

# CATALYTIC COAL GASIFICATION-PART I: MECHANISM OF THE REACTION OF CO<sub>2</sub> WITH CHAR

By

AMIR ATTAR AND DANIEL C. BAKER  
Department of Chemical Engineering  
University of Houston  
Houston, Texas 77004  
December 1979

Catalytic coal gasification (CCG) can provide a competitive source of gas for domestic and industrial uses, consequently, CCG has been the subject of numerous studies. However, the mechanism of CCG, with catalysts like potassium carbonate is not clear, since no simple mechanism is known by which a solid can catalyze the rate of reaction of another solid.

Taylor and Neville (1921) reviewed the older literature on CCG and presented some rate data. More recently, Johnson (1976) and Cusumano et al. (1978) reviewed some of the modern literature on CCG. The thermodynamics and kinetics of gasification reactions were reviewed by von Fredersdorff and Elliot (1963).

Haynes et al. (1974) screened various materials as catalysts for coal gasification. They confirmed that alkali carbonates, like K<sub>2</sub>CO<sub>3</sub> are very effective catalysts for coal gasification. Wilson et al. (1974) examined the effect of mixing nickel with alkali carbonates on the rate of gasification. They too found that alkali carbonates enhance the rate of gasification. Wilson et al. (1974) found that nickel that was added to the char, enhanced predominantly the methanation reaction of the gasification products, CO and H<sub>2</sub>. Chauhan et al. (1977) examined the effect of incorporation of calcium and sodium on the rate of coal gasification. They also examined the effect of the particle size and the impregnation period of the coal on its rate of gasification. They found that small particles are consumed at faster rates than large particles and that the rate of gasification levels off after a given fraction of the coal has been gasified. Wilks et al. (1975) compared the time needed to gasify 90% of one char and two coals using various catalysts. They observed that impregnation of the coal with the catalyst is much more effective than adding the catalyst to the coal. The methane yield was the same whether a catalyst was added to the coal or not. Addition of 30% CO to steam suppressed the rate of gasification. A major study of various gasification catalysts and the rate of gasification has been conducted by Exxon Research and Engineering. Recently Nahas and Gallagher (1978) published data on the rate of CCG using K<sub>2</sub>CO<sub>3</sub> and Vadovic and Eakman (1978) published a model for the rate of CCG. Tomita et al. (1977) added five minerals to coal and examined their effect on the rate of gasification. The results of Tomita et al. (1977) confirmed that all common minerals enhance to a limited extent the rate of coal gasification.

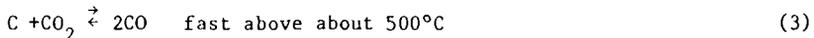
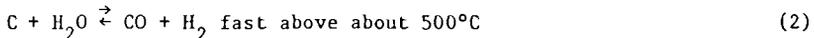
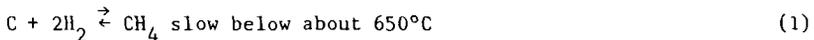
Since no simple mechanism is known by which one can explain the catalytic effect of one solid on the rate of reaction of another solid with a gas, we attempted to examine the mechanisms and rates of catalytic char gasification with different gases. Five possible rate enhancement modes were considered for the catalytic system char-K<sub>2</sub>CO<sub>3</sub>:

1. Catalysis by the chemical interaction of K<sub>2</sub>CO<sub>3</sub> with oxygen functional groups in the char, and generation of more active sites.

2. Catalysis by generating a dipole due to electrical charges on the surface of the  $K_2CO_3$ .
3. Catalysis by the chemical interaction of  $K_2CO_3$  with the gases, to yield more reactive gaseous species.
4. Catalysis by interference of the  $K_2CO_3$  with the temperature field associated with the reacting char particle.
5. Catalysis by interference of the  $K_2CO_3$  with the rate of adsorption of gases onto the char.

