2. BENCH SCALE STUDIES (Reporting Category 2)

2.1 CONTINUOUS GASIFICATION UNIT (CGU) OPERATIONS

The Continuous Gasification Unit (CGU) is a very small fluidized bed unit designed for continuous coal feeding and withdrawal of ash/char residue. It was built so that kinetic data could be obtained in a fluidized mode at a lower cost and with less manpower than that required for the FBG. Construction of the CGU was completed with Exxon funding prior to the start of the Predevelopment Program.

Although the CGU is smaller than the FBG, it has the expanded capability of operating at high pressure, with 1000 psig being the design maximum. The primary source of synthesis gas was intended to be cylinder gas; however, the capability does exist for synthesis gas recycle. A flow plan of the unit is shown in Figure 2.1-1. The solid feed is conveyed into the bottom of the unit using the synthesis gas/steam mixture. The gas rates are very low, and the design superficial velocity in the gasifier is near minimum fluidization. The overhead gas is filtered for solids removal and water scrubbed to condense unreacted steam. The flow and composition of the gas are then measured. For the option in which synthesis gas recycle is employed, the gasifier product is treated to remove acid gases and then cryogenically separated into product methane and recycle gas.

Operation of the CGU is expedited by the use of a programmable controller for logic control of start-up, alarm, and emergency sequences, and a 50 channel digital process controller. In addition, all instrumentation, including a continuous process gas chromatograph, is interfaced with an on-line computer for data logging and monitoring. Material balance, equilibrium calculations, and flow calculations are also performed by the computer, with operating condition set point feedback to the operator.

2.1.1 CGU Operating Experience

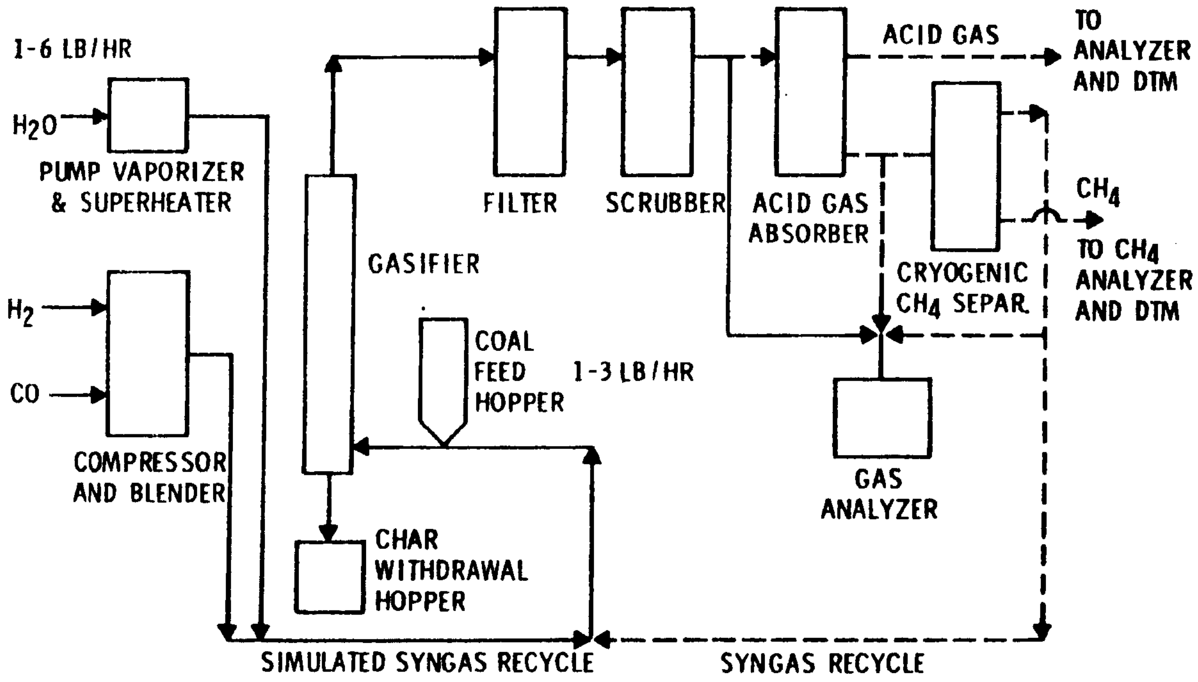
Start-up and initial operations of the CGU were completed during the third quarter of 1976. Because of operating difficulties, the periods of continuous unit operation were limited to a maximum of 26 hours. As a result, true steady-state conditions were not reached. Data were obtained for four continuous yield periods of up to six hours length. In addition, two batch-type yield periods with a captive fluid bed were conducted for comparison with previous fixed-bed experiments.

This work completed the CGU operations. Operating difficulties which were experienced during the start-up phase are discussed below. An analysis of the data obtained is presented in Section 2.1.2.

The CGU operating problems generally were related to the small size of the unit although normal pilot plant mechanical problems (e.g., compressor failures) were also encountered. One major CGU constraint is the low feed gas rate. This low rate requires a small feed line diameter (0.25 inches) in order to provide sufficient velocity to convey the feed char to the gasifier.

FIGURE 2.1-1

CONTINUOUS GASIFICATION UNIT (CGU) FLOW PLAN



The gas velocity in the feed line is very close to the theoretical saltation velocity. Thus, momentary upsets, caused for example by fluctuations in synthesis gas supply pressure, occasionally resulted in a solids plug in the feed line. This problem was corrected by modifying the syngas supply pressure regulation system to assure very steady flow and by operating at higher than design syngas rates. However, the higher rates did result in gas residence times lower than those projected for commercial operations and consequently in lower steam conversions. To correct this, it is planned that for future operations, the gasifier diameter will be increased to give a 1.8 fold increase in gasifier volume and a corresponding increase in gas residence time. This is within the capability of the present heater system.

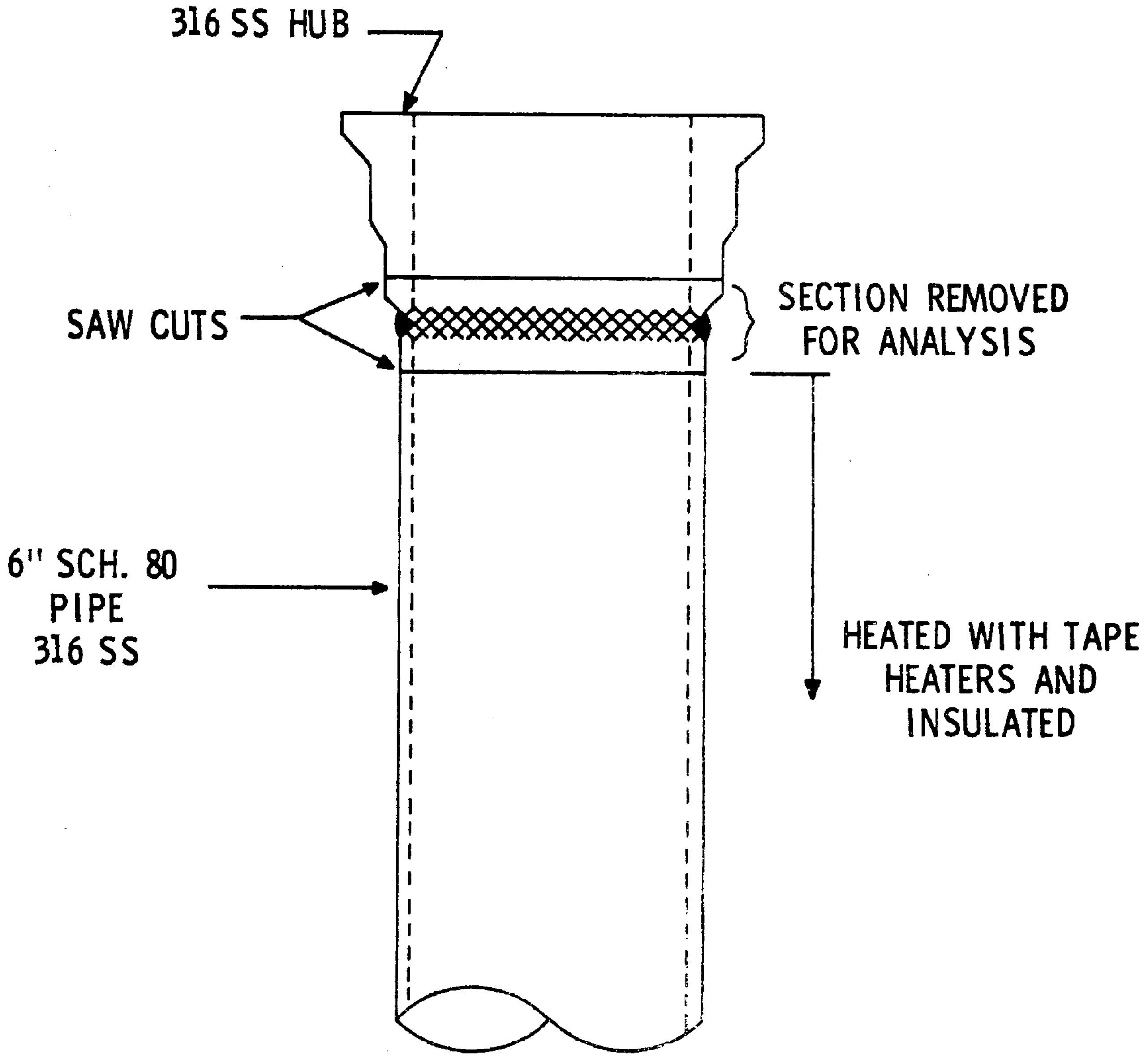
Occasional plugging problems also were experienced in the gasifier pressure taps used to indicate the level of the fluidized char bed. Since synthesis gas is used for the pressure tap bleed gas, the greater the volume of bleed gas the less the volume available to the feed line. To maximize the feed line gas, small diameter pressure taps (0.055 inches I.D.) were used with low gas velocities in the taps. Again, upsets in the syngas supply pressure or gasifier occasionally resulted in solids backing into the taps and plugging them. For future operations, it is proposed to modify the bleed gas supply system to simplify blowing out the taps in the event of solids plugging.

