

SYNTHESIS OF HYDROCARBONS BY THE HIGH INTENSITY ARC

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This report summarizes some of the results of an investigation into the use of a novel type of arc applied to hydrocarbon synthesis. The principal reacting system was carbon and hydrogen. Later substitutions for the hydrogen were employed in a limited way. These included, in turn, a 50-50 volume percent mixture of CO and H₂, steam, and a solid petroleum residue essentially (CH₂)_x.

The type of arc is one which was developed in our laboratory and whose properties for applications of the type reported here we have studied intensively for several years. It is a type of high intensity arc discharge characterized by a number of unique features, of which an important one is the fact that a relatively high rate of continuous through-put of feed material can be achieved. The feed is a fluid, is raised to high temperatures, and itself comprises the plasma environment of the discharge, particularly the electric conduction column maintained between the electrodes. As result it will be appreciated that the composition of the plasma is derived from that of the feed; however, the atomic, molecular, or free radical species comprising the plasma may differ significantly from the molecular composition of the feed.

Distinctive features of the High Intensity Arc

Conventional arcs, consisting of a gaseous electrically

conducting column joining two electrodes, a positive anode and a negative cathode, are used as a source of heat, as for example in electric smelting processes. The mechanism by which heat is usefully transferred to feed materials occurs by radiation and conduction from the hot column. The column is the zone of primary energy dissipation in which the input electrical energy is converted into radiant energy and sensible heat, both of which flow out in all directions through the intervening layer of atmosphere. The maximum temperature which may thereby be achieved and maintained in the surrounding charge is limited by practical considerations to about 2500°C.

In such arcs little if any of the material to be treated enters the energy dissipating region within the arc conduction column itself. The opportunity for successfully accomplishing this became available with the discovery in 1910 by Beck¹ of the type of discharge now known as the "high intensity arc". The use of this type of arc to treat materials to temperatures higher than 2500°C in a continuous and practical manner is one of the central themes of this paper. ²⁻⁶

In the high intensity arc, significant amounts of feed material can penetrate and pass through the conduction column, and are thereby heated with high energy transfer efficiency to very high temperatures; i.e., up to 10,000°K or more. In the early forms of the high intensity arc this was accomplished by incorporating the feed into the anode and allowing the anode to vaporize continuously into the arc. This is suitable however only for the treatment of normally solid feed materials.

Recently a means was developed in this Laboratory whereby the injection of large quantities of gases into the arc column can be made to operate in a practical manner, even for reactive gases. In this modification, the gas is injected from the cathode end rather than through the anode of the discharge, by means of a specially designed annular nozzle surrounding the cathode. This device has been termed the "fluid convection cathode".

Basis of the Fluid Convection Cathode

Referring to Figure 1, the arc column at the cathode is characterized by a converging shape to a small tip at the cathode surface. This convergence, representing an inhomogeneous electric current flux, therefore defines a zone of inhomogeneity in the accompanying magnetic field. This in turn has the effect of producing a fluid mechanical thrust away from the cathode in the direction of the anode, thus giving rise to a pressure gradient away from the cathode tip. To stabilize this gradient, ambient gas is aspirated into the arc column in the region of inhomogeneity. This region represents the only portion of the arc other than the anode crater through which appreciable quantities of gas may be injected without disturbing the stability and maintenance of the arc discharge.

The FCC was developed during an investigation⁷ of the influence of gas convection into the base of the arc column near the cathode of a high intensity arc. The technique consists essentially in surrounding the conical tip of the cathode with an annular nozzle which terminates upstream of the tip and which directs the gas in a converging high speed layer into the

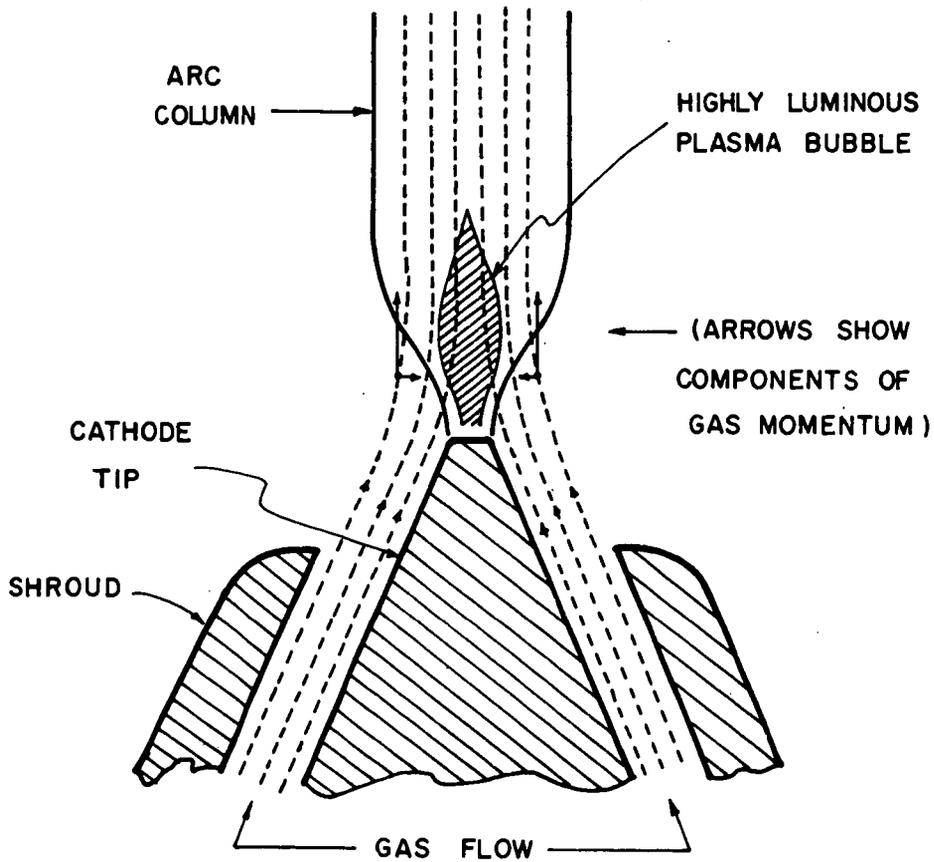


Fig. 1. Sketch of FCB showing compressive effect of gas flow on base of arc column.