Mechanisms (1) and (3) attribute the catalytic effect to changes in the chemistry of the reaction, while mechanisms (2), (4), and (5) suggest physical effects as an explanation to the catalytic activity of  $K_2CO_3$ . Since  $K_2CO_3$  enhances the rate of reactions of char with chemically different gases, e.g.  $CO_2$ ,  $H_2O$  and  $H_2$ , one may expect the mechanisms of the catalysis to be insensitive to the nature of the gas. This observation tends to support catalytic mechanisms which rely more on changes in the physics of the reaction system. However, as will be demonstrated, the most likely catalytic effect relies on a synergist interaction between the chemistry and the physics of the catalytic system  $K_2CO_3$ -char.

The main reactions which are associated with char gasification are:



Two additional reactions which take place in a gasifier are the shift reaction:



and the methanation of carbon monoxide:



Figure 1 shows the Gibbs free energy (GFE), of the reactions vs. the temperature. The carbon used was graphite. Since the equilibrium constant,  $K$ , is related to the GFE by:

$$\Delta G^\circ = -RT \ln k \quad (6)$$

it is obvious that gasification can proceed to  $CH_4$  according to reaction 1 only at temperatures below about  $838^\circ K$  or  $565^\circ C$ . Reactions (2) and (3) can gasify graphite only at temperatures above  $926^\circ K$  ( $653^\circ C$ ) and  $947^\circ K$  ( $674^\circ C$ ) respectively. None of these three chemical reactions can be used to gasify graphite to any appreciable extent in the temperature range  $565$ - $653^\circ C$ ! While the rate of char gasification is expected to be different than that of graphite, the overall qualitative behavior may be similar.

### Experimental

Figure 2 shows a schematic diagram of the experimental system. The system consists of five major parts:

1. A reactor
2. A gas chromatograph for gas analysis
3. A microprocessor-controlled pulse injector
4. A temperature monitor and programmer
5. A recorder and an interator.

Two types of reactors were used:

- A. A microreactor with an optic fiber in it, which allowed examination of light emission from the surface of the sample (Figure 3).
- B. A fixed-bed reactor, packed with char or treated char.

The system allows us to conduct isothermal and temperature-programmed tests, in addition to runs at different pressures. The operational range of temperature was 25-900°C and of pressures 0.1-0.5 MPa. The system allows the injection of pulses of gas of variable sizes between 0.517 cm<sup>3</sup> and 10 cm<sup>3</sup>. The range of temperature programming is 0-20°C/min. More detailed description of the system was published by Attar and Dupuis (1979).

During each run, a continuous stream of an inert gas was flowing through the reactor; as appropriate, a pulse of the reactive gas was injected into the reactor and gaseous products were obtained. The concentrations of CO, CO<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub> were determined using a thermal conductivity detector and a microprocessor-controlled integrator. Carbon monoxide and carbon dioxide were separated on a 200 cm x 0.3 cm column packed with 60-80 mesh Chromosorb<sup>R</sup> 105 at 65°C and with a nominal flowrate of 25 ml/min helium as a carrier gas. Methane and hydrogen were separated on a 200 cm x 0.3 cm column packed with 60-80 mesh molecular sieves 5 A at 80°C and with a nominal flowrate of 25 ml/min nitrogen as carrier.

A fixed sample of solid was placed in the reactor into which two thermocouples and an optic fiber were inserted. The radiation intensity coming from the reactor through the optic fiber was determined using a photomultiplier and an amplifier. The reactor internal temperature and a signal corresponding to the radiation intensity in the wavelength range of 200-750 nm were recorded vs. time. The photomultiplier produced a monotonically increasing signal relative to the radiation intensity which impinged on the optic fiber.

The fixed bed reactor consisted of 8 mm OD SS 316 tube packed with a known quantity of sample with a known particle size. Typically 30 cm length of tube were adequate.

Two types of analysis were done on the products of each pulse of reactive gas: analysis of the distribution of products by first separating them on a GC column, and analysis of the shape of the pulse of products as determined using a TC detector at the end of the fixed bed reactor.

