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

Work has continued on the kinetic reactivity of coal/char in CO_2. One viable mechanism has been suggested involving hydrogen abstraction by calcium oxide to explain this effect. The importance of diffusion resistance in mesopores/micropores indicates the need for a diffusion solid-gas reaction model.

Work has continued on the poisoning effect of CO gas on the CO_2 - C reaction. For several chars the effect has been found. Slight variations in $1/(1 - x)\ dx/dt$ vs x curves result for the different chars.

Construction of the high pressure atmospheric and fluidized beds is complete. A study of jet phenomena in a two-dimensional bed has resulted in a new, suggested correlation.

OBJECTIVE AND SCOPE OF WORK

The basic motive for this project is to provide fundamental data required for the design of coal gasifiers and MHD generators.

A major goal of the present work is to experimentally and theoretically investigate the kinetics of coal and char gasification reactions. Dependence of rate on such parameters as CO_2, CO, H_2O, H_2, concentrations, temperature, pressure, surface properties, and coal minerals will be obtained. A quantitative understanding of these dependencies will allow improved gasifier design for conversion processes and MHD generators. Improved prediction of the performance of various coals will be possible with knowledge of the effects of surface properties and minerals. The experimental investigation of the pressure dependence of these reactions up to 1000 psig will provide for confident design of the higher pressure gasifiers presently under development.

Fundamental data on the fluidization of coal and char particles will be obtained at pressure, as many of the gasification schemes call for fluidized gasifiers under pressure. Bubble sizes, expansion, elutriation etc., will be obtained on a 12" bed operated at ambient temperature.

SUMMARY OF PROGRESS

Below is a written summary of the technical progress. On the attached graph is a visual summary of the expended effort and costs.

A linear relationship between oxygen content, free swelling index, and calcium (doped or native) content and coal/char reactivity with CO_2 has been shown. A mechanism involving diffusion effects appears needed.

The effect of carbon monoxide is pronounced on the $C\text{-}CO_2$ reaction. At lower temperatures, a poison effect is observed at low CO concentrations with several chars. This effect varies slightly from char to char. At higher concentrations and temperatures, a mass-action law effect is observed as the CO_2 concentration is decreased.

Work on jet phenomena in 2-dimensional fluidized beds has been finished. Relationships between stagnant area, and jet velocity and jet spacing have been determined for a 2-dimensional fluidized bed. A correlation for jet height has been developed.