Another major problem encountered in the CGU, but one easily correctable, was steam condensation at some locations. This was caused by inadequate electrical trace heating and resulted in two types of operating difficulties - formation of soft plugs and metal failure. The soft plugs in the unit formed in the char sample and char withdrawal lines. At 500 psig, the steam saturation temperature is 471°F. Char impregnated with K_2CO_3 catalyst may stick at temperatures higher than the saturation temperature due to the hygroscopic character of K_2CO_3. The prevention of wet spots in very small lines and especially around valves and thermocouples where heat losses are concentrated is particularly difficult with a unit as small as the CGU. Nevertheless, additional heaters and insulation were used and the plugging problems were apparently solved.

Two instances of metal failure were encountered. The first was in the product gas filter vessel in the weld region between a 316 SS pipe and a 316 SS butt welded hub. Figure 2.1-2 is a sketch of the vessel showing the position of the affected area. While in service, tape heaters and insulation were wrapped around the pipe in the weld area. The hub and clamps were not heated. Analysis of a piece of scale from the weld area showed 5,000 ppm chloride. Radial cracks initiating at the inner metal wall were found in a ring containing the weld area cut from the vessel. Characteristic branching transgranular chloride-stress cracks were seen. The ring sprang open when cut, indicating that a high tensile stress state existed in the crack region due to the residual weld stresses. Since chloride stress cracking could not occur without a liquid phase, it is clear that steam was condensing. After the vessel was rebuilt, heaters were added to the weld and flange area to prevent steam condensation. The second stress-chloride cracking failure was in the char-sampling line in a weld area between a 316 SS male connector and a 316 SS half coupling. This line had been fully wrapped with tape heaters and insulation and held at 600-650°F. Steam evidently condensed at some time, however, probably during a shutdown as a result of inadequate purging.

FIGURE 2.1-2

CGU FILTER VESSEL FLANGE END



2.1.2 CGU Data Analysis

Material balances for the four CGU continuous yield periods (101-104) are presented in Table 2.1-1. For all four yield periods, the fluid bed temperature was in the range of 1300°F. In three cases, the pressure was 500 psig and in one case, it was 350 psig. The feedstock was Illinois coal char catalyzed with 20% K_2CO_3. The gasification medium was a steam/H_2/CO mixture. Because of the operating problems discussed above, it was not possible to obtain a representative sample of the ash-char residue. Thus, the unconverted carbon in the residue was estimated by carbon balance assuming no accumulation or depletion of carbon in the bed. The inlet and outlet gas compositions and the measured steam condensate collected in the scrubber were used to check the overall hydrogen and oxygen balances. These balances closed to within five percent in over half of the cases and to within ten percent in all cases.

The calculated carbon conversions for yield periods 102-104 vary from 60-90 percent. The calculated carbon conversion of 99 percent for Yield Period 101 is almost certainly in error as a result of carbon depletion in the bed. The percent carbon in the residue is an important parameter because, assuming a well mixed bed, it determines the carbon holdup in the bed. This in turn determines the steam residence time (steam feed rate/carbon holdup), a parameter used in correlating the data. The percent carbon on residue and residence time for Yield Period 101 appear to be low by an order of magnitude.

Material balances for the two captive fluid-bed yield periods (105 and 106) are summarized in Table 2.1-2. One run was made with pure steam as the gasification medium. In the other run, a mixture of steam and synthesis gas was used. The feed was devolatilized Illinois coal catalyzed with 20% K_2CO_3. The pressure was 500 psig and the temperature was 1250°F. With the captive fluid-bed operation, which is similar to the fixed-bed operation, the steam or steam/synthesis gas mixture flow rate is kept constant throughout a run. As the run proceeds and the carbon is gasified, the carbon content of the bed decreases, and the relative residence time decreases. In runs of this type, the gas composition is changing. Therefore, it is not possible to make an accurate measurement of the water content of the outlet gas by collecting the condensate produced. Thus, the product H_2O is calculated from the inlet and outlet dry gas analyses using an oxygen balance. Since no carbon is withdrawn, the carbon gasification rate is calculated by carbon balance. A check of the hydrogen balance is possible for each time period and this is shown in Table 2.1-2. The hydrogen balances close within ± 5% in essentially all cases.

The gasification rates for the three good continuous yield periods (102-104) and both captive bed yield periods (105 and 106) are compared with fixed bed gasification data obtained during the previous Exxon-sponsored research phase in Figure 2.1-3. The fixed-bed data were obtained in multiple runs at 1200-1300°F and 100-500 psig with catalyzed devolatilized coal containing 20% K_2CO_3. The fixed-bed correlation lines are shown for 1250°F and 1300°F. The moles of carbon gasified per mole of steam fed is plotted on the ordinate. Since the moles of carbon gasified are related to the moles of steam consumed, the ordinate can also be thought of as the fraction of steam converted by reaction with carbon. When operating in synthesis gas balance,

TABLE 2.1-1

MATERIAL BALANCES FOR CGU CONTINUOUS YIELD PERIODS

	Yield Period 101					Yield Period 102					Yield Period 103					Yield Period 104				
Temperature, °F	1280					1310					1310					1304				
Pressure, psig	350					500					500					500				
	Total	C	H	O	N	Total	C	H	O	N	Total	C	H	O	N	Total	C	H	O	N
Input (lbs/hr)																				
Char	2.500	1.213	0.015			2.500	1.213	0.015			2.500	1.213	0.015			2.000	0.970	0.012		
H_2O	5.300		0.593	4.707		4.907		0.549	4.358		5.000		0.560	4.440		5.060		0.566	4.494	
H_2	0.502		0.502			0.738		0.738			0.865		0.865			1.197		1.197		
CO																0.287	0.123		0.164	
N_2(5)						0.174				0.174	0.207				0.207	0.281				0.281
Total	8.302	1.213	1.110	4.707	0.000	8.320	1.213	1.302	4.358	0.174	8.572	1.213	1.440	4.440	0.207	8.825	1.093	1.775	4.658	0.281
Output (lbs/hr)																				
Char	1.285(1)	0.012(2)				1.740(1)	0.469(2)				1.387(1)	0.114(2)				1.135(1)	0.118(2)			
H_2O	4.200		0.470	3.730		4.430		0.496	3.934		4.620		0.517	4.102		4.819		0.539	4.280	
H_2	0.548		0.548			0.621		0.621			0.625		0.625			0.878		0.878		
CO	0.532	0.228		0.304		0.191	0.082		0.109		0.157	0.067		0.090		0.180	0.077		0.103	
N_2						0.174				0.174	0.207				0.207	0.281				0.281
CH_4	0.738	0.553	0.186			0.654	0.489	0.164			1.109	0.830	0.279			1.087	0.814	0.273		
CO_2	1.540	0.420		1.120		0.636	0.173		0.463		0.739	0.202		0.538		0.308	0.084		0.224	
Total	8.843	1.213	1.204	5.154	0.000	8.446	1.213	1.281	4.506	0.174	8.844	1.213	1.421	4.730	0.207	8.688	1.093	1.690	4.607	0.281
Material Balance,%	107		108	110		102		98	103		103		99	107		98		95	99	

	Yield Period 101		Yield Period 102		Yield Period 103		Yield Period 104	
Carbon Conversion, %(3)	99(4)		61		91		89	
Relative Steam Residence Time	0.13		0.41		0.12		0.14	
Mol Carbon Gasified/ Mol Steam Fed	0.34		0.23		0.33		0.26	
Product Gas Comp. (Mol %)	Measured	Calc. Gas Phase Equil.	Measured	Calc. Gas Phase Equil.	Measured	Calc. Gas Phase Equil.	Measured	Calc. Gas Phase Equil.
H_2O	38.52	45.37	39.53	42.94	38.54	38.77	33.67	34.83
H_2	44.96	35.41	49.50	45.82	46.60	46.09	54.05	53.87
CO	3.14	2.19	1.10	0.53	0.84	0.75	0.81	0.27
N_2	-	-	1.00	1.02	1.11	1.13	1.26	1.22
CH_4	7.60	12.53	6.55	8.95	10.38	12.27	8.83	9.54
CO_2	5.78	4.50	2.32	0.74	2.53	0.99	0.88	0.27
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