The char was prepared from the 1.4 gm/cm<sup>3</sup> float fraction of Kentucky #9 coal. The coal was pyrolyzed at 806°C for 10 sec. The char was impregnated with solutions of the various catalysts and dried in vacuum at 70°C for 12 hours. Unless stated otherwise, the char particles used were smaller than 44 microns.

"Demineralization" of the char was done in a mixture of 2 vol. of concentrated HCl and 3 vol. water for 30 min at 40°C.

Silylation of the char was done by a 3:3:6 mixture of hexamethyldisilazane: trimethyl-chloro-silane in dry pyridine at 40°C for 30 min 10 ml of solution were used for each 5 gm char. The excess reagent was washed successively with pyridine and dry methanol and dried in vacuum oven for 12 hrs at 70°C.

When char reacts with CO<sub>2</sub>



two molecules of CO are obtained for each molecule of CO<sub>2</sub> which reacts. Therefore, the reliability of the experimental measurement can be checked by the closure of the material balance on the oxygen. Figure 4 shows the combined measured amounts of CO and CO<sub>2</sub> for pulses of fixed size which were injected at different reactor temperatures. The data show that the precision is excellent both in the case of graphite and char. The dimensionless standard deviations on the closure of the material balance on the oxygen are 1.1 and 2.6% respectively for the temperature range of 200-700°C. In this range of temperatures the rates of CO<sub>2</sub> to CO varied over several orders of magnitude. Larger error was obtained when slow desorption occurred, due to inconsistencies in the integration procedure of the GC peaks. However, in general, it was possible to close material balance on each pulse with 5% or better.

### Preliminary Results and Discussion

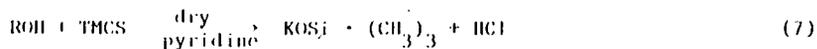
An attempt was made to screen the various possible mechanisms relative to their influence on the rate of the gasification. The results of experiments that were conducted in order to prove or disprove each mechanism are presented and discussed individually.

#### Mechanism 1. Catalysis by increased site activity.

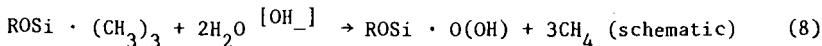
Although char is predominantly carbon, it has some oxygen and hydrogen. Part of the oxygen is present as adsorbed O<sub>2</sub>, CO<sub>2</sub> and CO, however it is believed that some is bound as surface -OH and -COOH groups. Impregnation of char with K<sub>2</sub>CO<sub>3</sub> using an aqueous solution produces much more active char than just adding K<sub>2</sub>CO<sub>3</sub> (Wilks et al. 1975). This suggested that K<sup>+</sup> may replace the H<sup>+</sup> on the surface oxygen functions and thus produces more active surface dipole charges which adsorb gases like CO<sub>2</sub> more actively.

#### Test of Mechanism 1.

Many compounds are known which react selectively with oxygen functional groups. For example, a mixture of trimethyl-chloro-silane (TMCS) and hexamethyldisilazane (HMDS) reactions with OH groups as follows (Friedman et al. (1961)):



such a reaction blocks the oxygen site and makes it unavailable for exchange with K<sup>+</sup>. Alkaline hydrolysis of the silicone compound yields inorganic silicates with OH groups NOT attached to the carbon.



Samples of char were silylated according to reaction (7) and then impregnated with  $\text{K}_2\text{CO}_3$ . The rate of gasification with  $\text{CO}_2$  of the silylated samples was slightly smaller than the rate of gasification of the non-silylated samples. Therefore, it was concluded that chemical interaction of K with the oxygen functions is not the dominant catalytic mechanism.

#### Mechanism 2. Catalysis by solid-solid polarization.

Potassium carbonate, like many other salts, has negative surface charges. Since char is a good conductor, an electric dipole is created when  $\text{K}_2\text{CO}_3$  touches char. It has been presumed that more active sites of high activity may be generated by such a contact.

