ROLE OF THE C--CO SUB 2 REACTION IN GASIFICATION OF COAL AND CHAR

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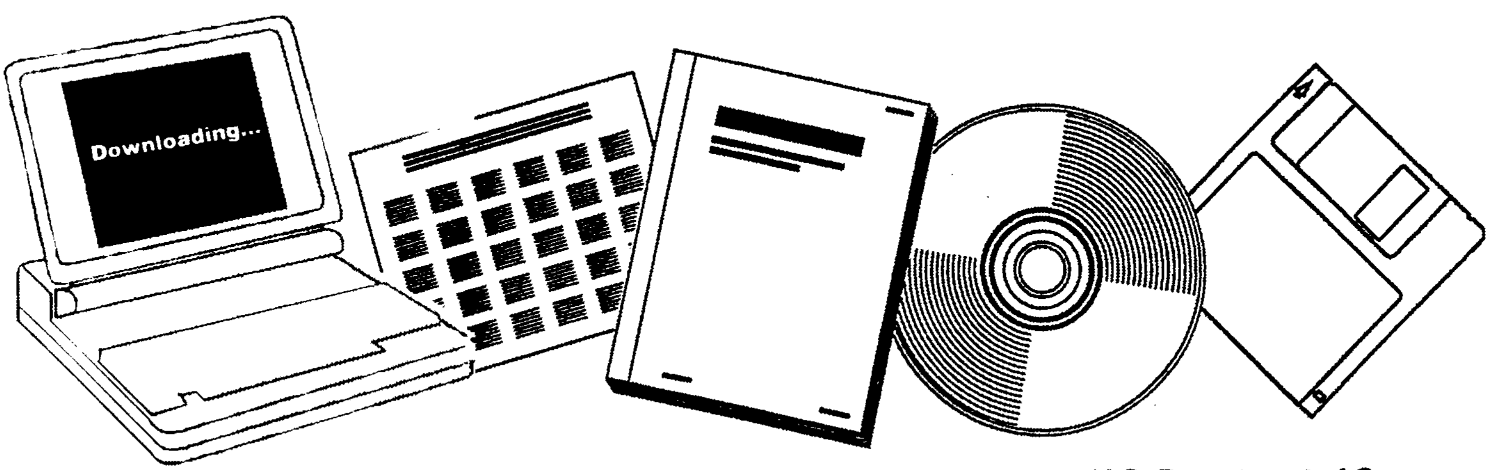

The Role of the C-CO_2 Reaction in Gasification of Coal and Char

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ABSTRACT

The initial reactivity of char with CO_2 was correlated with char composition by the equation:

$$\frac{1}{W}\frac{dW}{dt}\left(\frac{gm}{gm\ hr}\right) = 0.164\ \frac{g}{g\,hr} + 0.072\ \{CaO\} + 0.479\ \{CaO\} \cdot \{O_2\}$$

where $\frac{dW}{dt}$ is the change in weight of the char, and CaO and O_2 are weight per cent. (T = 900°C)

The pyrolysis technique employed to obtain the char can change the oxygen content by a factor of 2, in going from pyrolysis at 900°C (2 min.) to pyrolysis at 1000°C (30 min.). The surface area also changes. It appears that the "available" surface area does affect the rate. Reactivity changes with char conversion were roughly proportional to changes in surface area (by CO_2 adsorption technique). In fluidization of a sand/char system, the elutriation rate constant for the char was up to an order of magnitude larger than values calculated from literature correlations.