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(1) Ash and catalyst balance estimated assuming no accumulation or depletion in bed

(2) Estimated by carbon balance assuming no carbon accumulation or depletion in bed

(3) From carbon balance. See Note (2)

(4) Appears to be in error because of carbon depletion during yield period

(5) N_2 from feeder blow-by calculated by N balance

TABLE 2.1-2

MATERIAL BALANCES FOR CGU CAPTIVE BED YIELD PERIODS

Temperature, °F			1250				1250		
Pressure, psig			500(1)				500		
Gasification Medium			H_2O				$H_2O/H_2/CO$		
	YIELD PERIOD 105					YIELD PERIOD 106			
Time, Hours	1	2	3	4	5	1	2	3	4
Input, Moles/Hr									
H_2O	0.295	0.295	0.295	0.295	0.295	0.229	0.229	0.229	0.229
H_2	0	0	0	0	0	0.092	0.092	0.092	0.092
CO	0	0	0	0	0	0.028	0.028	0.028	0.028
Output, Moles/Hr									
H_2O(2)	0.122	0.122	0.145	0.201	0.232		0.115	0.156	0.191
N_2	0.098	0.083	0.081	0.071	0.051		-	-	-
H_2	0.073	0.081	0.086	0.072	0.055		0.092	0.086	0.074
CO	0.038	0.033	0.024	0.011	0.004	See	0.032	0.015	0.007
CH_4	0.054	0.050	0.036	0.012	0.004	Note	0.051	0.035	0.020
CO_2	0.068	0.070	0.063	0.042	0.029	(5)	0.055	0.043	0.030
Carbon Gasified, Mole/Hr(3)	0.160	0.153	0.123	0.065	0.037		0.110	0.065	0.029
Steam Conversion, %(2)	58.6	58.6	51.0	32.0	21.3	-	49.7	31.8	16.7
Hydrogen Balance, %(4)	96	97	98	98	99	-	93	95	94
Relative Steam Residence Time	1.43	0.91	0.49	0.27	0.15		0.52	0.24	0.11

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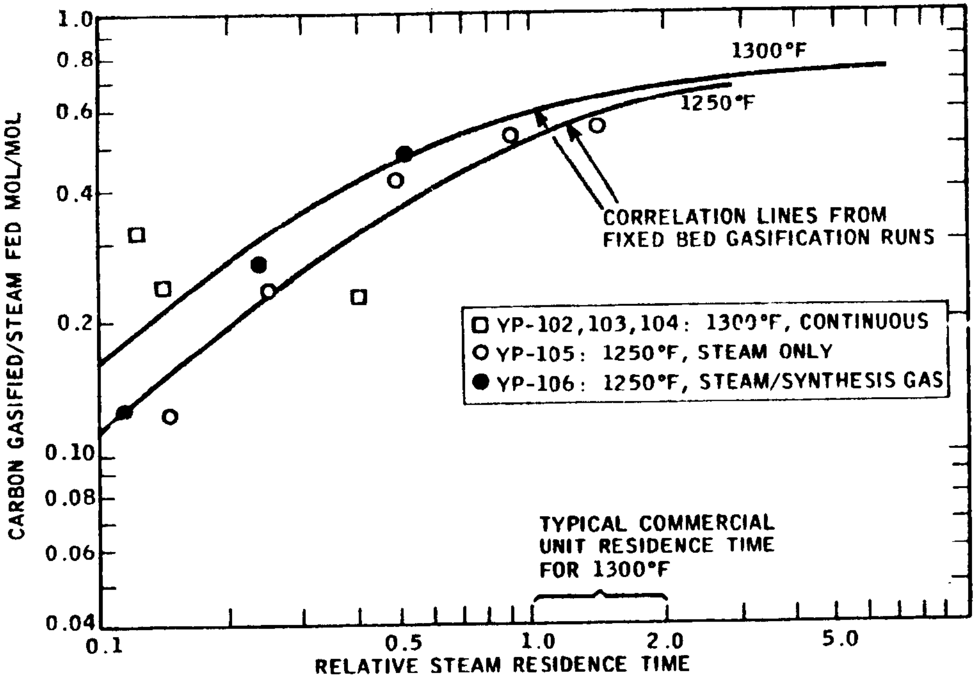
(1) Bleed N reduced effective pressure to 420 psig.
(2) H_2O by O balance
(3) By carbon balance
(4) Based upon feed char with 0.02 H/C weight ratio.
(5) Gas chromatograph problems were encountered during this first hour of operation.

FIGURE 2.1-3

COMPARISON OF CGU AND PREVIOUS FIXED BED DATA

EXTENT OF STEAM-CARBON REACTION vs. RESIDENCE TIME



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this quantity becomes identical to the overall steam conversion. On the abscissa, the relative steam residence time is plotted.. At low residence times, the extent of gasification is a strong function of residence time. At higher residence times, the extent of gasificatation approaches a plateau as carbon-steam equilibrium is reached.

In general, the CGU data fall very close to the fixed-bed correlation lines. This indicates that contacting is excellent in the CGU. This is not surprising since the CGU operates at very low superficial velocities. Since the captive bed runs were not at steady state, they show considerably more scatter than the continuous runs.

Also shown in Table 2.1-1 are the measured gas compositions for the continuous CGU yield periods as well as the gas compositions which would be obtained if the product gas were at gas phase methanation equilibrium. In Figure 2.1-4, the continuous and captive-bed data are compared with the correlation line for previous fixed-bed data on the approach to methane equilibrium. Methane in the product expressed as a percent of equilibrium is plotted against relative steam residence time. The data were obtained at 500 psig and 1200-1300°F. At the higher residence times, the CGU data are in fairly good agreement with the fixed bed correlation line. At 1300°F and relative steam residence times between 1 and 2, conditions typical of commercial unit operations, the correlation line shows that gas phase methane equilibrium is very closely approached.

At low residence times, the methane production exceeds that observed in the fixed-bed runs. The reason for this is not clear. It is possible that a small amount of methanation is occurring downstream of the gasification bed in cooler zones. This would tend to increase methane yields. At the low residence times where the steam conversions are relatively low, the absolute level of methane produced even at equilibrium is low; thus, the effect could be more pronounced.

2.2 FIXED BED GASIFICATION REACTION STUDIES

Design of the gasifier for the Exxon Catalytic Coal Gasification process requires a quantitative description of the kinetics of the catalytic gasification reaction. Bench scale studies were conducted in a fixed bed reactor tc provide the necessary data for the development of the rate equation and to determine the reactivity of other catalyst systems (*e.g*. mixed Na_2CO_3/K_2CO_3) relative to the K_2CO_3 base case.

2.2.1 Experimental Apparatus and Procedure

The high pressure apparatus used in this study is shown in Figure 2.2-1. The main components of the system are the fixed bed reactor, water pump and steam generation equipment, pressure and temperature control systems, unreacted steam condenser, a gas chromatograph, and a dry gas flow measurement system. Provisions were included for the optional addition of an inert or reactant gas (such as H_2 + CO) to the feed steam.

A high pressure pump was used to supply H_2O at a constant rate to the steam generator which consisted of 1/4" stainless steel tubing coiled

