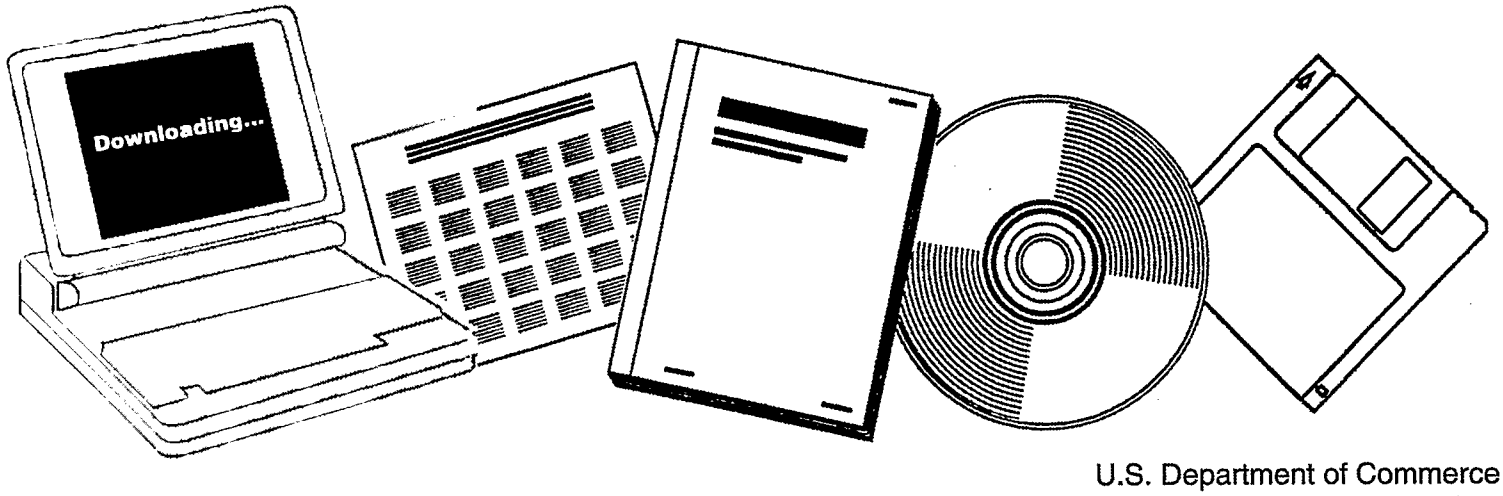
ROLE OF C--CO SUB 2 IN GASIFICATION OF COAL AND CHAR. ANNUAL REPORT, AUGUST 16--DECEMBER 31, 1978

WEST VIRGINIA UNIV., MORGANTOWN. DEPT. OF CHEMICAL ENGINEERING

1978



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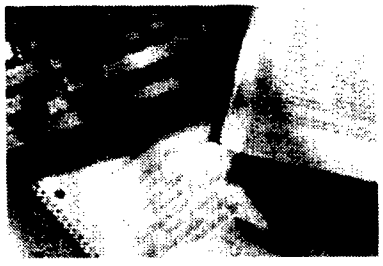

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The Role of C-CO_2 in Gasification of Coal and Char

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ANNUAL REPORT
For Period Aug. 16-Dec. 31, 1978

Prepared for the United States
Department of Energy
Under Contract ET-78-S-01-3253

ABSTRACT

Reactivity of chars obtained by physical mixing of coal with catalyst additives followed by pyrolysis show increased reactivity with K_2CO_3 additive, but not with CaO. The E_{act} for CO_2 reaction with char-additive K_2CO_3 is 20,000cal/mole in the temperature range 600-800°C, and reactivity has increased 5-10 times. Caution should be used in interpretation of these results because of complications from particle size effects and from variations in char oxygen with pyrolysis temlperature.