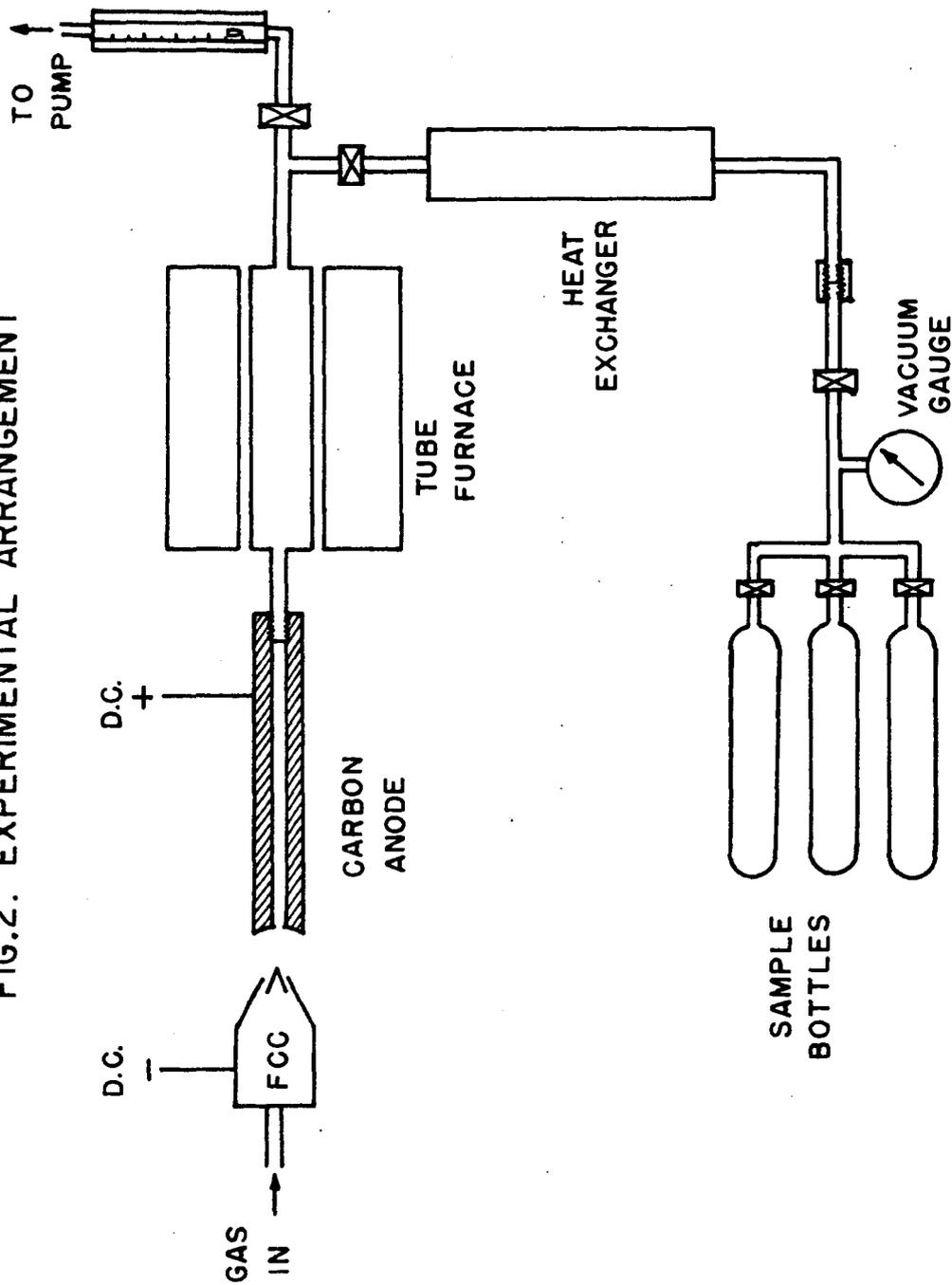
column of the arc very close to the point where it originates on the cathode. It was found that if this were done in a manner which causes the gas to impinge on the arc column in the region just in front of the cathode where the column is converging from the broader discharge column, then the gas will preferentially enter the column and can be injected at 10 to 20 times the aspiration rate, whereas, if an attempt were made in the classical manner, to force the gas into the arc column proper in order to energize the gas, such impingement is fruitless and tends to unstabilize and blow out the arc.

Again, with conventional confined arcs, where stability is sought by enclosing the arc discharge within a water-cooled chamber, and forcing the gas into the chamber with the intention of imparting arc energy to it, both theoretical and experimental results have proven that over 70% of the injected gas never enters the column⁹, and does not obtain any significant amount of activation energy from the arc.

Experimental Method

Figure 2 is a diagram of the D.C. high intensity arc apparatus, showing an FCC cathode through which the hydrogen gas is injected into the conduction column and a 1" diameter cylindrical carbon anode. The anode has a 1/4" diameter hole along its longitudinal axis. The anode is connected at its back end by 3/16" I.D. metal tubing to a 1-1/6" diameter Type 304 stainless steel tube surrounded by an electrically heated laboratory tube furnace. Leaving the furnace is a water-cooled heat exchanger following a tee-connection valved to permit the gas stream to go in either of two directions: (1) to a flowmeter

FIG.2. EXPERIMENTAL ARRANGEMENT



and laboratory pump, or (2) to a manifold of a large-dialled mechanical vacuum gauge and several valved 500 cc gas sampling bottles. These are evacuated prior to use. The carbon anode can thus serve as a combination source of solid carbon, and of carbon vapor issuing from the anodic arc terminus into the plasma column, as well as an arc crater gas sampling probe.