#### Test of Mechanism 2.

If the catalytic activity of  $\text{K}_2\text{CO}_3$  was due to the dipolarization, one would expect every material with negative surface charges to have a similar catalytic effect to  $\text{K}_2\text{CO}_3$ . Since this is not observed experimentally it must be concluded that solid-solid dipolarization is not the dominant catalytic mechanism.

#### Mechanism 3. Catalysis by interaction between the $\text{K}_2\text{CO}_3$ and the gas which forms more reactive species.

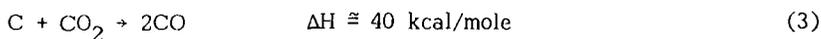
It has been postulated that  $\text{K}_2\text{CO}_3$  may interact with the gaseous molecules to form more reactive ones, which subsequently react with the char.

#### Test of Mechanism 3.

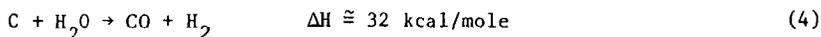
Potassium carbonate was found to catalyze the rate of reaction of char with many chemically and physically different gases. No products of binary interactions of activated species were found and it seems highly unplausible that the same solid will catalyze the formation of activated species from many different gases. Therefore, mechanism three has to be ruled out also. Additional data on this aspect were discussed by Thomas (1965).

#### Mechanism 4. Catalysis by the interaction of $\text{K}_2\text{CO}_3$ with the temperature field.

In ordinary gasification reactors the "reactor temperature" is measured and it is supposed that this temperature represents the reaction temperature. A catalytic effect is noted when higher rates of gasification of the solid are observed at the same MEASURED temperature. For the endothermic gasification reactions



and



heat has to be supplied to the char particle in order to maintain its gasification. If the rate of gasification is limited by the rate of heat transport, the temperature of the char,  $T_p$ , will be lower than the gas temperature,  $T_g$  or possibly the measured<sup>p</sup> temperature,  $T_m$ . If  $K_2CO_3$  impregnation enhances the rate of heat transport to the char, e.g. by absorbing more heat as radiation, one may conceive that conditions can exist, for which:

$$T_p < T_c < T_m \quad (9)$$

The temperature of the char particles with catalyst,  $T_c$ , may effectively be larger than the temperature of the char with no catalyst, AT THE SAME MEASURED TEMPERATURE. This phenomenon will be recognized as "catalysis" since the rate of gasification is an increasing function of the temperature. The ratio of the rate of reaction of a particle with catalyst to that without one,  $r$ , will be approximately

$$r \cong \exp - \frac{E}{R} \left( \frac{1}{T_c} - \frac{1}{T_p} \right) > 1 \quad (11)$$

#### Text of Mechanism 4.

Three tests were done to examine this mechanism:

- A. The total radiation intensity in the reactor was measured using an optic fiber which was inserted into the char.
- B. Pulses of  $CO_2$  were injected into the reactor and the concentrations of  $CO_2$  and  $CO$  were determined in the products. The approach function,  $\phi_a$ , which measures how close the concentration of the gases approach equilibrium was plotted vs. the measured temperature,  $T_m$

$$\phi_a = Y_{CO}^2 P/Y_{CO2} \quad (12)$$

- C. Calculations were made to estimate the possible effect of the rate of heat transport by radiation on the particle temperature.

Figure 5 shows the radiation emitted from chars treated by various reagents vs. the measured temperature. The data shows that at the same measured temperature samples of char impregnated with more active catalysts emit less radiation than samples of char treated with less reactive catalysts. Based on this observation, it is tempting to assume that the effect of the  $K_2CO_3$  is to enhance the rate of absorption of energy as radiation. Consequently, one would assume that the temperature of the  $K_2CO_3$ -treated char is larger than the temperature of the untreated char, at the same measured temperature. Since the reaction with  $CO_2$  is endothermic, one must maintain that  $T_p < T_c < T_m$ .