FIGURE 2.1-4

COMPARISON OF CGU AND PREVIOUS FIXED BED DATA

APPROACH TO EQUILIBRIUM vs. RESIDENCE TIME

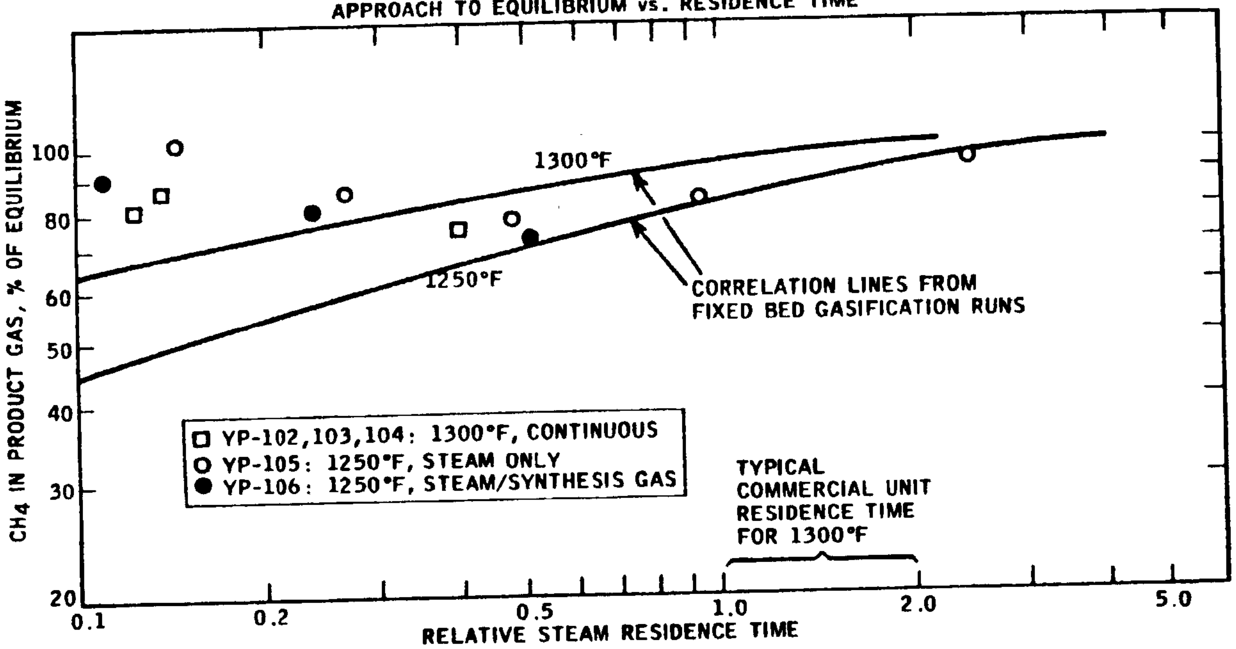

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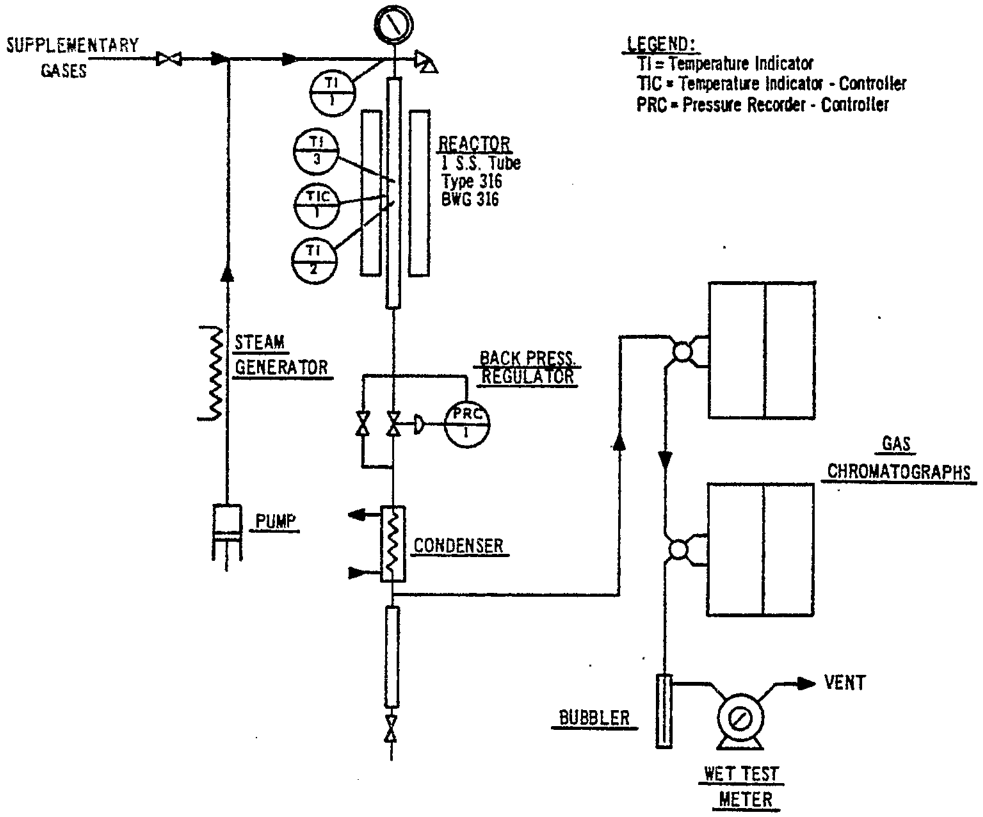
FIGURE 2.2-1

SCHEMATIC DIAGRAM OF BENCH SCALE FIXED BED GASIFICATION UNIT



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around the fixed bed reactor. Both the steam generator and the reactor were mounted vertically in a split tube furnace. The reactor temperature was measured and controlled at the center of the bed of char. The product gas stream, consisting primarily of H_2, CO, CH_4, CO_2, and unreacted H_2O, was filtered and then depressurized through the pressure control valve. The unreacted H_2O was condensed and the gas stream was further dried with calcium sulfate. The dry gas stream passed through a gas chromatograph sampling system which provided automatic sampling at 15 minute intervals. The dry gas flow was measured by a wet test meter connected to a pulse generator. The signals from the pulse generator were accumulated as a measure of total gas volume produced. The fixed bed reactor was constructed from 1-inch Schedule 80 stainless steel pipe and was approximately 30 inches in length. The reactor was filled to a depth of 15 inches by 1/8-inch mullite beads which supported the bed of char.

Samples were prepared by soaking 30 to 100 mesh Illinois No. 6 coal in a solution containing the desired weight of catalyst. This weight was typically between 10 and 20 gms K_2CO_3/100 gms of coal (referred to as 10 and 20% K_2CO_3). Normally, the weight ratio of water to coal was slightly greater than one. The samples were then dried overnight in a vacuum oven. A scanning electron microscope study showed a fairly even dispersion of potassium throughout the coal particle. The impregnated coal samples were then devolatilized at atmospheric pressure for 30 minutes in a muffle furnace under a nitrogen atmosphere at 1200°F. The resulting char samples were allowed to cool to room temperature and then stored in bottles under nitrogen.

A typical run was made by loading the reactor with a 20 gram char sample. The reactor was purged with helium and the temperature raised to the desired level. At that point the pressure in the reactor was raised to operating conditions by manually injecting water through the pump. When run pressure was achieved, the pump was set in the automatic mode. The supplementary gas valve was also opened at the start of the run if syngas was used. Steam and syngas (if used) were then fed to the reactor. At the end of a run, the feed was shut off and the unit depressured.

During the run, gas analyses and cumulative dry gas volumes were obtained. From these data the carbon gasified was calculated. Assuming that the oxygen content of the char is small in relation to the oxygen content of the steam fed, the steam conversion was obtained by oxygen balance around the reactor.

For the reaction kinetics study, runs were made in the fixed bed reactor with Illinois coal catalyzed with 10 percent and 20 percent K_2CO_3 with steam as the gasifying medium. Temperatures of 1200°F and 1300°F were used and pressures varied from 0 to 500 psig. Steam flows ranged from 3 to 100 gm/hr. With these conditions, steam conversions from 10 to 80 percent and total carbon conversions from 50 to 100 percent were obtained. Material balances on hydrogen were used to check the consistency of the data. The balance closures ranged from 100 to 105 percent for typical runs.

During the runs, it was observed that the steam gasification rate was independent of pressure. The gasification rate was found to increase with an increasing rate of steam fed to the reactor. Additionally, at high steam flow rates, or low steam conversions, the gasification rate was directly proportional to the catalyst loading. One explanation for these observations is that the kinetics are controlled by a strong product inhibition. This suggests that a kinetic expression in the classical Langmuir-Hinshelwood form may be used to fit the data. It was further seen that methane and carbon dioxide were in chemical equilibrium with the other gas phase components for the conditions studied, i.e., the methanation and shift reactions are at equilibrium.

2.2.2 Kinetic Data Interpretation

The data which resulted from the above experiments were correlated using standard procedures for interpreting the results from fixed-bed, integral reactors, i.e., a measure of the extent of conversion was plotted as a function of a residence time where the residence time is defined as the reactor capacity divided by the reactant feed rate. For this work, the most meaningful measure of x, the extent of reaction, is moles carbon gasified per mole steam fed. The reactant feed rate is simply moles steam fed per unit time, $N^{\circ}_{H_2O}$. A number of measures of reactor capacity can be examined, e.g., volume, moles carbon in bed, moles potassium in bed, surface area, etc.

One series of experiments was conducted at 1300°F, 500 psig, and 20 percent K_2CO_3 on Illinois coal using six different steam rates (3, 6, 12, 24, 50, and 100 gm/hr). The measure of bed capacity which best correlates the resulting data is moles carbon remaining in the bed. These results are given in Figure 2.2-2 where x, moles carbon gasified per mole steam fed, is plotted as a function of holding time, θ, moles instantaneous bed carbon per molar steam flow rate. The data for x as a function of θ collected for different steam flow rates all mesh together to give a single curve for the fixed temperature, pressure, and catalyst loading. For each experimental run, the initial data points are at the right and move to the left as carbon is depleted from the bed. The flat region in the data at the upper right of Figure 2.2-2 represents the equilibrium limit for the carbon-steam reaction. This limit corresponds to a carbon activity of about twice that of β-graphite. The region at the lower left of the diagram shows the carbon conversions limited by the rate of reaction. The data points at the different steam rates overlap in the required manner over three orders of magnitude of residence time.

A mathematical model for the fixed bed reactor was developed based upon the observed behavior. Plug flow of gas through the bed is assumed. It is also assumed that strong product inhibition results in a high rate of gasification over a very short distance of the bed followed by a slower rate over the remaining length of the bed where higher partial pressures of products exist. This assumption leads to a simplified picture for the fixed bed reactor shown in Figure 2.2-3 which is consistent with all the observed behavior. Note, in particular, that the appropriate measure of bed capacity is the moles carbon remaining in the bed. However, it should also be noted that future work may lead to alternate models which better explain the data. In this model, the reaction proceeds so as to form a sharp "carbon burnoff front". If little or no carbon is present, gasification will not take place. Therefore, the potassium catalyst which is left behind this "burnoff front" does not contribute to the reaction rate.