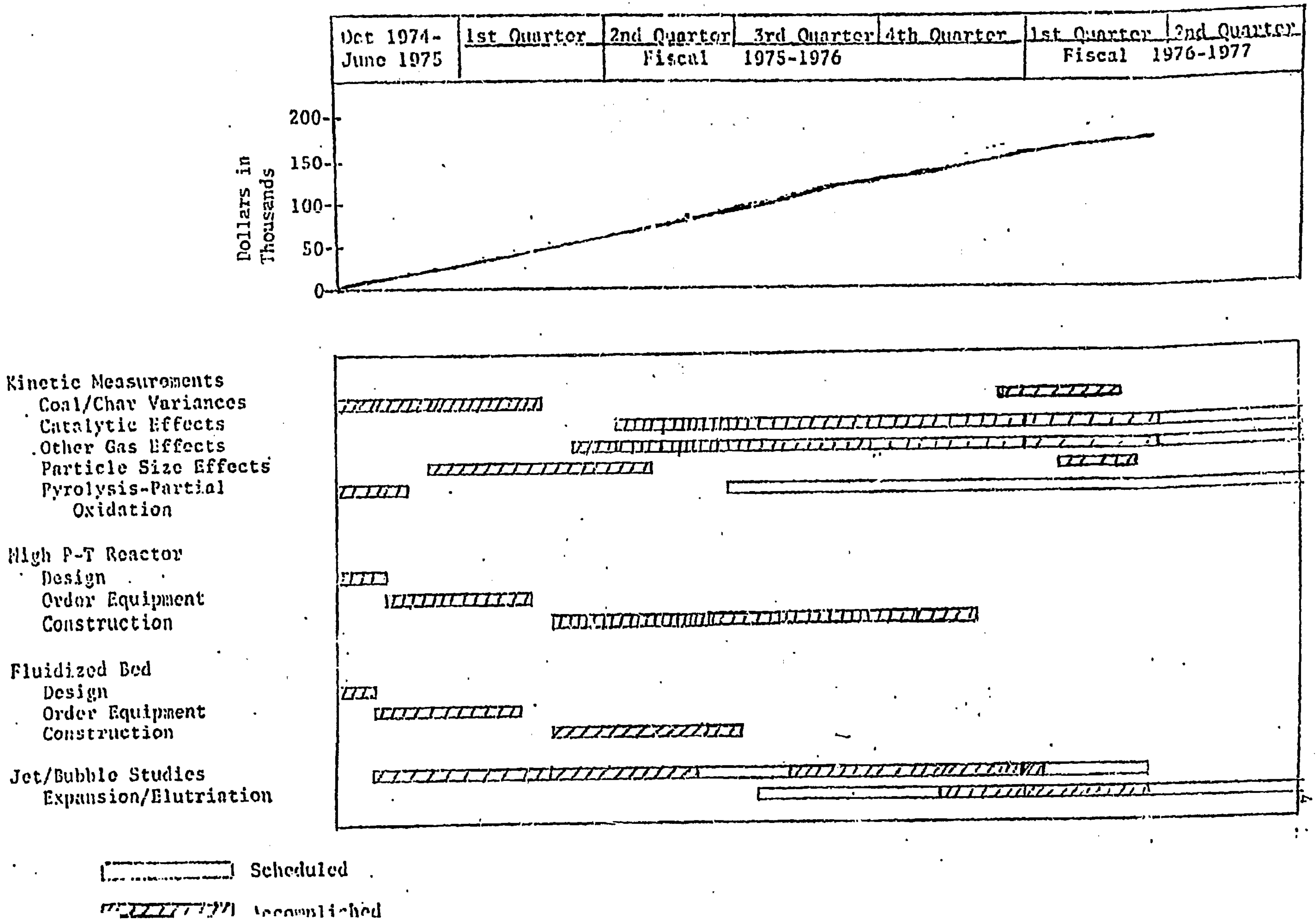
Coal/Char Reactivity

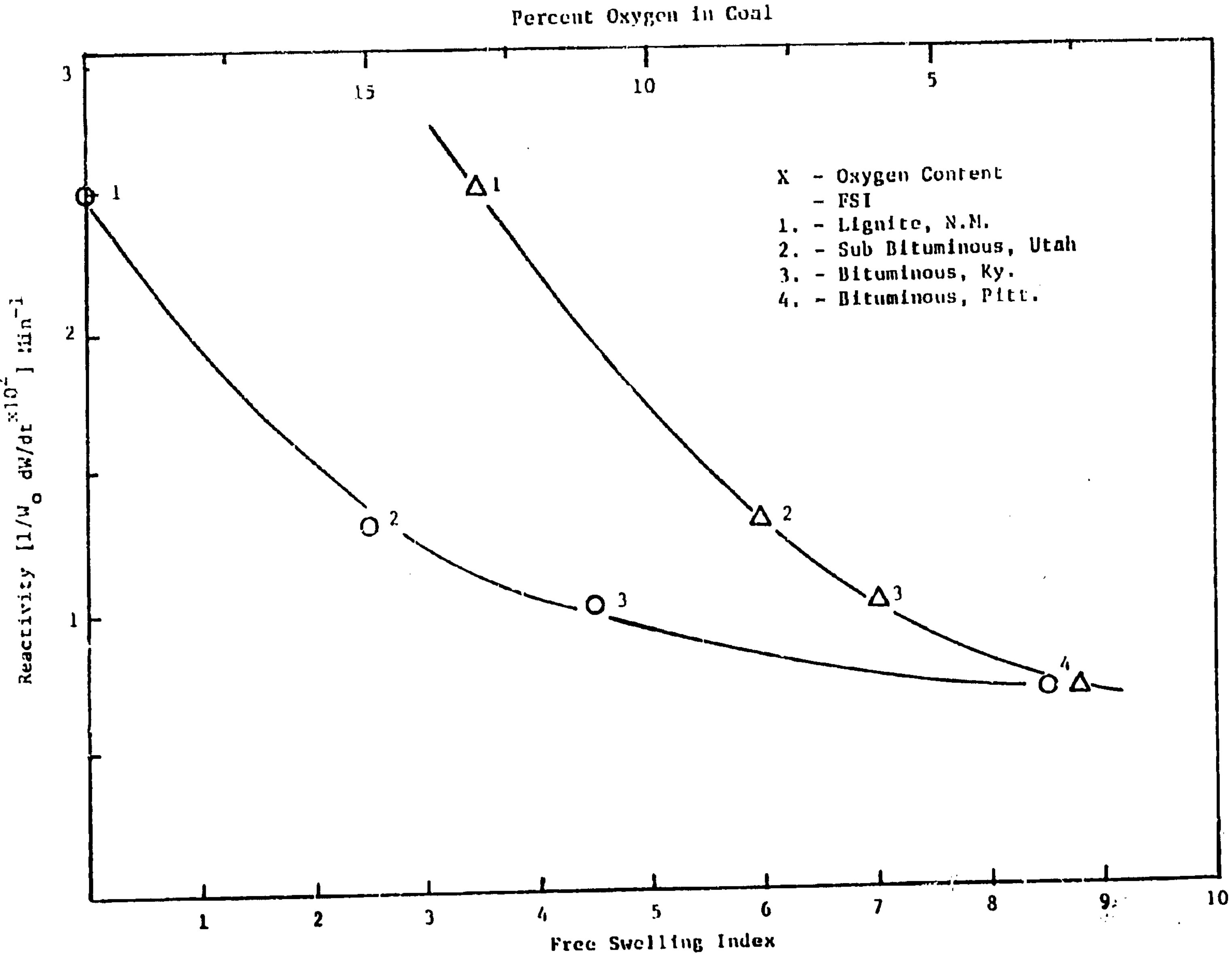
Work Accomplished:

The reactivity of coals with CO_2 has been shown to increase almost linearly with the amount of calcium present in coal, free swelling index, and oxygen content (Figure 1). Previous work had noted a particle size effect. The latest results indicate that the magnitude and direction of this effect depends on the manner of pyrolysis and char preparation. Work will continue on this effect in order to obtain a more definitive understanding.

These experimental results, and results from the literature on pore-size distribution as a function of conversion, indicate that diffusion through mesopores and particularly micropores should be incorporated into a model to predict reactivity. Preliminary calculations indicate that the small micropores are a major factor in determining reactivity. A sieving effect has been shown not to be major as crushing of larger particles (previously sieved) to -325 mesh has also found an increased reactivity. Electron - photographs have not found any difference in distribution of mineral matter crystals and pore openings between crushed particles and -35 + 60 mesh particles.