Figure 6 shows the logarithm of the approach plotted vs.  $10^3/T$  for graphite, untreated char and treated chars. The data show that larger approach is observed in the case of  $K_2CO_3$ -treated char than that which corresponds to graphite char, and to chars treated with  $Ca(OH)_2$  and  $Na_2CO_3$ , all at the same reactor temperature.

Thermodynamics limits the value of the approach which can be obtained to the equilibrium value AT THE SAME TEMPERATURE. To explain the data, one must assume that either the char temperature is larger than the measured temperature, or that char has much larger activity than graphite and that equilibrium values derived based on graphite can not be applied to char. The char temperature can not be larger than the gas temperature because the gasification reaction is endothermic.

Two questions are addressed:

- A. Under which circumstances the rate of heat transport may limit the rate of gasification by the endothermic reactions (2) and (3), and
- B. Can the effect of heat transport by radiation be of sufficient magnitude to influence the temperature of the particle?

The answer to both problems is obtained using a simple steady-state energy balance on a coal particle.

$$\begin{aligned}
 &\text{Rate of heat transport} && \text{Rate of heat transport} \\
 &\text{by conduction +} && \text{by radiation} \\
 &\text{convection} && \\
 & && + \\
 &= && \text{Rate of absorption of heat} && (13) \\
 & && \text{by the reaction}
 \end{aligned}$$

The complete mathematical analysis has been submitted for publication, the analysis shows that for particles of about  $100 \mu$  an increase in the rate of gasification by a factor of 1000-3000 will result in the rate of heat transfer limiting the rate of gasification. Heat transfer by radiation contributes 1-10% of the convection term near  $700^\circ C$ .

#### Mechanism 5. Catalysis by absorbing gas and retaining it near the surface of the char

Gas can be absorbed in a thin layer of coating present on the surface of solid supports. Thus, the system gas-solid will have a more "concentrated" gas-support interaction.

It is conceivable that if  $K_2CO_3$  can dissolve  $CO_2$ ,  $H_2O$  and  $H_2$ , then  $K_2CO_3$  treatment of the char may result in larger surface concentrations of these gases and therefore in larger rates of gasification.

#### Test of Mechanism 5.

Packed beds of char with  $K_2CO_3$  and without  $K_2CO_3$  were prepared as described in the experimental section and used in the reactor. Pulses of gases were injected into the reactor and the pulses of products were analyzed. The conversion of each pulse, its shape and its retention in the

reactor were used to infer on the mechanism of the catalysis. The main conclusions from these tests are:

- A. The pulses of gas are retained for a longer time in a reactor with treated-char relative to reactor with untreated char.
- B. The shape of the pulses which came out of a reactor with treated char suggests that the gas desorbes from the  $K_2CO_3$ -treated char much slower than from the surface of untreated char. Figure 7 shows the forms of pulses of  $CO_2$  injected to packed-bed reactors with char and with  $K_2CO_3$ -treated char at  $650^\circ C$ . The pulses coming out of the reactor with the  $K_2CO_3$ -treated char are flat and tailing. It takes as long as 10-20 minutes to completely desorb the pulse out. Figure 8 shows the shape of hydrogen pulses injected to the differential reactor at  $700^\circ C$ . Again, it is obvious that the residence time of  $H_2$  on  $K_2CO_3$ -treated char is substantially longer than that on untreated char. Figure 9 shows the output signals from the gas chromatograph, when equal pulses of  $CO_2$  were injected to columns packed with char and with  $K_2CO_3$ -treated char. The figure demonstrates three points: 1. more of the  $CO_2$  is converted to CO when columns packed with  $K_2CO_3$ -treated char are used. 2. the  $CO_2$  and the CO are retained on the  $K_2CO_3$ -treated char longer time than on the untreated char. 3. the pulses coming out of the  $K_2CO_3$ -treated char are tailing. These observations are consistent with mechanism five. The data show clearly that pulse of  $CO_2$  stay in the reactor longer time when the reactor contains  $K_2CO_3$ -treated char, relative to when it contains untreated char. Silylation of char slightly reduces the residence time of pulses of  $CO_2$  and the activity of the char. Treatment of silylated char with  $K_2CO_3$  increases the activity of the char beyond that of untreated char, but not quite to the level of unsilylated char treated with  $K_2CO_3$ . Taylor and Neville (1921) observed that better catalysts absorb more  $CO_2$  than poorer catalysts. However, they attributed the catalytic effect to the formation of surface carbon-oxygen complexes. Had surface complexes been formed, one would expect exchange of carbon from the gaseous carbon dioxide and the solid char. However, Yergey and Lampe (1974), who did tracer experiments using  $C^{13}$  on the gasification of char with  $C^{13}O_2$ , found that  $C^{13}O$  and  $C^{12}O$  evolve from the char simultaneously and at equal rates. These observations tend to support gasification mechanisms which do not permit exchange of carbon between the gas and the solid, or the formation of chemical bonds due to carbon-oxygen complexes.