FIGURE 2.2-2

EXTENT OF CARBON-STEAM REACTION AS A FUNCTION OF RESIDENCE TIME

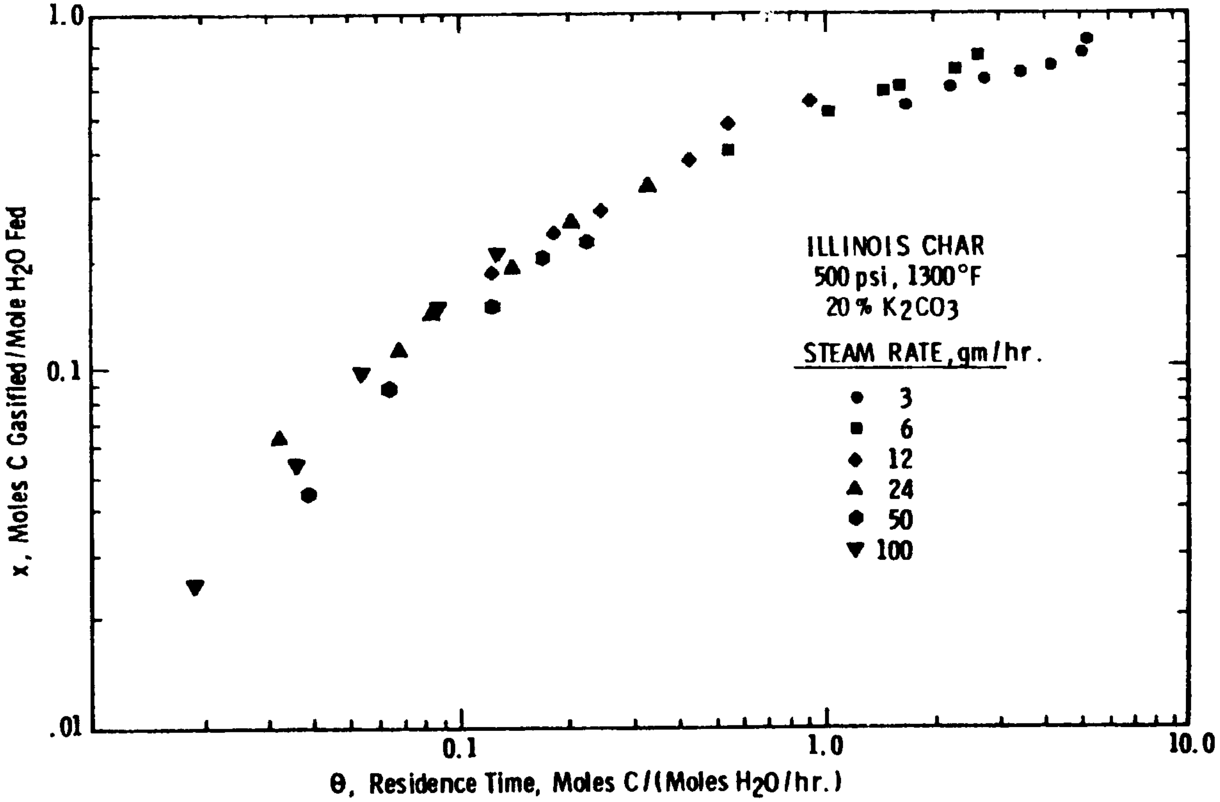
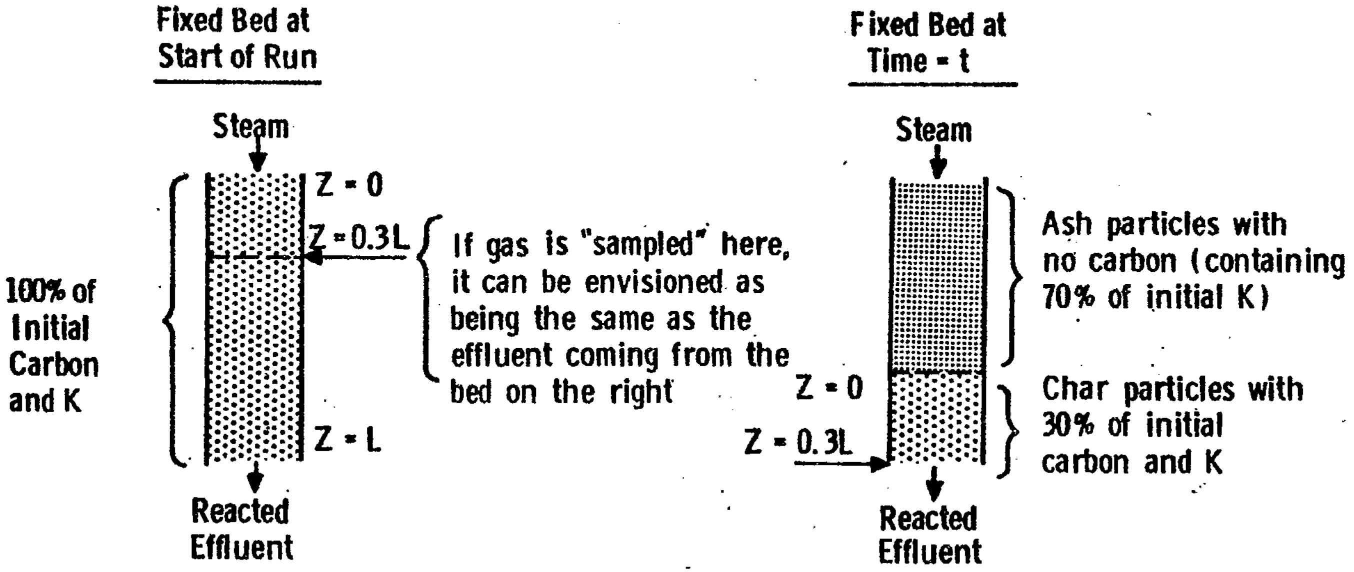


FIGURE 2.2-3

SIMPLIFIED MODEL FOR FIXED BED REACTOR IN POTASSIUM CATALYZED STEAM GASIFICATION



The equation describing conversion in the plug flow reactor is

$$\int_0^V \frac{dV}{\overset{\circ}{N}_{H_2O}} = \int_0^x \frac{dx}{-r_G} \qquad (2.2\text{-}1)$$

where V is the reactor volume, $\overset{\circ}{N}_{H_2O}$ is the molar rate of steam fed to the reactor, r_G is the molar rate of the carbon-steam gasification reaction per unit volume, and x is the extent of reaction defined as moles carbon gasified per mole steam fed. The sharp burnoff front model provides a relationship between the carbon remaining in the bed and the effective fixed bed reactor volume, i.e.,

$$n_C = C_C\, V \qquad (2.2\text{-}2)$$

where n_C is the instantaneous moles of carbon in the bed, V is the effective reactor volume, and C_C is the proportionality constant with the dimension moles carbon per unit volume. Based upon initial bed conditions, C_C will have a value of approximately 0.045 gmole/cc. Substitution of Equation (2.2-2) into Equation (2.2-1) provides

$$\frac{n_C}{\overset{\circ}{N}_{H_2O}\, C_C} = \int_0^x \frac{dx}{-r_G} \qquad (2.2\text{-}3)$$

This model may now be used for the identification of acceptable forms for the rate, r_G, and to obtain best fit values for the parameters in these expressions.

A Langmuir-Hinshelwood type expression for heterogeneous catalytic kinetics as applied to the carbon-steam reaction may be written in the generalized form,

$$r_G = \frac{k[p_{H_2O} - p_{CO}\, p_{H_2}/K_G]}{1 + \sum_i (b_i p_i + \sum_j b_{ij} p_i\, p_j)} \qquad (2.2\text{-}4)$$

where p_{H_2O}, p_{CO}, p_{H_2}, etc., represent the partial pressures of the components, k is the kinetic rate constant for the carbon-steam reaction, K_G is the equilibrium constant for this reaction (equal to twice the value of the equilibrium constant for the β-graphite-steam reaction), and the b's represent the adsorption constants, no more than four of which will be allowed to be nonzero in any one model being tested.

Equation (2.2-4), when substituted into Equation (2.2-3), gives

$$\theta = \frac{n_c}{N^{\bullet}_{H_2O}} = \frac{C_c}{k}\int_0^x \frac{dx}{R_G} + \sum_i \frac{b_i C_c}{k}\int_0^x \frac{p_i}{R_G}\,dx + \sum_i \sum_j \frac{b_{ij} C_c}{k}\int_0^x \frac{p_i p_j}{R_G}\,dx \qquad (2.2\text{-}5)$$

where the reaction driving force term in the denominator of each of the integrals is given by

$$R_G = -[p_{H_2O} - p_{CO}p_{H_2}/K_G] \qquad (2.2\text{-}6)$$

For a given conversion, the shift and methanation equilibrium relationships are sufficient to calculate the partial pressures of all components (H_2, CO, CH_4, CO_2, H_2O) in the gas phase. Using a closely spaced series of incremental values for x, the partial pressures were accurately mapped over a range of conversions. This needed to be done only once. These partial pressures were then substituted as required into the expressions under the integrals shown in Equation (2.2-5). The values of these integrals for any specified conversion are then obtained by a Simpson's rule numerical integration of the expression under the integrals.