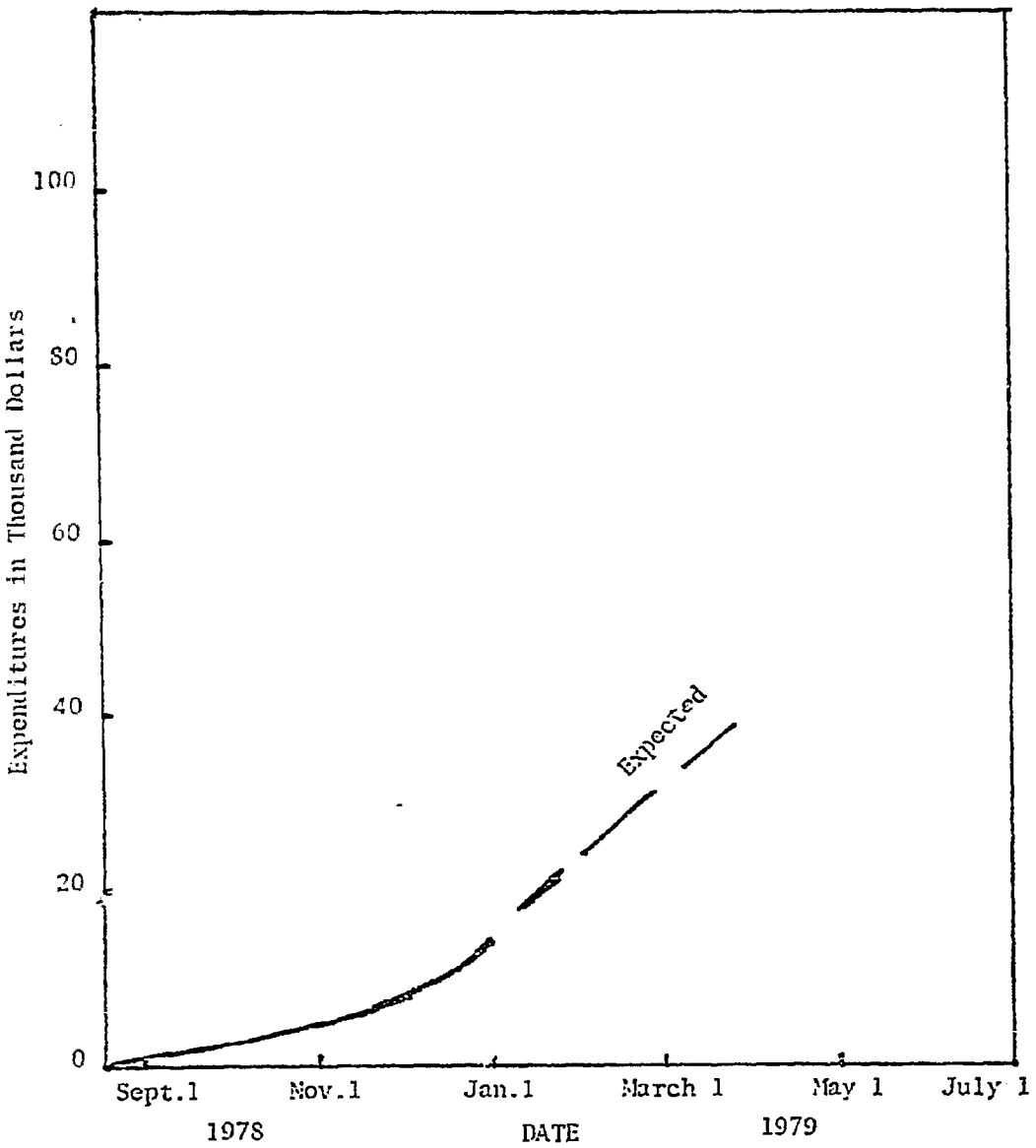
The LED-light probe for bubble detection in fluidised beds has been shown to work effectively. However, non-uniform gas distribution and non-vertical bubble rise make the use of the probe complicated.

Future work will center on char reactivity, pore and surface area development with conversion, and measurement of effective diffusivities.