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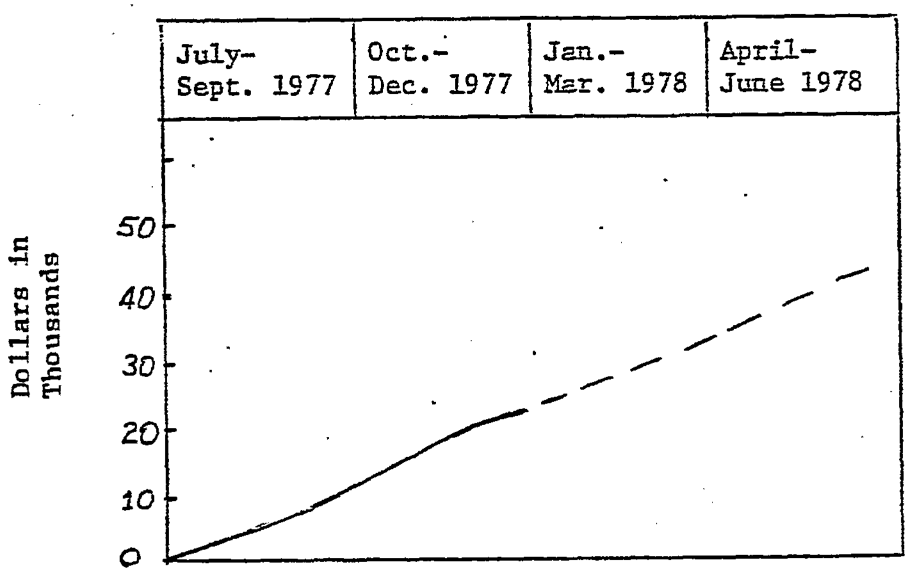
SUMMARY OF PROGRESS

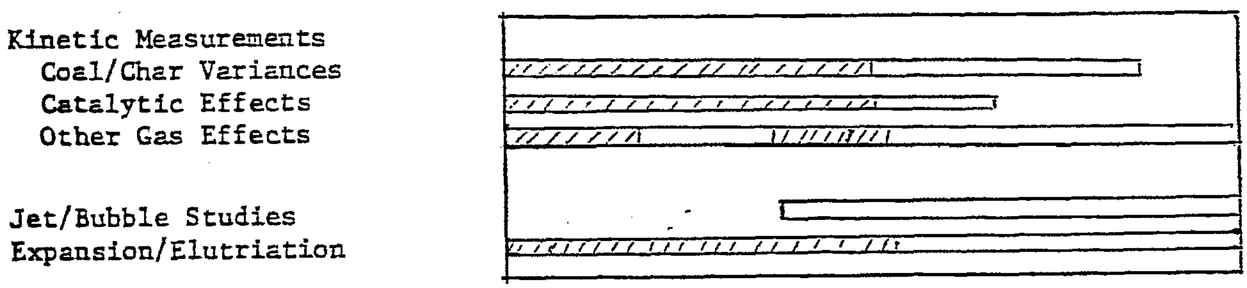
Below is a visual summary of the expended effort and costs on the extension EF-76-C-01-0497.

Cost and Performance Chart: The Role of the C-CO_2 Reaction in Gasification

Costs:



Goals:



Accomplished

Scheduled

General:

The relation between char reactivity with CO_2 and composition has been statistically correlated. Differences in char reactivity due to char preparation method can be mostly explained by changes in char oxygen and surface area due to the different methods. The change in char reactivity with conversion follows the change in surface area.

The fluidization of inert/char at 1 atom appears somewhat similar to other solid particle systems.

Work Accomplished:

A series of 15 experiments on reactivity of various chars were run. The calcium (as calcium oxide) and oxygen (by difference) were determined for each of the chars. The chars were prepared by pyrolysis for 2 minutes in carbon dioxide by a furnace heating a small sample to 900°C, followed immediately by reaction. A correlation of reactivity with these two composition variables was statisically obtained:

$$(1)\quad \frac{1}{W}\frac{dW}{dt}\ \left(\frac{mg}{mg\,hr}\right) = 0.1636 + 0.072\ (\%CaO) + 0.479\ (\%CaO)(\%O)$$

where the % CaO and %O are wieght per cents of these materials in the char.