#### Acknowledgement:

The authors wish to thank Dow Chemical Co. and Texas Energy Advisory Council for their generous support of this work.

#### References

1. Attar, A. and Dupuis, F., *Ind. Eng. Chem., Proc. Des. and Dev.*, **18**, 607-618 (1979).
2. Attar, A. and Robinson, R., submitted for publication.

3. Ayling, A. B., and Smith, I. W., *Combust. and Flame.*, 18, 173-184 (1972).
4. Chauhan, S. P., Feldman, H. F., Stambaugh, E. P., and Oxley, J. H., *Prep. Div. Fuel Chem., ACS*, 22 (1) 38-52 (1977).
5. Cusumano, J. A., Dalla Betta, R. A., and Levy, R. B., *Acad. Press.*, N.Y. 1978, Chapt. 10, p. 233.
6. Friedman, S., Kaufman, M. L., Steiner, W. A., and Wender, I., *Fuel* 40, 33-46 (1961).
7. Gardner, N., Samuels, E., and Wilks, K., P. 217-237 ("Coal Gasification", *Adv. in Chem., Ser. 131, ACS, Washington* (1974)).
8. Haynes, W. P., Gasior, S. J., and Forney, A. J., p. 179-203, "Coal Gasification", *Adv. in Chem., Ser. 131, ACS, Washington* (1974).
9. Hill, F. B., and Wilhelm, R. H., *AIChE J.*, 5 (41), 486-496 (1959).
10. Johnson, J. L., *Catal. Rev. Sci. Eng.*, 14 (1), 131-152 (1976).
11. Nahas, N. C. and Gallagher, J. E., Jr., paper presented in the 19th Intersociety Energy Conversion Engineering Conference, Aug. 1978, San Diego, California.
12. Taylor, H. S. and Neville, H. A., *J. Am. Chem. Soc.*, 43, 2055 (1921).
13. Thomas, J. M., p. 122-203 in "Chemistry and Physics of Carbon", Vol. 1, Walker, P. L., Jr., (ed), Marcel Dekker, N. Y. (1965).
14. Tomita, A., Mahajan, O. P., and Walker, P. L. Jr., *Prep. Div. Fuel Chem. ACS*, 22 (1), 4-6 (1977).
15. Vadovic, C. J., and Eakman, J. M., *Prep. Div. Fuel Chem., ACS*, 23 (1978).
16. Von Fredersdorff and Elliot, M. A., Chap. 20 p. 892-1022, in "Chemistry of Coal Utilization", Lowry H. H. (ed) *Suppl. vol.*, Wiley, H. Y. (1963).
17. Wilks, K. A., Gardner, N. C., and Angus, J. C., *Prep. Div. Fuel Chem., ACS*, 20 (3), 52-60 (1975).
18. Wilson, W. G., Sealock, L. J., Jr., Hoodmaker, F. C., Hoffman, R. W., Stinson, D. L., and Cox, J. L., p. 203-217 in "Coal Gasification", *Adv. in Chem., Ser. 131, ACS, Washington* (1974)
19. Yergey, A. L., and Lampe, F. W., *Fuel* 93, 280-281 (1974).

