE vs. TEMPERATURE:

COAL FUME (80 PSIG); DEVOLATIZED COAL (300PSIG)

FIG. 5

note: see legend on fig. 5



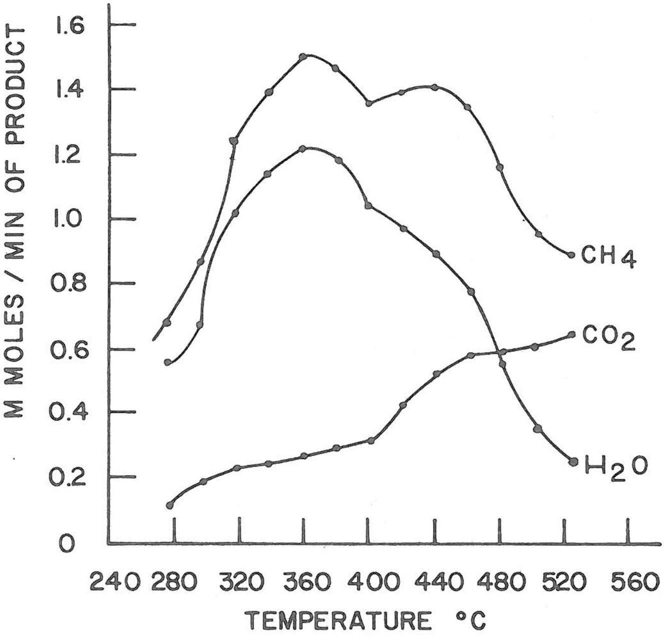
GAS COMPOSITION vs. TEMPERATURE

COAL FUME (80 PSIG); DEVOLATIZED COAL (300 PSIG)

FIG. 6

$H_2 + CO = 6.0 \pm 0.8$ M MOLES / MIN

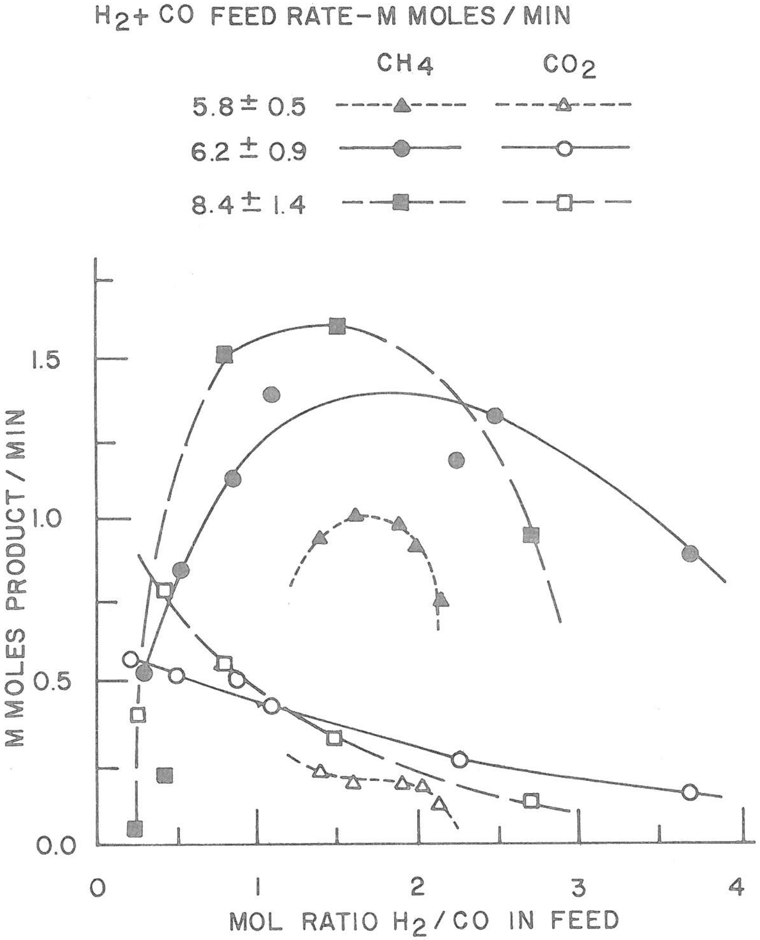
$H_2 / CO = 1.4 \pm 0.7$



METHANATION RATE vs. TEMPERATURE

CATALYST - 1 g CABOSIL + IRON

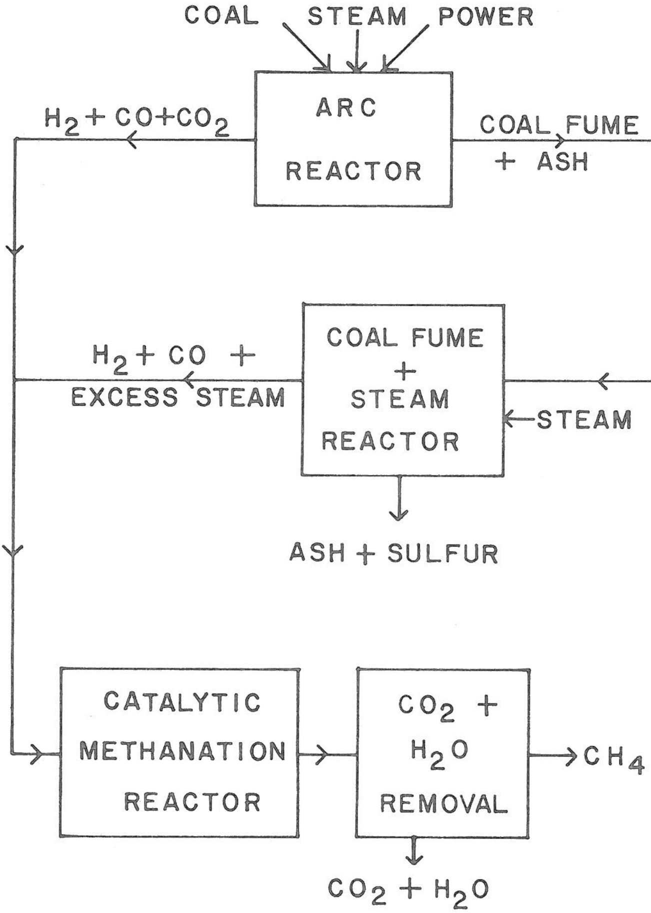
FIG. 7



METHANATION RATE vs. FEED COMPOSITION

CATALYST - 1 g CABOSIL - IRON

FIG. 8



SCHEMATIC OF PROCESS FOR
ARC GASIFICATION OF COAL

FIG. 9