This equation fit the data within a 0.96 correlation coefficient. It had previously been determined that iron and magnesium were non-important as catalysts, while sodium and potassium are effective catalysts but were in small concentrations and their contribution was minimal. This correlation has an implicit assumption of constant effect from pore size distribution/surface area.

The method of pyrolysis has a significant effect on the amount of oxygen and surface area, as measured by CO_2 adsorption techniques. Table I shows the char surface area and amounts of oxygen in the char.

Table I

Differences in Char Properties from Pyrolysis at 900 C and 1000 C

Type Coal	Pyrolysis	Oxygen in Char (Wt.%)	Surface Area (CO_2 Gas, m^2/gm)
Lignite	@ 900°C (2 min.)	2.8	220
	@ 1000°C (30 min.)	1.43	137
Pittsburgh (#7)	@ 900°C (2 min.)	1.07	
	@ 1000°C (30 min.)	0.50	

TABLE II

COMPARISON OF REACTIVITY DATA OF CARBON - CO_2 REACTIONS

T = 900°C

P = 1atm

Char Type	Investigators	Experimental Rate corrected Mg/mg hr Old	New	Rate Predicted from correlation(1) $R=I + aCaO + b[CaO]\cdot[O_2]$ mg/mg-hr	Comments
Lignite, Montana	Walker et al(3)	5.25	9.45	8.1	The chars were prepared at 1000°C for 30 minutes in N_2 atmosphere. The oxygen content obtained from the coal con was corrected to 50% of its original value, (2) and substituted in the correlation. The original data was for -40+100 mesh. Therefore the reactivity (experimental) was multiplied by a factor of 1.5. The effect of bed weight has already been taken by the investigators. The symbols Old and New refer to the types of TGA used and the difference from Old to New is in the direction of flow of gas (upward or downward). As surface area is somewhat less because of the char preparation method (2) than in the present work, it is expected the rate predictions would tend to be high.
Lignite, ND	"	5.40	8.40	10.765	
Lignite, ND	"	4.05	17.05	4.92	
Sbb. C. Wyoming	"	4.95	6.90	5.90	
Sbb. A. Wyoming	"	2.55	1.95	2.80	
HVC. Ill.	"	1.00	0.90	1.70	
Lignite, Tx	"	1.80	2.85	1.40	
HVA: Ky	"	0.285	0.12	0.24	

(1) The values for this equation are I = 0.1636 mg/mg-hr, a = 0.072 mg/mg-hr-wt%, b = 0.479 mg/mg-hr-wt%-wt%

(2) A correlation between coal composition oxygen and char composition oxygen was developed for relatively rapid pyrolysis. Maintaining the temperature for 30 minutes to one hour reduces the oxygen in the char by 50 % and changes the surface area as measured by CO_2 adsorption.

(3) Hippo, E., and Walker, P. L. Jr., Preprints Am. Chem. Soc. Mtg, Fuels Div., August 1975.

TABLE II - Continued

Char Type	Investigators	Experimental Rate etc.	Rate Predicted etc.	
Hydrane 49	Dutta and Wen(4)	0.48	0.68† 0.19*	†The values of oxygen and CaO in the char were obtained by knowing their amounts in original coal. *The numbers with the asterisk represent values which were obtained by taking the values of oxygen reported by the authors. The effect of particle size was not considered as it was not observed by the investigators. The bed weight effect was not taken because of the low reactivity of chars.
Synthane 122	"	0.51	0.60† 0.60*	
IGT 155	"	0.42	0.56† 0.25*	
ILL. 6	"	0.46	0.58†	
Hydrale 150	"	0.24	0.3416†	
Helper Coke Sbb	Blake et al(5)	0.75	1.68*	*The reported value of oxygen is 2%. Then the coke was soaked for 1 hr at 1000°C. Therefore the assumed per cent oxygen reported was 1.7% by wt of oxygen. ‡This coke was soaked for 1 hr at 1000°C. Therefore 0.85% O_2 was assumed based on their data. Effect of bed weight and particle size was considered.
Elkol Coke Sbb Wyo	"	0.42 to 0.63	0.73‡	
Artificial graphite from petroleum pitch	Petersen and Wright (6)	≥0.12 [0.06 for long cylinderical rods.]	I=0.1636 When (% CaO) = 0 (% oxygen) = 0	The intrinsic char reactivity is present when the char has zero per cent CaO and zero per cent organic oxygen content. This value compares well with artificial graphite. Effect of particle size and bed weight was taken into account.