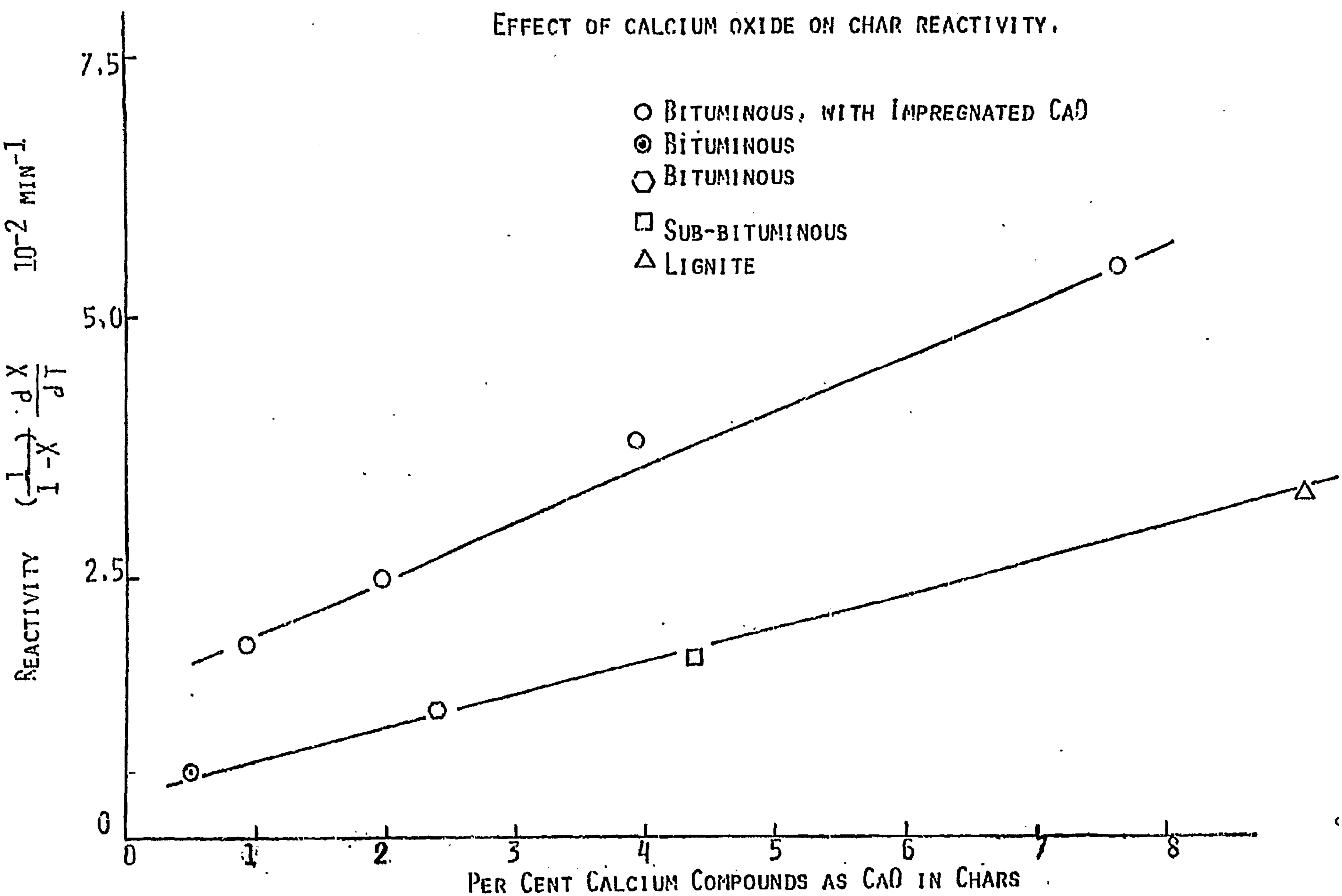
Cost and Performance Chart: The Role of the C-CO_2 Reaction in Gasification





1 FACTORS AFFECTING REACTIVITY OF COALS WITH CO_2

Fig. 1b. FACTORS AFFECTING REACTIVITY OF COALS WITH CO_2



Neutron activation results on oxygen content as a function of conversion found no change in oxygen content from x = 0 to x = 0.2. The interpretation of these results is uncertain, but it would appear that there are not oxygen-carbon reactive sites already in the char.

Work with different concentrations of CO_2-CO [i.e., (100:0), (98.9:1.1), (95.1:4.9), (80.3:19.7), and (51:49)] was carried out in the temperature range 850°C - 1100°C. Char was prepared by devolatilizing coal in a N_2 atmosphere at 1000°C for 25 minutes and then crushing it to -400 mesh size. Differences in particle size effects were noted from our previous work. This work must be further delineated.

At all temperatures and CO_2-CO concentrations, the reactivity increases with conversion, which may be partly attributed to a surface area increase as the reaction proceeds. Note that this intrinsic rate increases with X to high conversions. However, the rate curves are not exactly the same. It may have to do with the pore size and mineral matter distribution causing differences in particle size effects.