SUMMARY OF PROGRESS

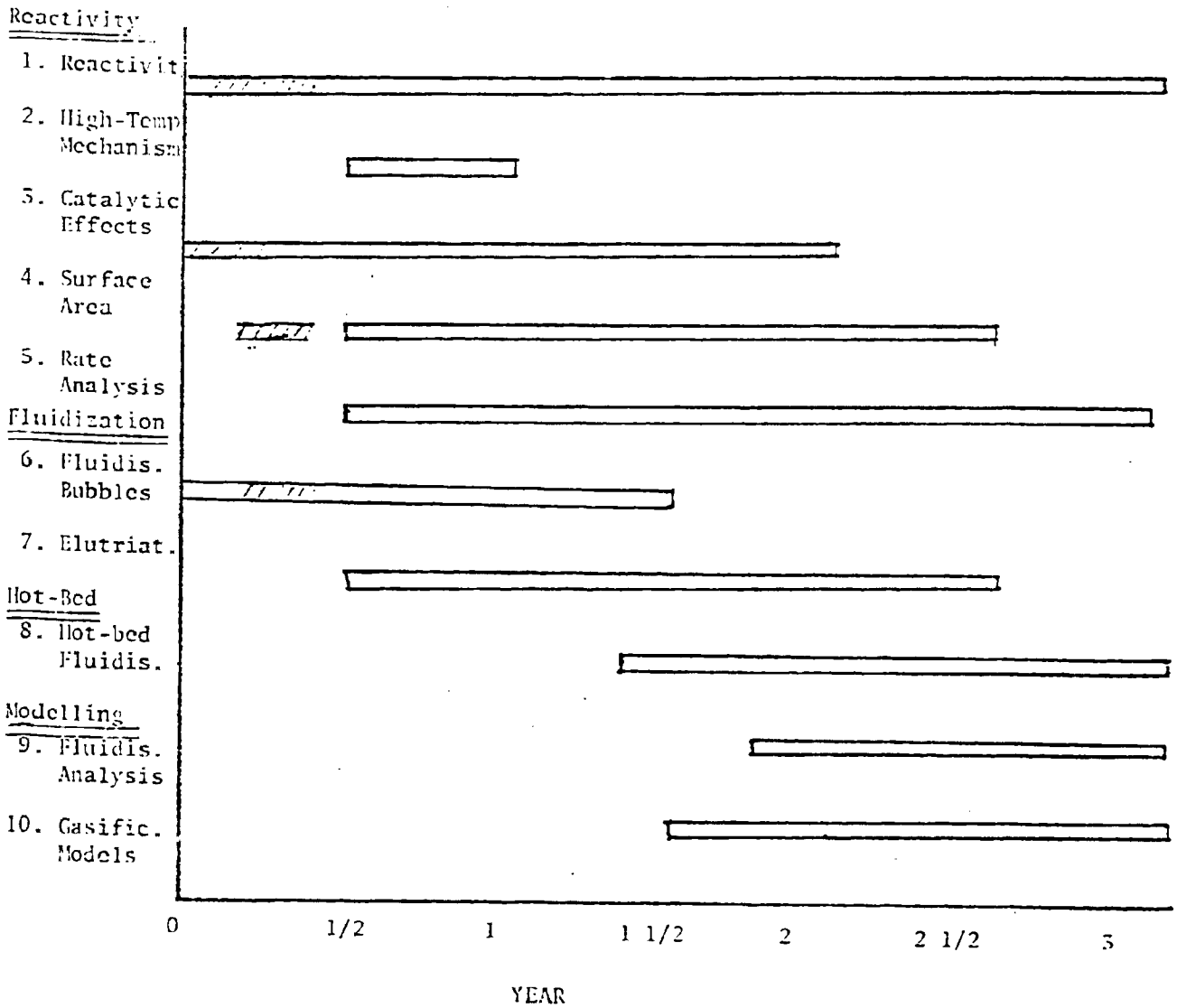
Below is a visual summary of expended effort and costs on the contract ET-78-S-01-3253.

Expenditure Time Chart



WORK SCHEDULE

Program Time Schedule



General

Three tasks were to be studied initially during the present report of this contract. The catalytic effects of CaO and other additives were to be investigated. A study of reactivity with CO_2 and other gases at temperature and pressure was to be started; and the flow characteristics of a coal and char particle will be investigated in cold fluidized beds.