Depending upon the pumping flow rate or timed pressure rise in the sampling branch, it is thus possible to draw an arc flame effluent gas stream from the reaction zone through the tube furnace to vary the residence time at any temperature up to about 1000°C, and thence through the heat exchanger and into the sample bottles in sequence.

In operation with diametrically opposed electrodes the FCC arc column bears directly on the carbon anode, which is completely covered by the arc crater at a current of 150 amperes or more. The pump valve is opened sufficiently to meter the plasma down through the anode hole, to purge and equilibrate the effluent hot zone in the tube furnace, and then to meter samples into the gas sampling bottles in sequence at timed rates, measuring the rise period of the vacuum gauge pressure.

Analysis of the samples was carried out by gas chromatography, using helium carrier gas and an air-hydrogen flame in a model 609 F and M Scientific Corporation flame ionization chromatograph with a Poropak Q column. A test gas mixture containing the aliphatic compounds CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 , and C_4H_8 was used to calibrate the analytical procedure.

Results

Since the early objectives of the program were primarily

exploratory, the results reported here are essentially qualitative, although within a given test series weight can be given to concentration ratios of components of a test sample mixture for purpose of comparison.

Series I. Hydrogen Flow Rate Through the FCC

This was effected by operating the arc at standard conditions of 150 amperes, maintaining the effluent hot zone at 800°C, sampling at about 30 - 60 seconds per sample, and varying the hydrogen flow rate into the FCC. Comparison of hydrocarbon composition is shown in Table 1, in terms of the relative distribution of the volume concentration of the products found. The distribution was obtained by calculating the percentage contribution which each chromatograph amplitude recording made to the sum of all, in arbitrary scale divisions. There appears to be a significant dependence of effluent hydrocarbon composition upon the amount of hydrogen fed into the FCC.

Series II. Time Factor

In this series, standard conditions of 150 amperes and 8.5 mols per minute of hydrogen were used, with varying sampling rates through the 800°C effluent hot zone. Results are tabulated in Table 2. No other hydrocarbons were observed. These data suggest that methane and acetylene are produced and disappear at different rates.

Series III. Hot Zone Temperature

In this series, standard conditions included 150 amperes, 8.5 mols H₂ per minute through the FCC, sampling rate through the effluent hot zone at 2 1/2 minutes, with variation of the hot zone temperature. Results are shown in Table 3. It is

TABLE I. RELATIVE DISTRIBUTION IN EFFLUENT
 vs. H₂ FLOW THROUGH FCC

H ₂ (MOLES/MIN.)	CH ₄	C ₂ H ₂	C ₃ H ₆
3.4	0	100	0
6	4.4	66.2	29.4
8.5	45.6	45.6	8.8
14.1	85	15	0

TABLE 2. RELATIVE DISTRIBUTION vs. SAMPLING
FLOW TIME THROUGH HOT ZONE

TIME	CH ₄	C ₂ H ₂
10 SECS	44	56
12	75.5	24.5
20	91.5	8.5
30	95.5	4.5
1-1/4 MIN.	93	7
2-1/2	100	0
4	0	0
12	0	0

TABLE 3. RELATIVE DISTRIBUTION vs. HOT ZONE
TEMPERATURE

TEMP. °C	CH ₄	C ₂ H ₂	C ₃ H ₆
800	100	0	0
500	35	65	0
400	40	60	0
200	2	87.5	10.5
25	0.5	99.5	0

evident that the hot zone temperature has a significant effect on the hydrocarbon composition of the effluent.

Series IV. Hot Zone Surface Area

Noting the result of increased time of flow in the sampling rate shown above in Series II, and assuming that 8.5 mols H₂ per minute through the FCC creates a steady state for carbon + hydrogen in the plasma at the arc crater, the sampling source, then the time of exposure to the hot zone wall of Type 304 stainless steel was observed. This was accomplished at 150 amperes, 8.5 mols H₂ per minute, and 800°C hot zone temperature, in two diameters of hot zone tubes, 1-1/6" and 9/16", -- a cross-sectional area ratio of 4:1. To equate the sample residence times, the sample flow periods were adjusted to this ratio. Results are shown in Table 4. No acetylene was found in the 9/16" diameter samples, while the small amounts in the 1-1/6" samples were consistent with the distribution for 20 and 30 seconds checked with similar times observed in the earlier Series II above.

Series V. Further Effect of Hot Zone Area

The result of Series IV was followed by further observations comparing hydrocarbon yields and ratios in two cases and at two temperatures, as follows:

- A. 1-1/16" diameter at 800° and at 500°C
- B. 1-1/16" diameter, into which tube a section of stainless steel wool was added, also at 800° and 500°C.

These conditions were compared, since any effect due to exposure to large surface of stainless steel would not require comparably rapid sampling flow. In other words, the effect of increased

TABLE 4. HYDROCARBON RATIO vs. HOT ZONE SURFACE

DIAMETERS	SAMPLING RATE (SEC)	CH ₄ RATIO
9/16, 1-1/16	80 : 20	1 : 11
	120 : 30	1 : 8

surface area alone could be observed. The hydrocarbon distribution at each temperature with and without added stainless steel wool is shown in Table 5. Table 5 indicates that the preponderance of methane and absence of acetylene is not affected at 800°C. To interpret the apparent shift, however, at 500°C, it is necessary to compare the relative concentrations of all samples. This is shown, in terms of their ratios, in Table 6. It will be noted that the effect of stainless steel hot zone is relatively constant and appreciable for the times and temperatures of exposure. At 800°C, no acetylene is present, as expected, for reasons of temperature, as shown in Table 3 above, while at 500°C, the time-related suppression of acetylene previously observed in Table 2 above is also seen to be more strongly enhanced by the increased stainless steel surface area. We interpret this to mean that acetylene disappears much more rapidly than methane under these conditions, and that the disappearance is related to the surface area of the stainless steel hot zone.