In Figure 2 are curves summarizing the change in rate as a function of added CO content for lignite and bituminous coals.

At higher temperatures there is only a dilution effect on the reactivity. At lower temperatures, there is not only a dilution effect but also a poisoning effect. The [Rate (CO_2-CO mixture)/Rate CO_2] ratio remains constant throughout the reaction from X = 0 to X = 0.9. At low temperatures, the rate sharply declines up to 1% CO and then follows a straight line of different slopes, depending on T. The slope of this line decreases with an increase in temperature. These results are consistent with the literature mechanism for carbon:

$$C + CO_{2(g)} \rightleftharpoons C(O) + CO(g)$$

$$C(O) \longrightarrow CO(g)$$

work on obtaining values for the rate constants is proceeding.

Future Work:

Continued work on the effect of oxygen and CaO content on coal reactivity will continue. Work on diffusion effects on particle reactivity will be developed. The effect of CO as a poison will be investigated with respect to catalytic activity and on different coals. Work at higher pressures and temperatures will commence in the new TGA reactor. Correlation of present work with earlier theories will be pursued.

Figure 2a. Lignite char reactivity as a function of CO_2-CO concentrations.

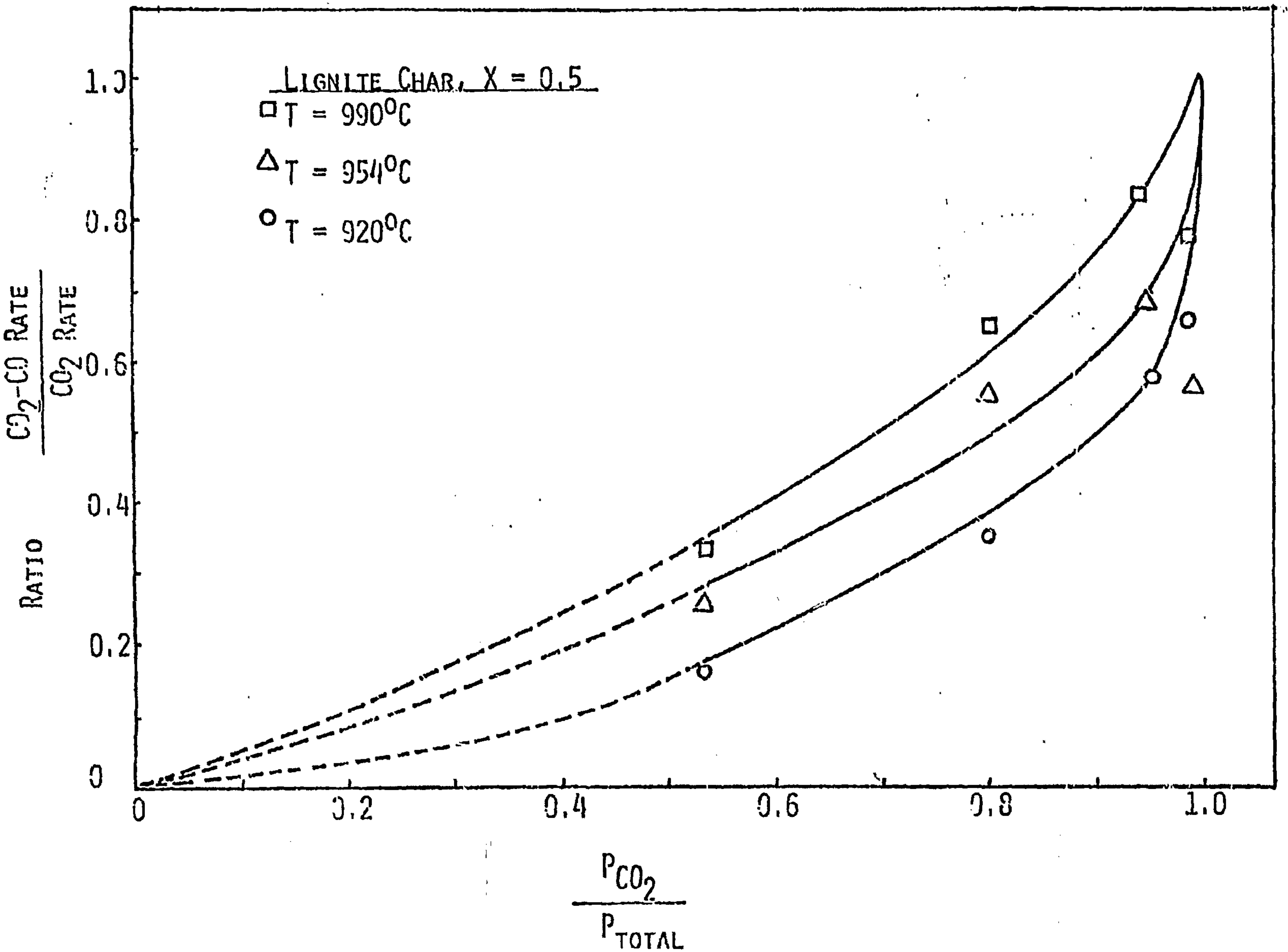
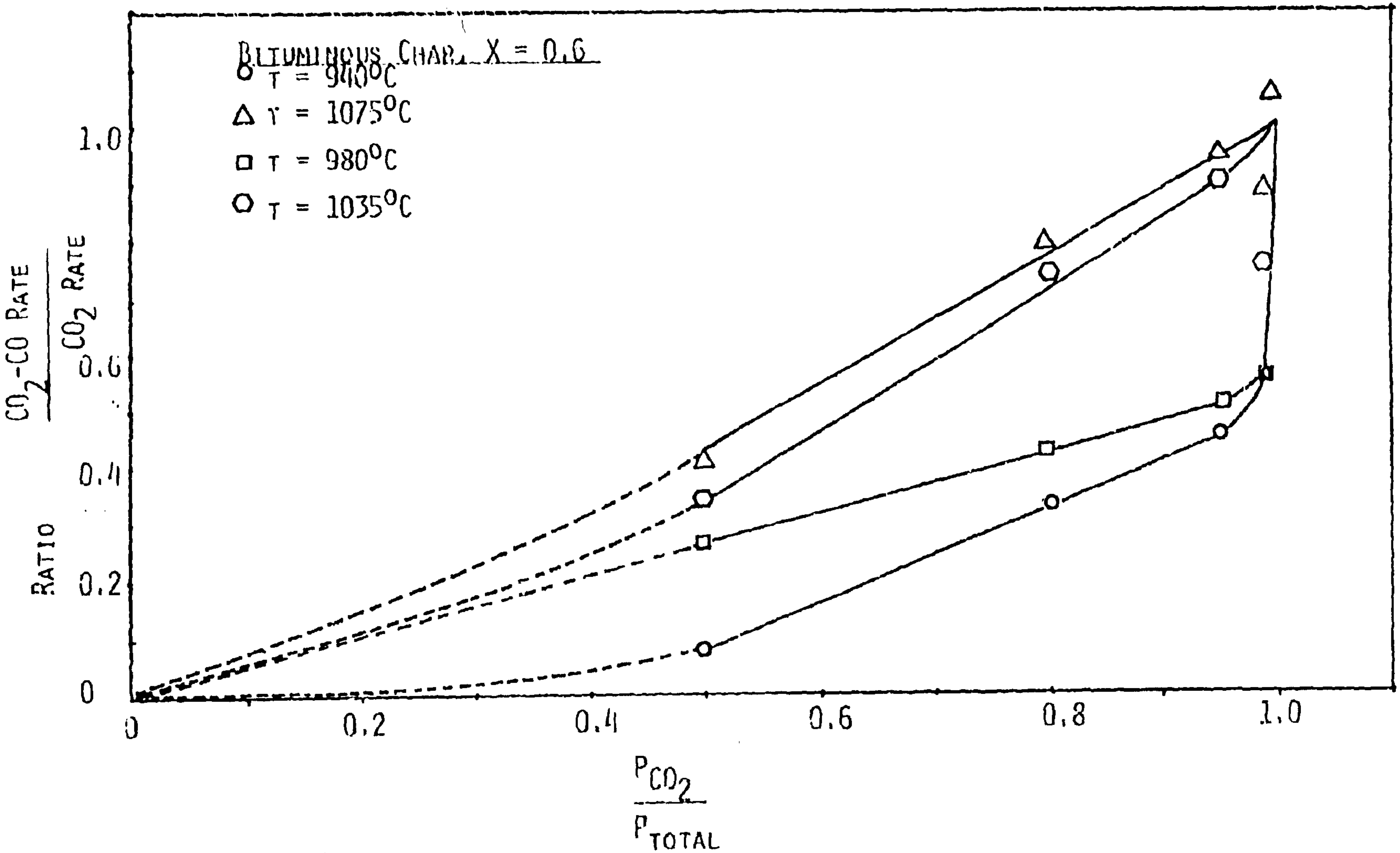