The coefficients in front of the integrals in a series of particular forms of Equation (2.2-5) were estimated by regression analysis. The regression data base used consisted of the results of the steam gasification runs at 500 psig described above, as well as runs at 0, 100, and 250 psig and at steam rates of 6, 12, and 24 gm H_2O/hr. Two additional series of runs were conducted at 500 psig and the same three steam rates. The first was at 1200°F and 20 percent K_2CO_3, and the second was at 1300°F and 10 percent K_2CO_3. The data from these runs were used to assess the effect of temperature and catalyst loading on gasification rate.

Numerous kinetic models were formulated and tested by regression for the constants in Equation (2.2-5). These models consisted of all combinations of from one to four terms involving the partial pressures of H_2, CO, and H_2O and the cross products of the partial pressures of H_2 and CO, and H_2 and H_2O. Those which gave negative coefficients on regression were discarded as being physically unreal. Four additional models were discarded because they gave an infinite rate in the limit of zero steam conversion. The three models which remained are:

(A) $$r_G = \frac{k(p_{H_2O} - p_{CO}\, p_{H_2}/K_G)}{p_{H_2} + b_1\, p_{H_2O}} \qquad (2.2\text{-}7)$$

(B) $$r_G = \frac{k(p_{H_2O} - p_{CO}\, p_{H_2}/K_G)}{p_{H_2} + b_1\, p_{H_2}\, p_{CO} + b_2\, p_{H_2O}} \qquad (2.2\text{-}8)$$

(C) $$r_G = \frac{k(p_{H_2O} - p_{CO}\, p_{H_2}/K_G)}{p_{H_2} + b_1\, p_{CO} + b_2\, p_{H_2O}} \qquad (2.2\text{-}9)$$

All are independent of pressure. The variance of the residuals around the regression line for these are A: 0.0556, B: 0.0519, and C: 0.0562. Since Model B has a smaller variance than model A or C, it was chosen as the basis for further analysis. However, further studies should be done to better discriminate between these and possibly other kinetic expressions. The coefficients obtained by regression of Model B are:

$$\frac{C_c}{k} = 1.60 \text{ hr}$$

$$\frac{b_1 C_c}{k} = 0.337 \text{ hr/atm}$$

$$\frac{b_2 C_c}{k} = 0.095 \text{ hr}$$

These coefficients were used in Equation (2.2-5) to compute the values of θ required to achieve the various measured conversion levels. These calculated values are compared to the actual holding times in Figure 2.2-4. While there is scatter to the data, it is seen that the model provides a reasonable fit over the broad range of pressures (0-500 psig) and flowrates (3-100 gm/hr) considered.

Using the approximate value of C_c = 0.045 gmole/cc, the values for the parameters at 1300°F and 20 percent K_2CO_3 loading may be expressed as:

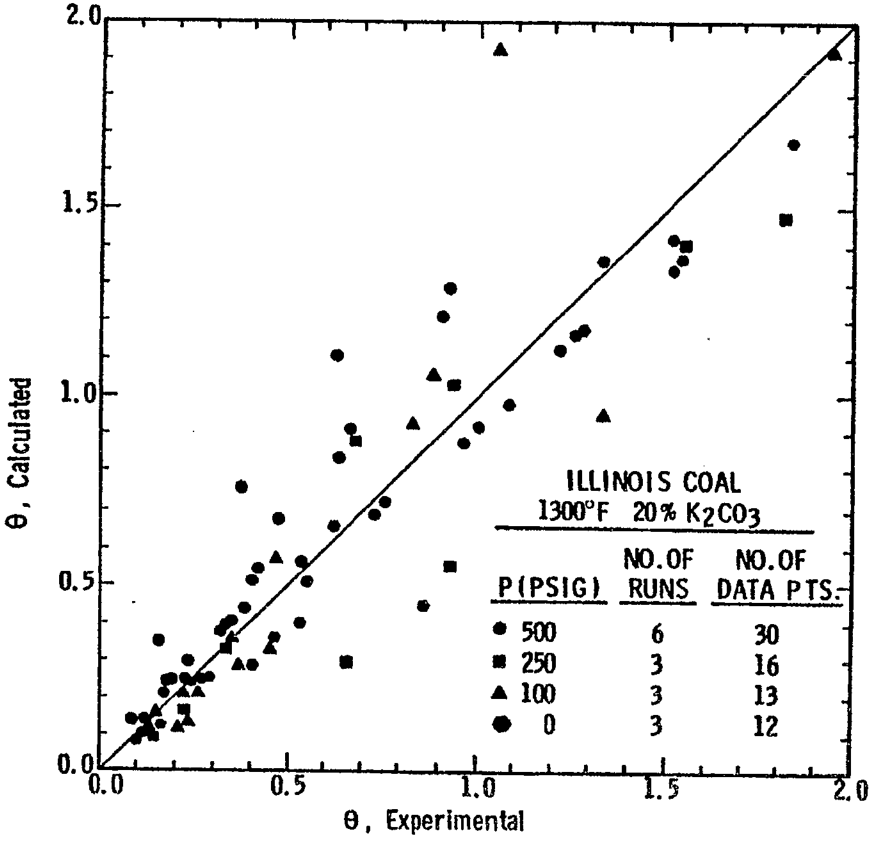
$$k = 0.0281 \ \frac{\text{gmole C}}{\text{hr}\cdot\text{cc}}$$

$$b_1 = 0.210 \text{ atm}^{-1}$$

$$b_2 = 0.0595$$

FIGURE 2.2-4

COMPARISON OF EXPERIMENTAL AND PREDICTED HOLDING TIME, θ, TO ATTAIN A GIVEN CONVERSION FOR MODEL "B"



It was found by comparing the 1200°F and 1300°F data that the rate constant, k, has an activation energy of 30 kcal/gmole in the Arrhenius expression. Furthermore, its value at the 10 percent K_2CO_3 loading was approximately half that at the 20 percent K_2CO_3 level. Hence, within this range k may be expressed as:

$$k = k_0 C_K \exp(-E/RT) \qquad (2.2\text{-}10)$$

where k_0 is the frequency factor, C_K is the moles of catalytically active potassium per unit volume, E is the activation energy, R is the universal gas constant, and T is the absolute temperature. For 20 percent K_2CO_3 on Illinois coal, the value of C_K for the fixed bed of char is typically

$$C_K = 0.0021 \text{ gmole/cc}$$

On this basis the value of the frequency factor may be computed as

$$k_0 = 6.80 \times 10^7 \text{ gmole C/hr·gmole K}$$

for

$$E = 30 \text{ kcal/gmole}$$

The ratio of holding times necessary to attain a given conversion level, x, at two different temperatures and catalyst levels is given by:

$$\frac{\theta_1}{\theta_2} = \frac{k_2}{k_1} = \frac{C_{K_2}}{C_{K_1}} \quad \exp\left[-\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \qquad (2.2\text{-}11)$$

This assumes that the temperature difference does not significantly affect the equilibrium calculation for the partial pressures. Equation (2.2-11) allows the definition of an "equivalent residence time", θ, which can be used to combine data collected at different temperatures and catalyst levels. The quantity θ^* is defined as the holding time at T^* and C_K^* which will give the same conversion as that obtained with a holding time θ at temperature T and catalyst concentration C_K. Specifically,

$$\theta^* = \theta \frac{C_K}{C_K^*} \quad \exp\left[-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \qquad (2.2\text{-}12)$$

This relationship was tested for its ability to correlate 500 psig fixed bed reaction data collected at 10 percent K_2CO_3-1300°F and 20 percent K_2CO_3-1200°F with the data base collected at 20 percent K_2CO_3-1300°F. The result is given by the data points shown in Figure 2.2-5 where conversion, x, is plotted as a function of equivalent residence time, θ^*, with all data adjusted if needed to 1300°F and 20 percent K_2CO_3. It is seen that the data appear uniformly correlated by this expression.

2.2.3 Generalized Fixed Bed Model

The above kinetic relationships apply to a pure steam feed. In order to apply them to the synthesis gas recycle case, they must be generalized for mixed gas input to the fixed bed. This may be done by writing the differential equations describing the molar flow of each molecular species through the bed and numerically integrating these over the effective volume. These equations are:

$$\frac{d\,N_{H_2}}{dz} = A\,(-3\,r_M + r_S + r_G) \qquad (2.2\text{-}13)$$

$$\frac{d\,N_{CO}}{dz} = A\,(-r_M - r_S + r_G) \qquad (2.2\text{-}14)$$

$$\frac{d\,N_{CH_4}}{dz} = A\,r_M \qquad (2.2\text{-}15)$$

$$\frac{d\,N_{CO_2}}{dz} = A\,r_S \qquad (2.2\text{-}16)$$

$$\frac{d\,N_{H_2O}}{dz} = A\,(r_M - r_S - r_G) \qquad (2.2\text{-}17)$$

where N_i is the molar flow rate of component i, z is the distance down the bed, A is the cross-sectional area of the bed, and r_M, r_S, and r_G are the rates of the methanation, shift, and carbon-steam gasification reactions, respectively, expressed as moles per unit reactor volume per unit time.