The effects of physical admixing of lime or K_2CO_3 and coal (200-500μ) was investigated and compared with undoped coal and solution impregnated coal. The reactivity of undoped coal with CO_2 at 900°C could be reached at 650°C with an admixture of K_2CO_3 and coal pyrolyzed and then reacted. With CaO admixed, the reactivity was only slightly increased, if at all.

The rate with K_2CO_3-solution-impregnated (1.25%) coal was found to increase by only a factor of two over undoped coal. The expansion of coal in these physical admixtures upon pyrolysis was found to increase the diameter by about 20-40%.

Shakedown runs of the high-temperature TGA system found that, through the arm introducing the frequency coils, natural-convection air currents introduced oxygen which could quickly consume the carbon present for induction heating when the system was between runs. The special brass flange msut be tightly sealed in order to obtain useful temperature-constant runs with no impurities.

Screening runs to measure bubbling phenomena in a sand/char fluidized bed were completed for several different bed velocities. Bubble-time duration and frequency were measured at various positions in the bed using the LED (light) probe. It was determined that differences in pressure as a function of gas velocity, in gas-distribution through the bed and non-vertical movement of rising bubbles made interpretation of results tenuous. The pressure changes are primarily due to outlet ΔP. The cyclone for the pressurized fluidized bed has been redesigned and a new unit is under construction in order to minimize pressure changes and aid in determination of the bubble phenomena.

Steps are proceeding to begin investigating changes in pore area and pore sizes with conversion for different coals. A TGA unit is being modified to also be used for surface area determination by measuring weight changes from adsorption of CO_2 at various partial pressures. A computer model is being developed for pore size and pore area expansion based on an initial pore-size distribution to include diffusional effects.

Details, Work Accomplished:

Catalysis:

Pittsburgh-seam coal particles (200-500 μm in diameter) and K_2CO_3 or CaO were physically mixed, pyrolyzed and reacted with CO_2 for sample sizes of 10-60 mg. The pyrolysis temperature was the reaction temperature, as samples were heated to temperature in CO_2 so reaction immediately followed pyrolysis. The temperatures employed were 600-900°C. The ratio of coal to K_2CO_3 (CaO) was roughly 1:1 or 3:1. Not much difference was noted between the reactivity induced with the two ratios (Table 1). As can be seen from Table 1, little char reactivity increase was noted with CaO, while K_2CO_3 produced a 5-10 increase in char reactivity at each temperature. It should be noted that K_2CO_3 melts at 891°C and produces a mobile species which can move to interact with the char matrix. Below that temperature some vapor movement may be possible.

A solution-impregnated coal, doped to a 1.25 wt% K, as determined by atomic absorption spectroscopy, was also reacted at 900°C. It increased the rate by a factor of two, similar to increases found by Exxon. A crude check on whether the presence of inerts (K_2CO_3, CaO) would inhibit free swelling was conducted (Table 2). Swelling through pyrolysis was still present, being 20-40%. A check on whether the act of pyrolysis swelling was necessary to cause catalysis, was done by reacting wood chips mixed with K_2CO_3. A high reactivity (Table 1) was obtained for the non-swelling wood char, indicating the probability that swelling was not required for catalysis.

Figure 1 indicates an activation energy of 16-20,000 kcal/gmole. However, as the last contract showed an increase in char oxygen at lower pyrolysis temperatures and which dramatically affect reactivity, a lower activation energy would be expected for char alone at T = 600-800°C than at 900-1100°C. A direct comparison with the activation energy of 65-70,000 kcal/gmole for bituminous char at these higher temperatures must be treated with caution. Interpretation of these results is still proceeding. Variations in particle size from free swelling also complicate the interpretation. However, a significant increase in rate was observed, and the rate obtained at 900°C can be obtained at 650°C.

Fluidization:

The LED (light) probe (Figure 2) for bubbles was tested and used in determining the presence and duration of bubbles at a specific point in the 2' x 2' fluidized bed. Bubble frequency and duration at

Table I - Reactivity of Physically Mixed Components.