Series VI. Effect of Hot Zone Surface Composition

Noting that the time-related suppression of methane and acetylene appeared to suggest a hot zone surface effect when stainless steel was used, this material was replaced by several others, using tubes of 1-1/16" diameter. Arc crater gas samples taken under otherwise identical conditions (viz., 150 amperes, 8.5 mols H₂ per minute, hot zone temperature 800°C, parallel sampling flow rates) produced hydrocarbon compositions as shown in Figures 3 through 6.

In the case of fused silica, it is seen in Figure 3 that

TABLE 5. HYDROCARBON DISTRIBUTION vs. SURFACE AREA

SAMPLING TIME (SECS)	300 °C				500 °C			
	WITHOUT ST. ST. WOOL		WITH ST. ST. WOOL		WITHOUT ST. ST. WOOL		WITH ST. ST. WOOL	
	CH ₄	C ₂ H ₂	CH ₄	C ₂ H ₂	CH ₄	C ₂ H ₂	CH ₄	C ₂ H ₂
30	94	6	100	0	18	82	84	16
150	100	0	100	0	35	65	100	0

TABLE 6. RATIO OF HYDROCARBON CONCENTRATIONS
IN SAMPLES

SAMPLING TIME (SECS)	800 °C		500 °C	
	RATIO +/-		RATIO +/-	
	CH ₄	C ₂ H ₂	CH ₄	C ₂ H ₂
30	1/1.3	0/0	1/1.7	1/27
150	1/4	0/0	1/4.8	1/200