(4) Dutta, S., Wen, C. Y., And Belt, R. J., I. E. C. Proc. Design and Development, 16, 20 (1977).
(5) Blake, J. H., et al., Fuel 45, 115 (1966).
(6) Petersen, E. E., and Wright, C. C., I. E. C. 47, 1624 (1955).

Presently, a study is being conducted of the hypothesis that a difference in reactivity of chars from the same coal is due to changes in oxygen and surface area. For example, the reactivity ratio for the lignite chars pyrolysed by the two methods is

$$(2) \quad \frac{r(CO_2)900°C}{r(CO_2)1000°C} = 3.0 \quad \text{experimental}$$

while the reactivity ratio predicted by using equation (1) and a direct proportionality with surface area is

$$(3) \quad \frac{r(CO_2)900°C}{r(CO_2)1000°C} = 2.95 \quad \text{predicted.}$$

It should be noted that from preliminary data such a close fit for the bituminous char (Pitt. #7) was not obtained, although the trend was similar.

Using corrections for (i) oxygen content based on pyrolysis method, (ii) particle size effects previously measured, and (iii) bed size effects, data from the literature were compared with the equation-(1) correlation in Table II. The comparison is quite good, considering (a) the errors in oxygen and CaO measurements and (b) the assumptions required to back out the data of other authors because they had not considered the corrections (i)-(iii).

Surface area changes as a function of char conversion. A lignite char (pyrolysis 1000°C) was reacted to various conversions and the surface area by CO_2 adsorption was measured. A surprising correspondence between reactivity and surface area changes was found (Table III).

Table III

Correspondence between Reactivity per Gram Char Remaining and Surface Area with Char Conversion

Char Conversion by Weight %	Reactivity Ratio* $\left(\frac{1}{w}\frac{dw}{dt}\right)_{x=0} \Big/ \left(\frac{1}{w}\frac{dw}{dt}\right)_x$	Surface Area by CO_2 (m^2/gm)	$\frac{S)x = o}{S)x}$
0	1.0	137	1.0
21.4	1.40	186	1.34
45.0	2.03	281	2.05
56.3	2.34	306	2.24
71.4	2.50	404	2.95

$\frac{1}{w}\frac{dw}{dt}$ = Rate of reaction based on the unreacted char.

Experiments on the fluidization of sand with char have continued in the 2' x 2' bed. There is good mixing of most of the char and sand. However, a thin layer ($\leq$ 1 cm) of the smaller, lighter char does form on the surface of the bed. This does not contribute substantially to the elutriation, as visual observations confirm that the elutriated char comes from the bulk of the bed proper. The elutriation rate constant that was measured was similar, but slightly higher than literature values for particles 74-104 μ. For char particles from 37-74 μ, the measured rate constant was an order-of-magnitude larger than calculated from literature correlations. Apparently there is a difference between the light char particles and the sand/glass particles generally used in the correlations.

CONCLUSIONS

The reactivity of chars with CO_2 can be correlated with just two composition parameters, CaO and oxygen in the char. The correlation has the form Rate = I + a{CaO} + b{CaO}·{O_2} where {CaO} and {O_2} are composition weight per cent. However, the surface area of a char was assumed roughly constant for this correlation. But it appears that available surface area (as measured by CO_2 adsorption) affects the rate. Increasing rate based on remaining char weight follows an increase in surface area. Fluidization with char exhibits a higher elutriation rate constant than predicted by literature correlations.

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