	SOLID REACTANTS[b]	PROPORTION	TECHNIQUE USED	REACTANT GAS	TEMPERATURE	INITIAL REACTION RATE (X=0)
1.	Coal-K_2CO_3	1-1	Physical Mixing	CO_2	600°C	0.033 mg/mg-min
2.	Coal-K_2CO_3	3-1	"	CO_2	600°C	0.037 "
3.	Coal-K_2CO_3	1-1	"	CO_2	700°C	0.077 "
4.	Coal-CaO	1-1	"	CO_2	700°C	0.0065 "
5.	Wood Chips-K_2CO_3	1-1	[a]"	CO_2	800°C	0.15 "
6.	Undoped Coal	----	-------	CO_2	800°C	0.025 "
7.	Coal-CaO	1-1	Physical Mixing	CO_2	800°C	0.038 "
8.	Coal-K_2CO_3	1-1	"	CO_2	800°C	0.21 "
9.	Coal-K_2CO_3 (Rerun)	1-1	"	CO_2	800°C	0.185 "
10.	Coal-K_2CO_3	3-1	"	CO_2	800°C	0.11 "
11.	Coal-K_2CO_3	1-1	Solution Impregnation	CO_2	900°C	0.11 "
12.	Undoped Coal	----	-------	CO_2	900°C	0.055 "

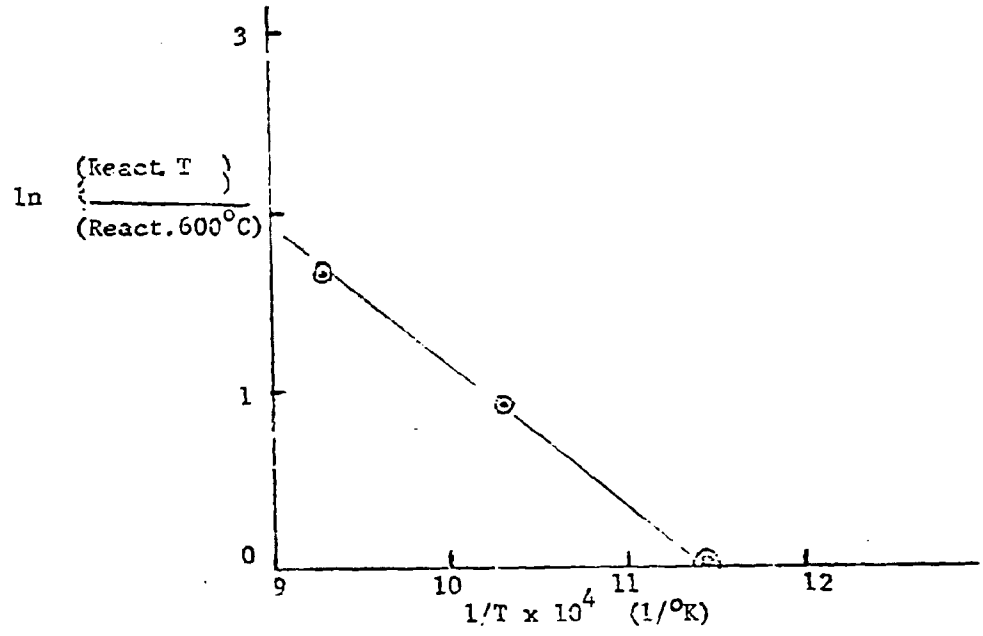
(a) Wood Chips were not crushed when mixed with coal.
(b) The coal was crushed to 2-500 μ.

Table 2
Particle Sizes Before and After Pyrolysis

Mixture	Before Pyrolysis (microns)	After Pyrolysis (microns)
1:1 Coal-Cao	494 ±144	614 ±251
1:1 Coal-K_2CO_3	346 ±128	462 ±200

Figure 1

Char-CO_2 Reactivity as a Function of Reciprocal Temperature for 1:1 Physically Mixed Coal-K_2CO_3