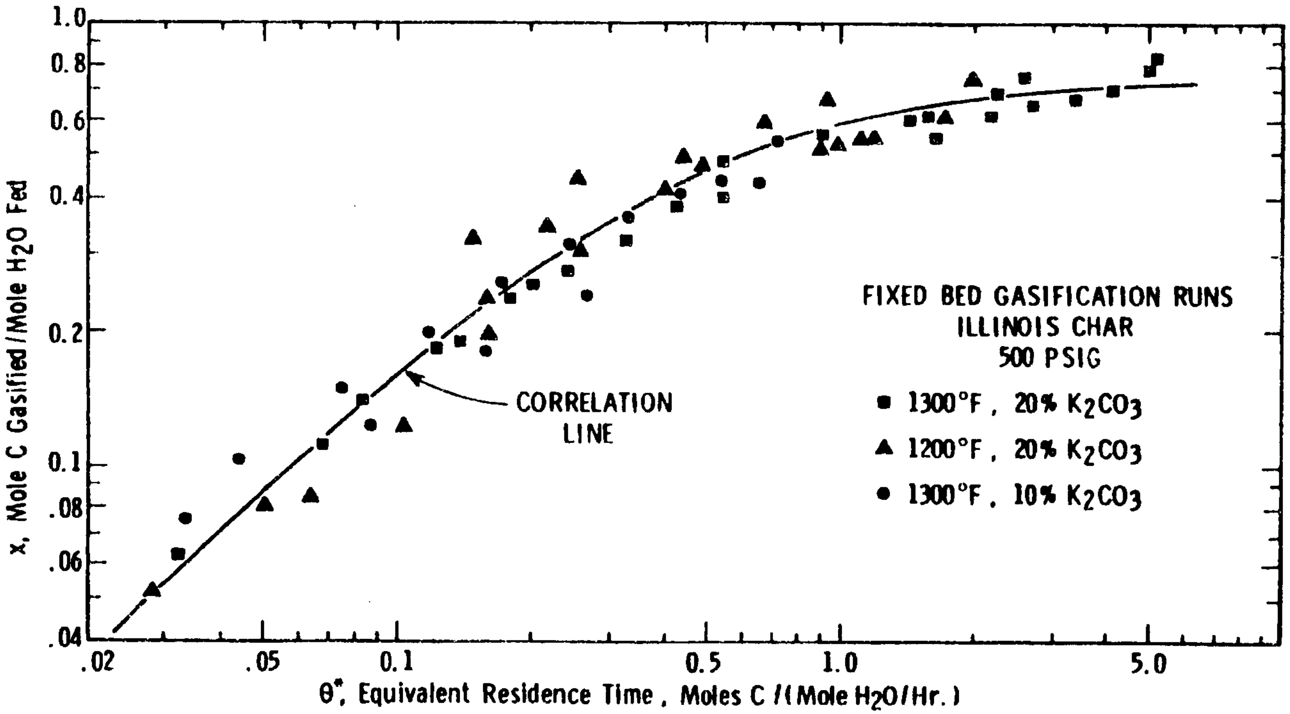
The reaction rate expressions used for the shift and methanation reactions are:

$$r_S = k_S\,(p_{CO}\,p_{H_2O} - p_{CO_2}\,p_{H_2}/K_S) \qquad (2.2\text{-}18)$$

$$r_M = k_M\,(p_{CO}\,p_{H_2}{}^3 - p_{CH_4}\,p_{H_2O}/K_M) \qquad (2.2\text{-}19)$$

FIGURE 2.2-5

COMPARISON OF FIXED BED DATA WITH MODEL PREDICTION FOR STEAM FEED



where k_S and k_M are the respective rate constants, and K_S and K_M are the respective equilibrium constants. These reactions may be forced essentially to equilibrium by assigning arbitrarily large values to the rate constants. The reaction rate expression used for the potassium catalyzed carbon-steam reaction is obtained by combining Equations (2.2-8) and (2.2-10):

$$r_G = \frac{k_0 C_K \exp(-E/RT) [p_{H_2O} - p_{CO} p_{H_2}/K_G]}{p_{H_2} + b_1 p_{CO} p_{H_2} + b_2 p_{H_2O}} \qquad (2.2\text{-}20)$$

The ordinary differential Equations (2.2-13)-(2.2-17) were numerically integrated by a Runga-Kutta-Fehlberg procedure for a series of cases considering pure steam fed to a fixed bed reactor at 500 psig, 1300°F, and $C_K = 0.0021$ gmoles potassium per cc (corresponding to 20 percent K_2CO_3 on Illinois coal). The conversion, x, was determined at various distances, z, down the bed from:

$$x = \frac{N_{CO} + N_{CH_4} + N_{CO_2}}{\overset{\circ}{N}_{H_2O}} \qquad (2.2\text{-}21)$$

The residence time corresponding to each conversion was computed as:

$$\theta = \frac{C_c A z}{\overset{\circ}{N}_{H_2O}} \qquad (2.2\text{-}22)$$

The integrations performed in this manner for various steam flowrates overlapped to give the single correlation line shown in Figure 2.2-5. This line is seen to provide a reasonable fit to the data.

To test the predictive capability of the kinetic model with a mixed gas feed, two fixed bed gasification runs were made with steam plus syngas (H_2 + CO) at 1300°F. One run was made with 5 liters per hour syngas at 500 psig. The second was made with 15 liters per hour syngas at 100 psig. Both runs were made with 12 grams per hour steam feed. In both cases the syngas composition was 75 mole percent H_2 and 25 mole percent CO. In these experiments the conversion, x, was computed as

$$x = \frac{N_{CO} + N_{CH_4} + N_{CO_2} - \overset{\circ}{N}_{CO}}{\overset{\circ}{N}_{H_2O}} \qquad (2.2\text{-}23)$$

where $\dot{N}_{CO}$ is the molar rate of carbon monoxide fed to the reactor. The residence time was computed by Equation (2.2-22). A comparison between the predicted and experimental conversions for these two experiments is shown in Figure 2.2-6. Good agreement is observed in the 500 psig case. The conversions obtained here are essentially the same as those observed above for pure steam feed. At 100 psig with higher syngas flow, the data show a lower conversion than at 500 psig for the same residence time. It is also seen that the model underpredicts the actual conversion. This may be due, in part, to the use of parameters which are derived from pure steam data.

In summary, an empirical Langmuir-Hinshelwood kinetic model for the potassium catalyzed gasification of Illinois No. 6 bituminous coal has been developed. This model provides a good fit to fixed bed reactor data over pressures ranging from atmospheric to 500 psig and a 30-fold range of steam flow rates. It also predicts conversions for the temperature range 1200°F to 1300°F and catalyst loadings from 0.1 to 0.2 grams K_2CO_3 per gram of coal. For the catalyst levels examined, the gasification rate was proportional to the amount of catalyst present. Additional studies need to be performed over a broader range of catalyst loadings to determine the limits of this relationship. It was also shown that these kinetics can be applied to predict trends in conversion for H_2O, H_2, and CO mixed gas feeds.

The kinetic expression obtained has been shown to have adequate predictive capabilities in the range of interest. It is in a form which can be used directly in the development of models for fluid bed gasification reactors, as previously discussed in Section 1.3.6 of this report. The correlation lines provided by the fixed bed potassium catalyzed material may also be used as a reference for comparison of the reactivities of other catalytic systems.

2.2.4 Alternate Catalyst Systems

Additional fixed bed gasification experiments focused on the use of Na_2CO_3 and mixed Na_2CO_3/K_2CO_3 catalysts. The incentive for using Na_2CO_3 is that its cost is only 20-30% of the cost of K_2CO_3. The activity of sodium carbonate was found to be significantly lower than that of potassium carbonate, especially at high pressure. Also, analysis of the char streams from the mixed catalyst runs showed that potassium is selectively tied up by coal minerals, reducing the incentive for using mixed catalyst. As a result of these findings, potassium carbonate was selected for catalyst recovery and recycle operations. The catalyst recovery operations identified KOH and K_2S, as well as K_2CO_3, as the predominant forms of potassium following gasification. The experimentally measured reactivity of KOH was essentially equivalent to K_2CO_3 while K_2S showed a lower reactivity. It was also determined that Wyodak coal is as reactive as Illinois coal when impregnated with K_2CO_3 or KOH.