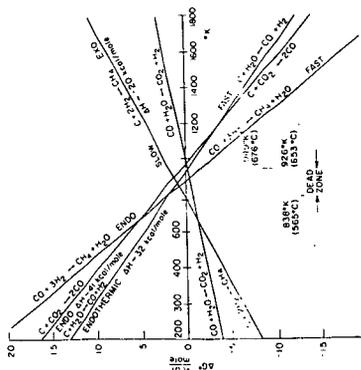


Fig. 1. Gibbs free energy of the main gasification reactions.

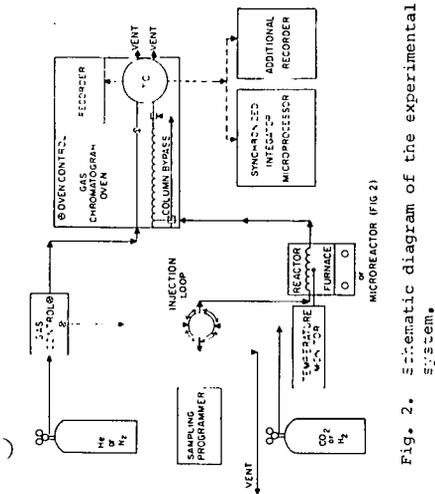


Fig. 2. Schematic diagram of the experimental system.

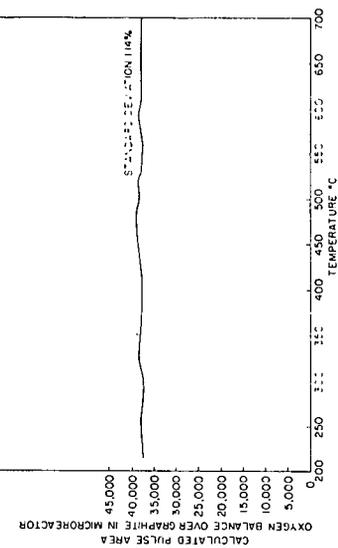


Fig. 4. Examination of the consistency of the results: closure of oxygen material balance.

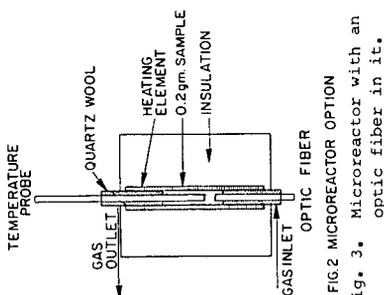


FIG. 3. MICROREACTOR OPTION

Fig. 3. Microreactor with an optic fiber in it.

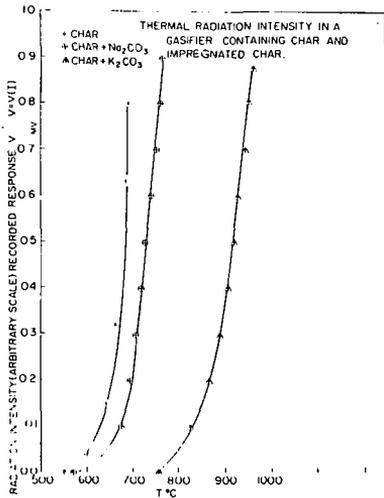


Fig. 5. The variation of the emission of light from the surface of char treated by various catalysis.