NOTE: + = WITH STAINLESS STEEL WOOL

- = WITHOUT STAINLESS STEEL WOOL

FIG. 3. SILICA

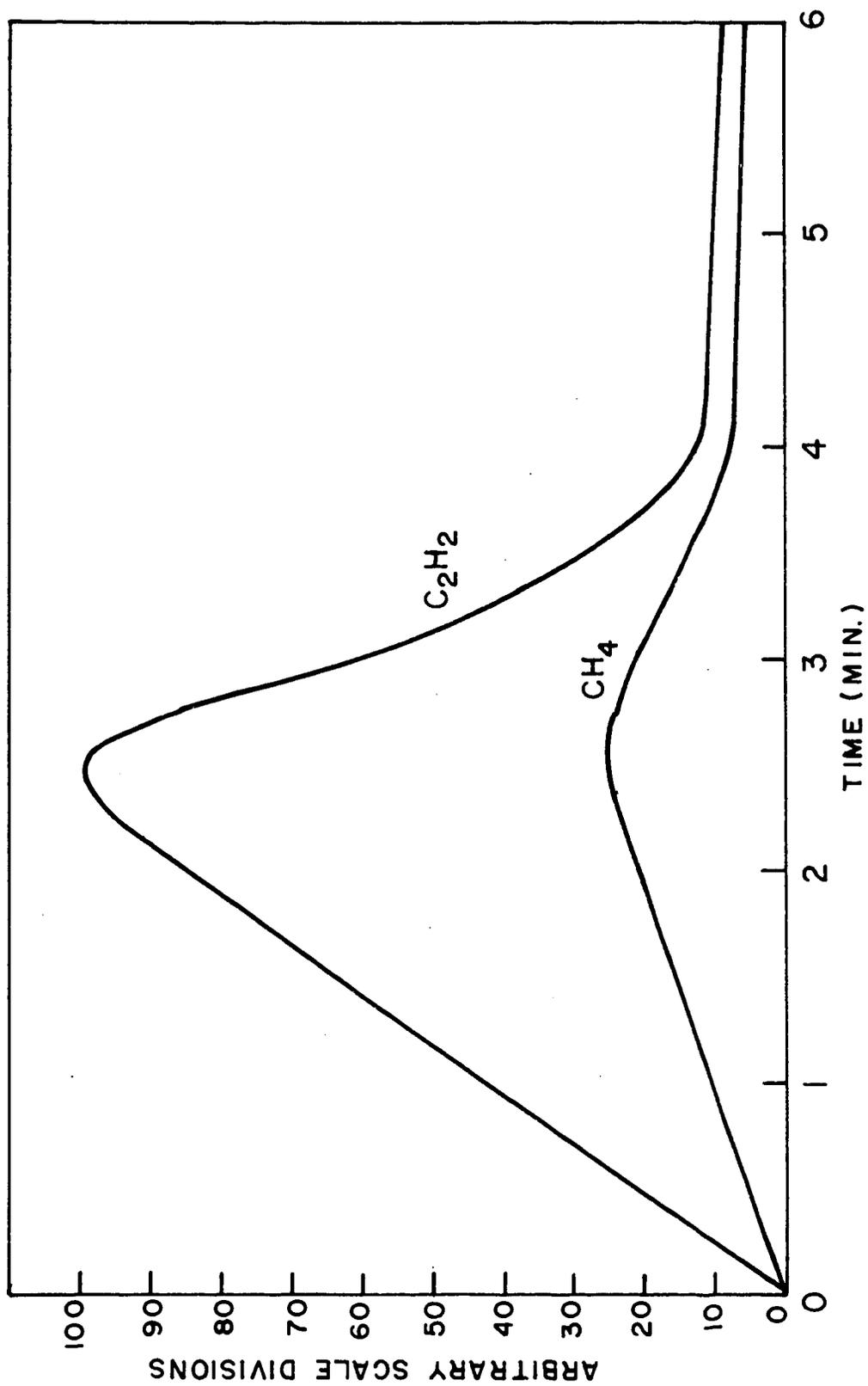


FIG. 4. IRON

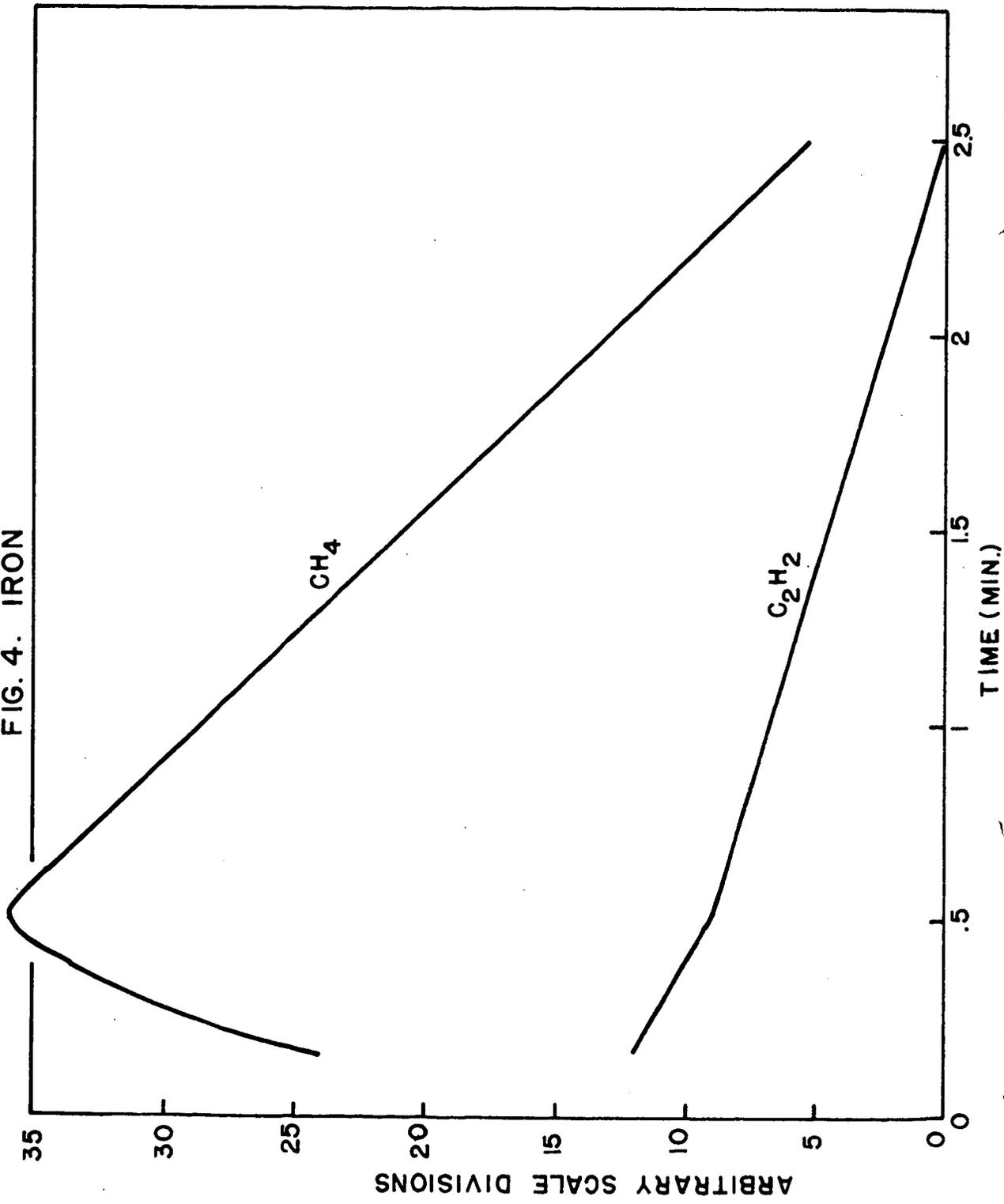


FIG. 5. STAINLESS STEEL TYPE 304 (8% NI, 74% Fe)