Figure 2b. Bituminous char reactivity as a function of CO_2-CO concentrations.



Pressure TGA for Reaction Studies

The reactor is complete, and operation and shake-down will begin. After debugging, initial experiments will be at 1atm., T = 1000 - 1300°C.

Fluidized Bed

Experimental, Jet Studies:

An investigation of the stagnant area of solids between openings for a given perforated distributor has been finished. The 2-D fluidized bed was 30.5 cm wide, 1.2 cm thick, which was made by separating two plexiglas sheets (9.5 mm thick) with 1.2 cm spacers. The apparatus arrangement was the same as previously reported. The bed was filled to various heights with different particles such as glass beads, P.V.C. beads sand and limestone.

Fluidization

Cinematic data were taken in a 2-dimensional bed to determine the maximum jet height from grid ports as a function of jet velocity. An improved correlation relating jet height as a function of fluidization parameters was statistically obtained:

$$\frac{H_j}{d_o} = 814.2 \left(\frac{p_p \, d_p}{p_g \, d_o}\right)^{-0.585} \left(\frac{p_g \, d_o \, U_j}{\mu}\right)^{-0.654} \left(\frac{U_j^2}{g d_o}\right)^{0.47}$$

H_j = maximum jet height

p = density, (p - particles, g - gas)

d = diameter (p - particles, o - orifice)

U_j = jet velocity

μ = viscosity

The effect of gas flow in the particulate phase on solids motion was investigated by having a separate flow of fluidizing gas through a diffusive distributor from the jet flow to the ports. This separate gas flow was found to have no effect on jet height, although a small variation in the angle of approach of the jet with the grid was found.

High Pressure Fluidized Bed-Construction:

i) Pressure Fluidized Bed

The construction of the fluidized bed is complete.

ii) Square Fluidized Bed

The construction of a 2 ft. square fluidized bed shell is complete. This system uses the same air compressor as the pressure fluidized bed.

The square fluidized bed was built to calibrate the probes for use in the pressure fluidized bed. The square bed is two feet by two feet in cross-section and six feet high (described in the previous progress report). Presently shake-down runs for pressure drop, minimum fluidization velocity, and jet heights in limestone and coal beds are being run.

iii) Probe for Bubble Studies

An optical probe has been constructed and shown in previous reports. This probe consists of a Light Emitting Detector (LED), L, and a Phototransistor, P, both encased in a stainless steel tube, S. The probe has been tested in two-dimensional transparent fluidized bed, and is operational. Experiments in the three-dimensional beds are to begin.

CONCLUSIONS

Kinetic reactivity of remaining char increase with char conversion up to conversions near 0.9. This increase occurs for reaction with CO_2 or with CO_2 + CO mixtures. This phenomena appears unrelated to variations in char site activity from changes such as sieving or bound oxygen.

An improved correlation of jet height from fluidized-bed grid ports as a function of jet velocity is presented.

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