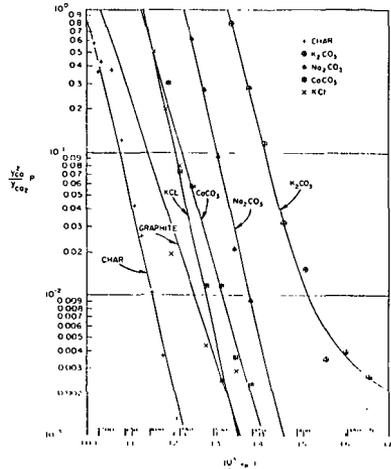


Fig. 6. The approach functions  $PY^2_{CO}/Y_{CO_2}$  plotted vs.  $10^3/T$  for chars treated by various catalysis.

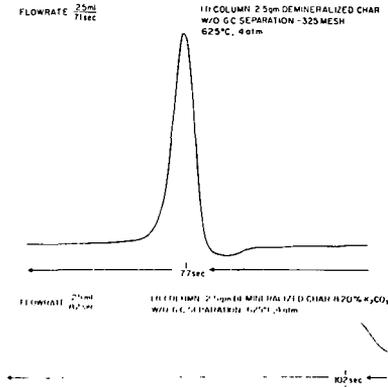


Fig. 7. The shape of pulses of  $CO_2$  at the outlet of the packed bed reactor.

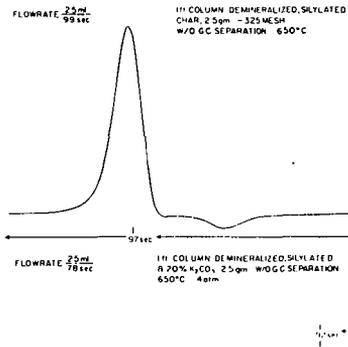
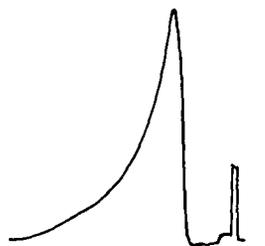


Fig. 8. The shape of pulses of  $CO_2$  at the outlet of the packed bed.

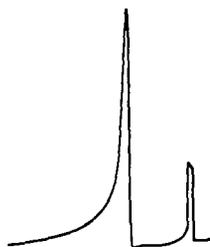
## H<sub>2</sub> STUDY IN MICROREACTOR

0.2 gm. DEMINERALIZED  
CHAR & 20% K<sub>2</sub>CO<sub>3</sub>  
700°C, 2.5 atm.



SENSITIVITY INCREASED  
BY A FACTOR OF 6  
A = 39,000

0.2 gm. DEMINERALIZED  
CHAR 700°C, 2.5 atm.



A = 40,000

Fig. 9. The shape of pulses of H<sub>2</sub> at the outlet of the microreactor.

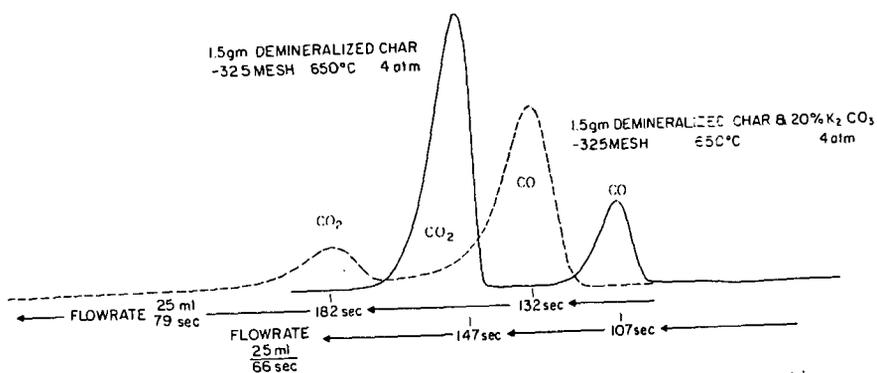


Fig. 10. Pulses of CO<sub>2</sub> from char and K<sub>2</sub>CO<sub>3</sub>-treated char after separation on the GC.