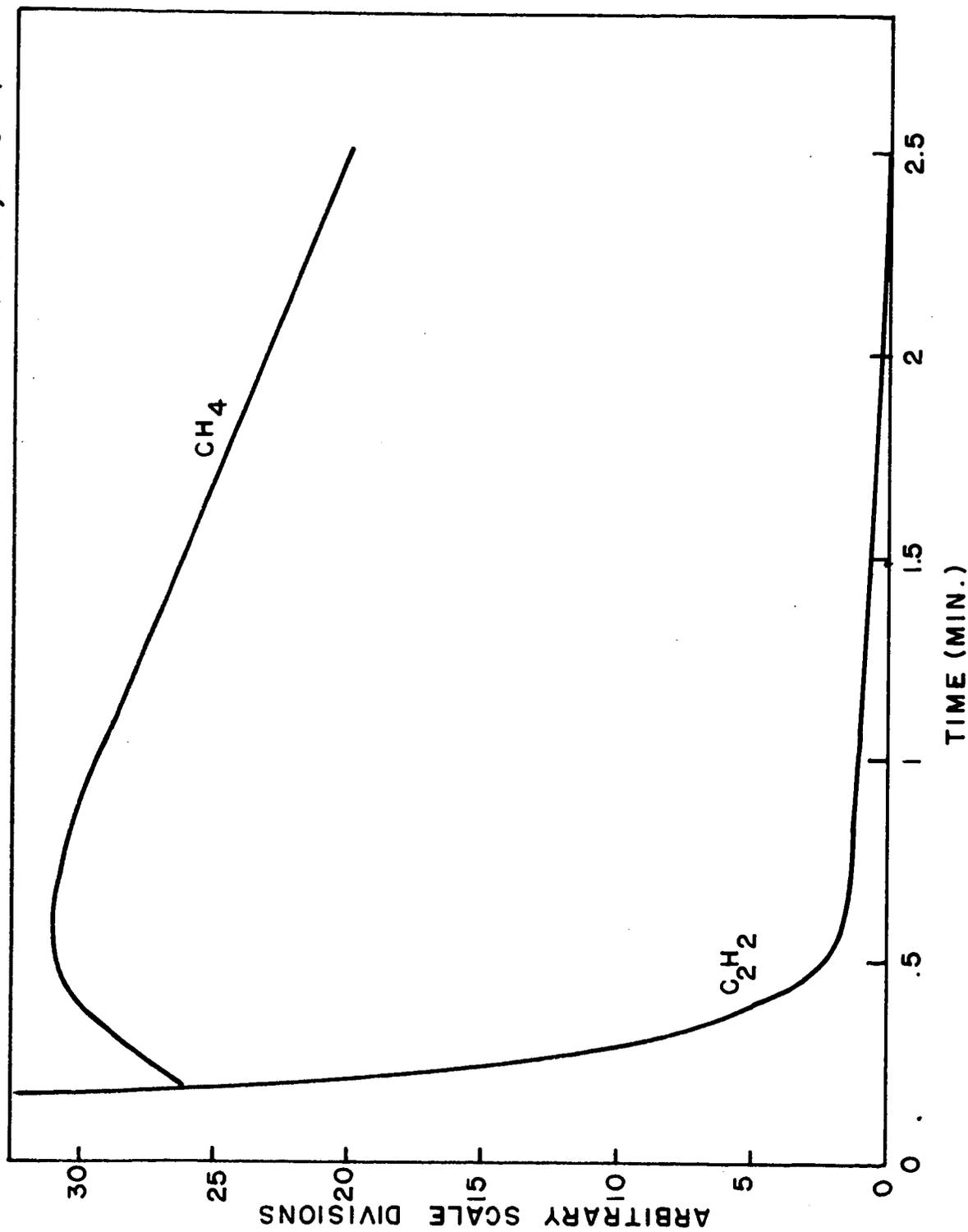
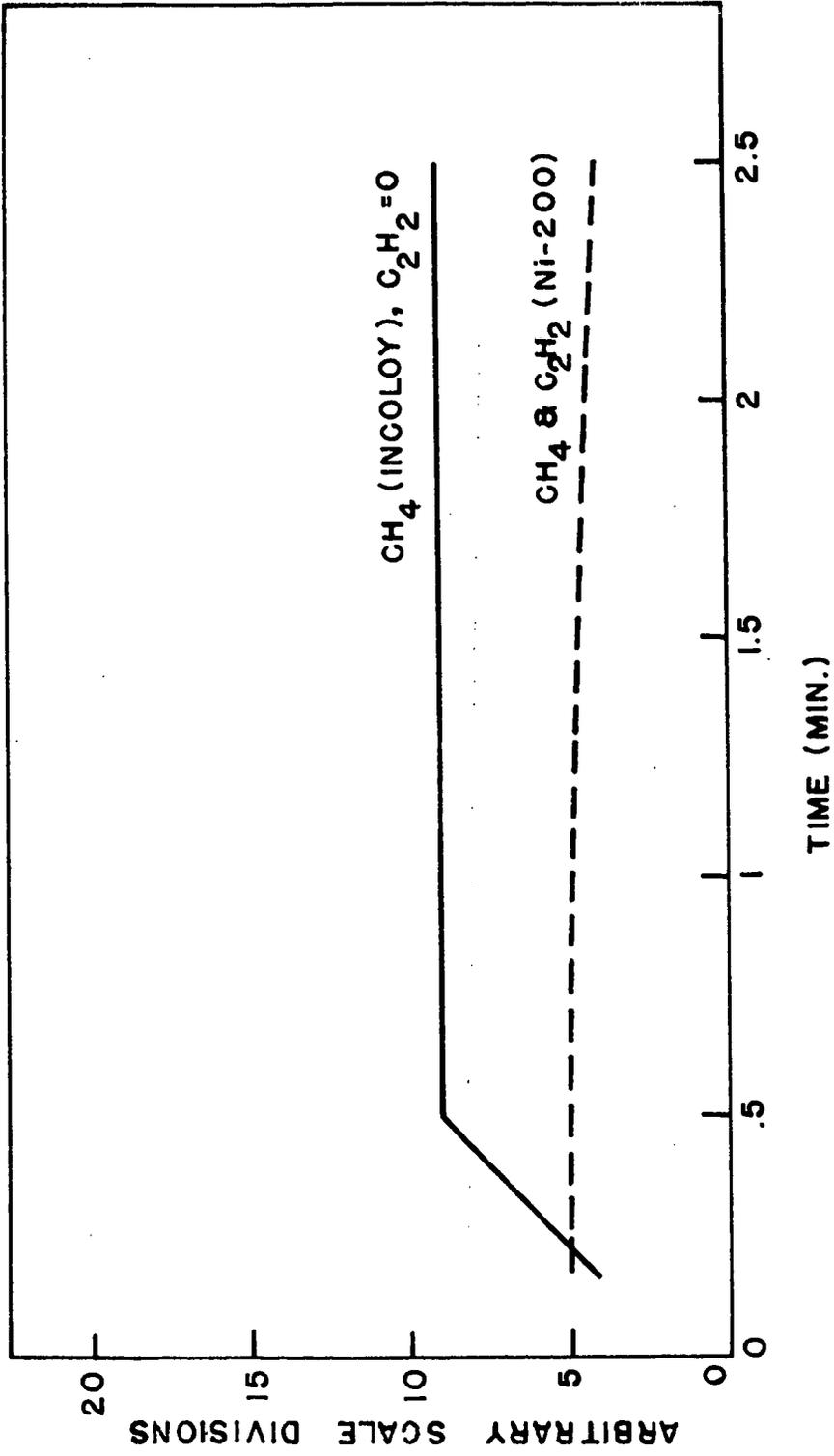


FIG. 6. INCOLOY 800(32% Ni, 46% Fe); NI-200(99.5% Ni)



the time of exposure in the 800°C hot zone has roughly parallel effects upon the presence and disappearance of both methane and acetylene.