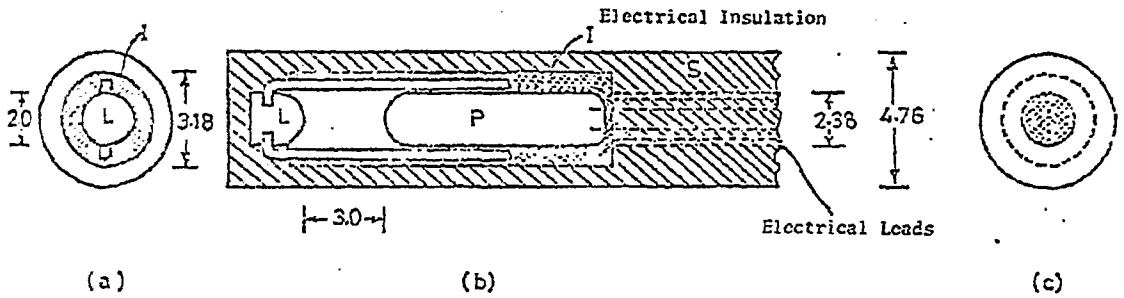


FIGURE 2. Bubble probe Design: a) left end view, b) cross sectional view, and c) right end view of the optical probe (Dimensions indicated are in mm).
L = Light Emitting Diode; P = Semi-Conductor; S = Solid Encasement
The presence of gas gaps is detected by allowing a signal connection between L and P.

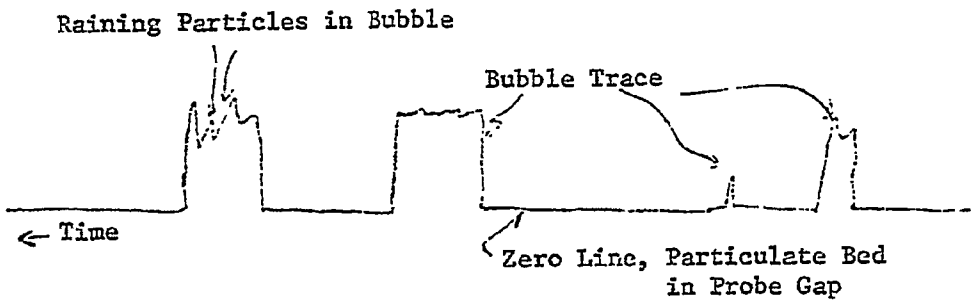


Figure 3. Schemeatic of Bubble Probe Output

various points in the 12" deep bed were determined at 100-300 SCFM by output on a fast dynograph. Figure 3 is a typical output. Figure 4 presents data of bubble frequency versus flowrate at three ascending positions in the bed. At low gas feedrates, the variability of the data indicate uneven, changing gas distribution through the bed. Growth of bubbles by combination seems not to have occurred as the bubbles transverse the height of the bed. Extreme scatter, both in magnitudes and changing trends with gas velocity, in gas bubble time at a particular point in the bed seem to indicate that bubble rise is not always vertical and bubbles rise at various angles with the vertical leading to the scatter. Bubbles are not present adjacent to the wall, and a distance of at least three horizontal inches into the bed is required before any stable bubble development is noted. An experimental program to position a series of probes above each other and to statistically consider these facts must be developed in order to adequately analyze and correlate bubble size, velocity and growth in an all-char fluidized bed.