This is in contrast with iron (Figure 4) and Type 304 stainless steel (Figure 5), where acetylene disappears rapidly while methane persists.

Increasing the nickel content by the use of Incoloy 800 (32% Ni, 46% Fe) and Nickel-200 (99.5% Ni) appears to produce further suppression of both acetylene and methane, -- an effect which does not appear to be especially time-sensitive.

Some Results with Other FCC Gas Feeds

Preliminary tests were carried out in which substitution was made for hydrogen as the FCC-injected gas. The first substitute was a H_2 - CO 50-50 volume percent mixture. The usual standard test conditions were employed, except that the gas volume flow rate was set to a value which included a relatively small amount of hydrogen (0.6 mol per minute). The results shown in Table 7 compares the (interpolated) analog distribution resulting from the same amount of pure hydrogen alone with the distribution using the mixture with CO. The absolute amount of acetylene in the CO - H_2 mixture tests also increased with time whereas the acetylene in the low rate pure hydrogen analog diminishes rapidly and no hydrocarbon was found after 10 seconds.

The next FCC gas used was steam, with corresponding results shown in Table 8. In comparing absolute concentrations by measuring chromatograph deflection amplitudes, the total product yield of hydrocarbon was found to have increased with increasing

TABLE 7. HYDROCARBON DISTRIBUTION : (CO+H₂) vs. H₂

SAMPLE TIME	(CO+H ₂)	H ₂
	CH ₄ :C ₂ H ₂ :C ₃ H ₆	
10 SECS	30 : 60 : 10	100 % C ₂ H ₂
30	40 : 60	0
2-1/2 MIN	16 : 81 : 3	0

TABLE 8. HYDROCARBON DISTRIBUTION RATIO FOR
FCC-STEAM+CARBON ANODE

STEAM GMS/MIN	CONTAINED H (GM/MIN)	SAMPLE TIME	DISTRIBUTION RATIO CH ₄ : C ₂ H ₂
2	.22	30 SEC	5 : 4
2	.22	90	3 : 5
4	.44	10	8 : 1
4	.44	30	CH ₄ ONLY
6.3	.7	10	4 : 1

flow rate of steam. As with the water gas tests, short time intervals with steam produced appreciable methane under conditions which would have yielded only a small amount of acetylene or no hydrocarbons, if the same amount of contained hydrogen were fed as pure H_2 in equivalent rates to the FCC arc.

Solid Carbonaceous Feed

Finally, preliminary tests were carried out in which a powdered solid was entrained in argon and injected into the FCC arc. The solid was a petroleum refinery "bottom" having a softening point of $327^\circ F$ and an approximate composition of $(CH_2)_x$. The argon was chosen as a neutral carrier to avoid ambiguity concerning the source of hydrogen in the product. For simplicity, no effluent hot zone was used, and so the sample gas was considered as being quenched to room temperature. As expected, in every instance the hydrocarbon product was preponderantly acetylene, although there were traces of methane also.

Discussion

Based upon the results of the tests described above, it is suggested that two distinct sets of processes are operative. One involves the phenomena within the arc and the other relates to the conditions to which arc-generated gases are exposed in the effluent stream.

Exploratory as this investigation is to this point, it affords no evidence which discloses the undoubtedly complex mechanisms underlying the observed effects. However it seems reasonable to assume that a time-related catalytic effect exists which is related to the composition and temperature of the hot

zone surface to which the arc sample effluent was exposed. The rapid transition in hydrocarbon composition from acetylene to methane in the presence of iron or stainless steel is one indication. Thermal effects and increased residence time in the presence of hydrogen were shown to lead to progressive diminution and disappearance of hydrocarbons, suggesting another slower process which may be pyrolytic or possibly inhibitory.

It is submitted, also, that effects which occur within the hot zone are not necessarily independent of the arc reactions. The composition of the effluent which leaves the arc crater and enters the hot zone has an important effect upon the ultimate product composition. For example, the contrast, under otherwise identical test conditions, which is evident as substitution was made for pure hydrogen as the FCC gas feed produced a noteworthy change. With a mixture of CO and H₂, or H combined with O as steam, hydrocarbons were produced with appreciable or major fractions of methane, where pure hydrogen yielded only small amounts of acetylene or no hydrocarbons at all. One may infer that the presence of CO or O within the plasma possibly alters the course of the reaction, and hence the effluent composition.

From our basic studies of FCC gas injection⁸ into the arc conduction column, together with concurrent temperature measurements, it is fairly certain that upwards of 80% of the injected gas penetrates the column and uniformly reaches temperatures in the range of 10,000° - 20,000°K. Our current investigations of this arc, using hydrogen as FCC gas feed and a carbon anode, indicates clearly that the hydrogen in the arc conduction

column approaching the anode is monatomic. We are presently studying the plasma composition in front of the anode crater, where this monatomic hydrogen is mixing with or impinging upon carbon at its sublimation temperature. The objective of identifying the plasma species in this zone, with hydrogen and ultimately with $H_2 + CO$ or with steam, offers the possibility of determining how the ultimate quenched effluent composition, as well as the function of the secondary species, such as CO or O, in altering the process, may be predicted.

Additionally the exposure of a carbonaceous solid into this plasma, producing acetylene in accordance with expectation, indicates in a preliminary way the probability of employing these arcs effectively for gasification involving coal or other carbonaceous feeds.

Summary

A novel type of arc discharge, the FCC high intensity arc, employing a carbon anode and a cathode designed to afford effective enhanced introduction of hydrogen-bearing gas feeds into the arc conduction column, was employed to study the synthesis of hydrocarbons. In the temperature range of this arc, -- that is, $10,000^\circ - 20,000^\circ K$ -- in the cathode conduction column, the hydrogen is monatomic and impinges on the carbon anode at its sublimation temperature (about $4000^\circ K$) in the arc crater.

Gas samples, drawn from this region during standard arc operation, were found by gas chromatography to contain hydrocarbons. The composition of these depended upon the flow rate of hydrogen fed into the arc column, the temperature and resi-

dence time of the arc effluent in a downstream hot zone, and the wall composition of the hot zone. Hydrogen, though always in excess of stoichiometry, caused a transition in the hydrocarbon product ranging from 100% acetylene, at low flow rate (3.4 mols H_2 /min) to mixtures of methane and acetylene with occasional presence of propylene, becoming predominantly methane at high flow rates (14.1 mols H_2 /min) for intermediate residence times (about 30 seconds) at 800°C in a Type 304 stainless steel hot zone. Shorter residence times (about 10 seconds) with adequate hydrogen (8.5 mols/min) at 800°C in stainless steel hot zone produced hydrocarbon mixtures which were predominantly acetylene. The effect of residence time thus also showed a transition in hydrocarbon composition from 100% acetylene at 10 seconds to 100% methane in from 30 seconds to 2-1/2 minutes.

Under the same test conditions, a similar transition was observed when the hot zone wall was iron instead of Type 304 stainless steel. When the wall was Incoloy 800 (32% Ni, 46% Fe) and Nickel-200 (99.5% Ni) both hydrocarbons were substantially suppressed regardless of residence time. With a fused silica wall, mixtures of acetylene and methane appeared in all time intervals.

In the transitional cases, acetylene diminished from the product time samples, dropping rapidly from 10 seconds and disappearing in 2-1/2 minutes, while methane rose to a maximum in 30 seconds and slowly diminished. No hydrocarbons were found after 4 minutes. With silica, both acetylene and methane

rose and diminished in parallel manner to constant low levels after 2-1/2 minutes, persisting after 6 minutes.

The effect of temperature in the hot zone was studied with the stainless steel wall at a residence time of 2-1/2 minutes. At 800°C, the only hydrocarbon produced was methane. At 25°C the product contained acetylene with a trace of methane. Intermediate temperatures produced mixtures of the two in transitional proportions.

Substitution of 50-50 volume percent mixture of CO and H₂ for pure H₂ for FCC-injection produced hydrocarbons which were mixtures of methane and acetylene (with a small amount of propylene in one 10-second sample), whereas the same fractional volume flow rate of contained hydrogen, if fed as pure hydrogen alone, would have produced only a small amount of acetylene or no hydrocarbons at all.

When steam was substituted for hydrogen into the FCC arc the principal hydrocarbon component was methane, increasing in proportion to acetylene with increasing steam flow, whereas, again, the equivalent H, if fed as pure hydrogen, would have shown a small amount of acetylene or no hydrocarbons.

A solid pulverized petroleum residue corresponding to (CH₂)_x, fed entrained in argon into the FCC, produced acetylene predictably under conditions corresponding to the analogous H₂ feed.

Two processes are believed to participate in determining the hydrocarbon composition of the effluent product. One process is thought of as interaction of the feed materials within

the arc column at the anode crater, transformed into high temperature plasma species. The resultant composition is believed to influence the course of the second process which is a time- and temperature-related catalysis occurring in a downstream hot zone, leading to the final effluent composition. Upon further exposure to the hot zone, the over-all quantity of hydrocarbons in the effluent diminishes. This is believed to be related principally to the temperature of the hot zone, as evidenced by the collateral diminution of acetylene and methane at 800°C in a fused silica hot zone. Differential transition from acetylene to methane occurred in the cases of iron and Type 304 stainless steel, and a time-independent constant suppression of both methane and acetylene was obtained when the hot zone wall at 800°C was either Incoloy 800 (32% Ni, 46% Fe) or Nickel-200 (99.5% Ni).

Preliminary tests with pulverized solid $(CH_2)_x$ entrained in argon and fed into the FCC arc, as well as the alteration in favor of methane in the steam cases, lend support to the belief that these results with the FCC high intensity arc may lead to practical applications in the gasification of coal and other carbonaceous feeds.

Acknowledgement

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References

1. Beck, H., *Elektrotech. Zeit.* 42, 1921, p. 993.
2. An informative discussion of the regions of the low intensity arc is given in The Electric Arc, by J. M. Somerville, John Wiley and Sons, N. Y., 1959, p. 5 et seq.
3. For further details on energy dissipation see "Arc Jets in Science and Technology", by Charles Sheer, Chap. 7 in Vistas in Science, ed. by D. L. Arm, Univ. of New Mexico Press, 1968 p. 140 et seq.
4. Finkelburg, W., Der Hochstromkohlebogen, Springer, Heidelberg, 1948.
5. Sheer, C. and Korman, S., "The High Intensity Arc in Process Chemistry", in Arcs in Inert Atmosphere and Vacuum, ed. by W. E. Kuhn, John Wiley and Sons, N. Y. 1956, p. 175 et seq.
6. Sheer, C., Korman, S., Stojanoff, C. G., and Tschang, P.S., Final Scientific Report, AFOSR 70-0195, Mechanics Division, Air Force Office of Scientific Research, p. 33 et seq.
7. To be published. Investigation supported by Aeromechanics Division, Air Force Office of Scientific Research.
8. To be published. Investigation supported by Aeromechanics Division, Air Force Office of Scientific Research.
9. Emmons, H. W., "Recent Developments in Plasma Heat Transfer", in "Modern Developments in Heat Transfer", Warren Ibele, ed., Academic Press, New York, 1963, p. 465 et seq.