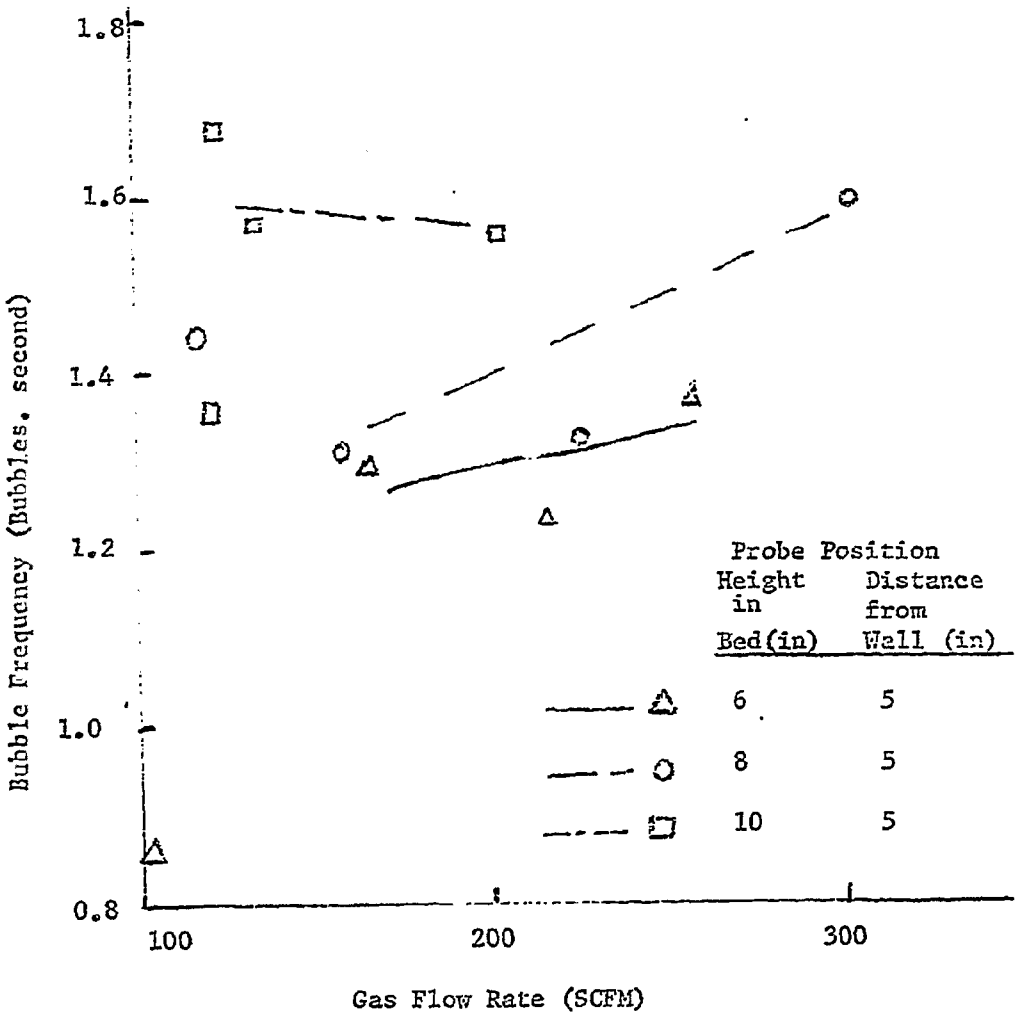


Figure 4. Bubble Frequency as Function of Gas Flow
Bed pressure = 1 + atm.; sand particles, 400 microns;
2 foot x 2 foot bed cross section.

Future Work:

Plans call for an emphasis on char reactivity studied. The areas to be specifically investigated initially include (1) char-H_2O reactivity at both 1 atm and pressure, (2) catalytic char reactivity of both impregnated and natural mineral matter, (3) development of surface area and pore size distribution with conversion of the above reactions, and (4) measurement of effective diffusivity in small pores by moment analysis of gas chromatographic adsorption of gases. The last area needs to be studied in order to develop a reactivity model to include diffusivity limitations at high reactivities or pressures.

Equipment will include an in-situ TGA system for measuring adsorption of CO_2 onto char for surface area analysis, and a char-packed column in a gas chromatograph for effective diffusivity determination. The large pressure TGA will be utilized for high pressure runs to compare with the reactivity model.

Immediate model development will center on a pore-development model based on uniform reactivity of surface area includes pores to about 4 diameter and development differences due to diffusivity will be incorporated.

Fluidization work will center on development of an experimental procedure and analysis for measuring bubble distribution, velocity, and size in char fluidized beds. As mentioned earlier, the maldistribution of gas through the grid plate and non-vertical rise of bubbles complicates the accurate quantitative analysis. In order to reduce a pressure variation with gas flow due to high cyclone pressure drop, a new cyclone has been redesigned and is being constructed. A careful program must be developed, so screening data on pure char fluidized beds will first be performed to detect other possible trouble spots.

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