Initially, carbon gasification rate data were obtained for catalyst loadings of 15 wt.% Na_2CO_3 and 5 wt.% Na_2CO_3/5 wt.% K_2CO_3. These data are compared in Figure 2.2-7 with correlation lines for K_2CO_3 catalyst from multiple runs made prior to the start of this predevelopment program. Some check runs were also made with 10 wt.% K_2CO_3. The moles of carbon gasified per mole of steam fed is plotted on the ordinate, and the relative steam

FIGURE 2.2-6

COMPARISON OF FIXED BED DATA WITH MODEL PREDICTIONS FOR STEAM/SYNGAS FEED

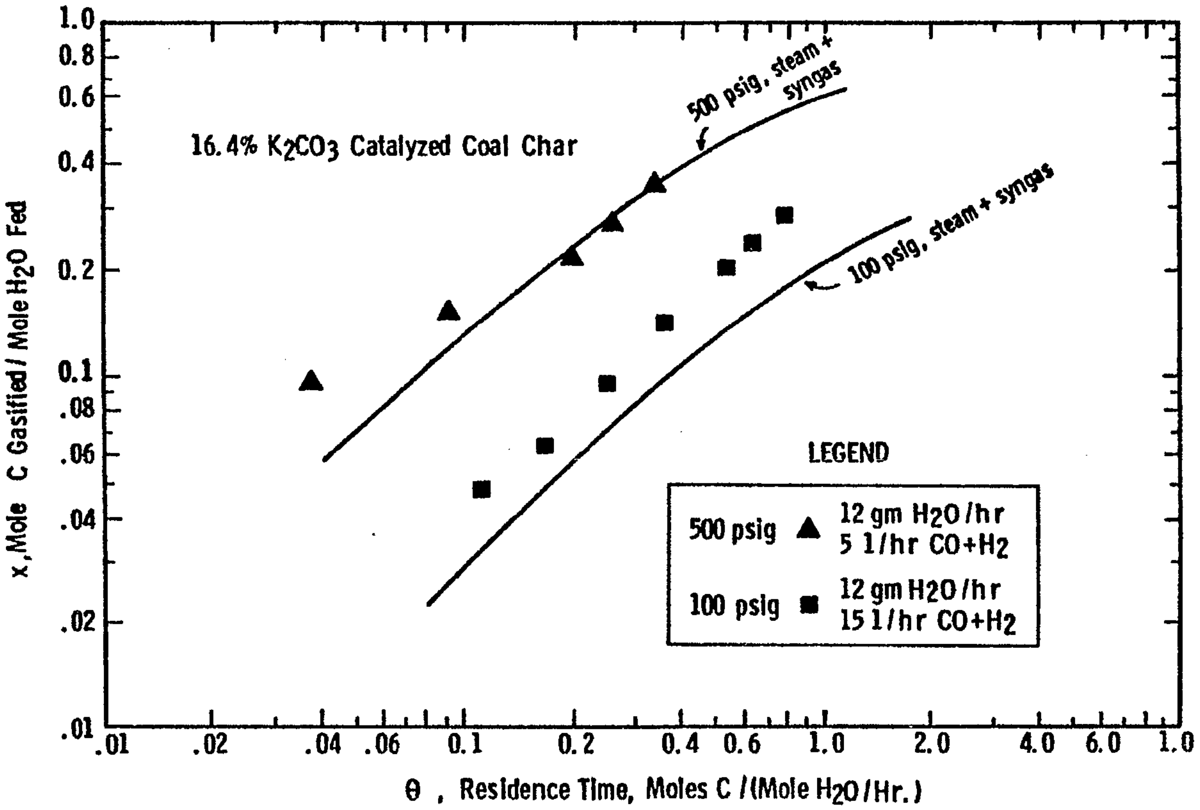
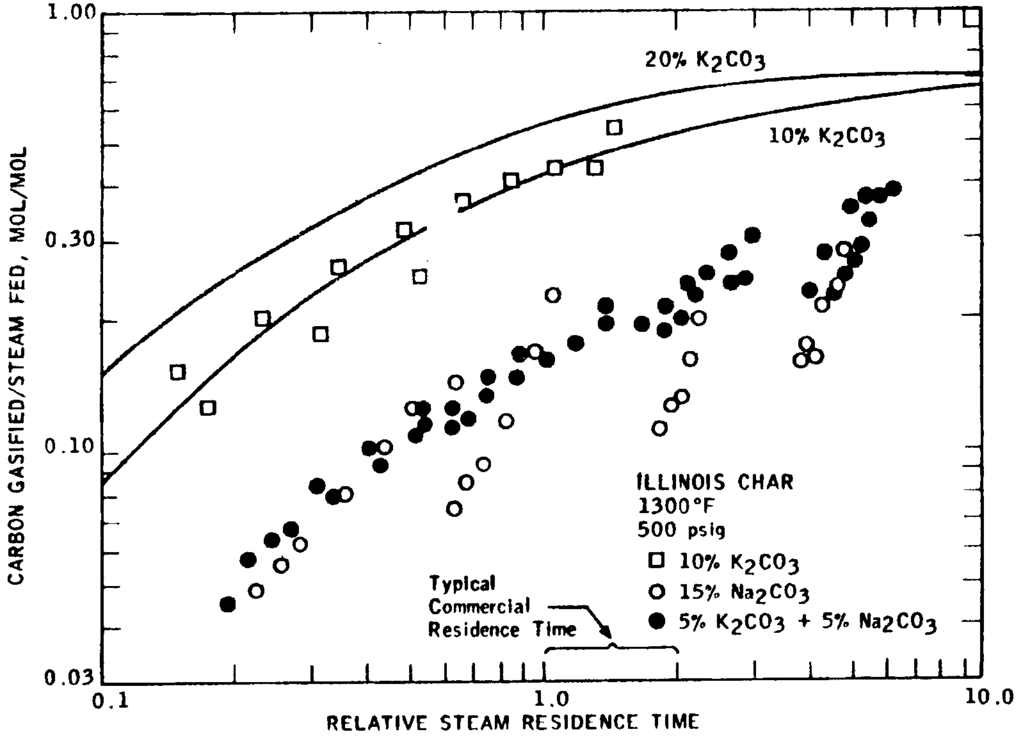


FIGURE 2.2-7

GASIFICATION RATES IN FIXED BED TESTS



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residence time is plotted on the abscissa. For all runs, the temperature was 1300°F, and the pressure was 500 psig.

The data from individual runs of the 5% K_2CO_3/5% Na_2CO_3 mixed catalyst form a continuous curve relating carbon gasified/steam fed to relative steam residence time over a wide range of initial steam rates. This curve is similar to that obtained using K_2CO_3 catalyst except that the curve has been displaced along the abscissa. This displacement is a measure of the reduced activity for the mixed catalyst. The data for the pure Na_2CO_3 catalyst, on the other hand, form discrete curves for each steam rate. Thus, these runs suggest that the Na_2CO_3 catalyst does not maintain its activity during a run as well as K_2CO_3.

Gasification rate data for 50/50 weight mixtures of Na_2CO_3 and K_2CO_3 at levels of 10, 15, and 20 total wt.% on coal are compared with the correlation line for multiple runs using 10% K_2CO_3 in Figure 2.2-8. A fundamental measure of the relative activity of the two catalysts is the ratio of residence times required to achieve a given level of moles carbon gasified/mole steam fed (effective steam conversion). As expected, reactivity increases as catalyst loading increases. Based upon the data obtained, the 5% Na_2CO_3/5% K_2CO_3 mixed catalyst has about 20-25 percent of the activity of the 10% K_2CO_3 catalyst. With 10% Na_2CO_3/10% K_2CO_3 catalyst, only about one-fourth the residence time is required to reach the same value of carbon gasified/steam fed as with 5% Na_2CO_3/5% K_2CO_3 catalyst. More importantly, however, the 10% Na_2CO_3/10% K_2CO_3 catalyst has essentially the same activity (within experimental accuracy) as 10% K_2CO_3 alone. Thus, at the reaction conditions of interest, Na_2CO_3 has little catalytic activity when used in combination with K_2CO_3.

One of the original incentives for using the mixed catalyst rather than K_2CO_3 alone was a belief that sodium would act as a scavenger for aluminum compounds in the coal. These aluminum compounds have been found to tie up a portion of the potassium catalyst as catalytically inactive aluminosilicates. Analysis of the char residues from the mixed catalyst runs revealed that while some sodium is initially tied up, the sodium is displaced by the more active potassium as carbon conversion increases. Figure 2.2-9 shows this progressive tie-up for the 20 wt.% mixed catalyst. Similar results obtained for the 15 wt.% and 10 wt.% mixed catalyst are shown in Figure 2.2-10 and 2.2-11. Thus, at high carbon conversions, only small amounts of sodium are present as aluminosilicates. Since with a mixed Na_2CO_3/K_2CO_3 catalyst, the makeup required to compensate for catalyst tied up with the ash would still be essentially all K_2CO_3, there is little incentive for using Na_2CO_3 in admixture with K_2CO_3.

Data have also been obtained in the fixed bed reactor on the steam gasification behavior of Illinois No. 6 coal impregnated with 16% K_2CO_3, 10% KOH, and 12% K_2S by weight on coal. In addition, data were obtained on the gasification rate of Wyodak coal impregnated with 15% K_2CO_3 and 12% KOH by weight. As discussed below, the results of these tests indicate that KOH is equivalent to K_2CO_3 on a molar basis when impregnated on both Illinois and Wyodak coal. Wyodak coal impregnated with either KOH or K_2CO_3 behaves essentially the same as Illinois coal. Illinois coal treated with K_2S yields a lower reactivity than coal treated with either KOH or K_2CO_3. This may be the result of the oxidation of K_2S to an inactive sulfate form by the pure steam atmosphere.

FIGURE 2.2-8

FIXED BED GASIFICATION RUNS

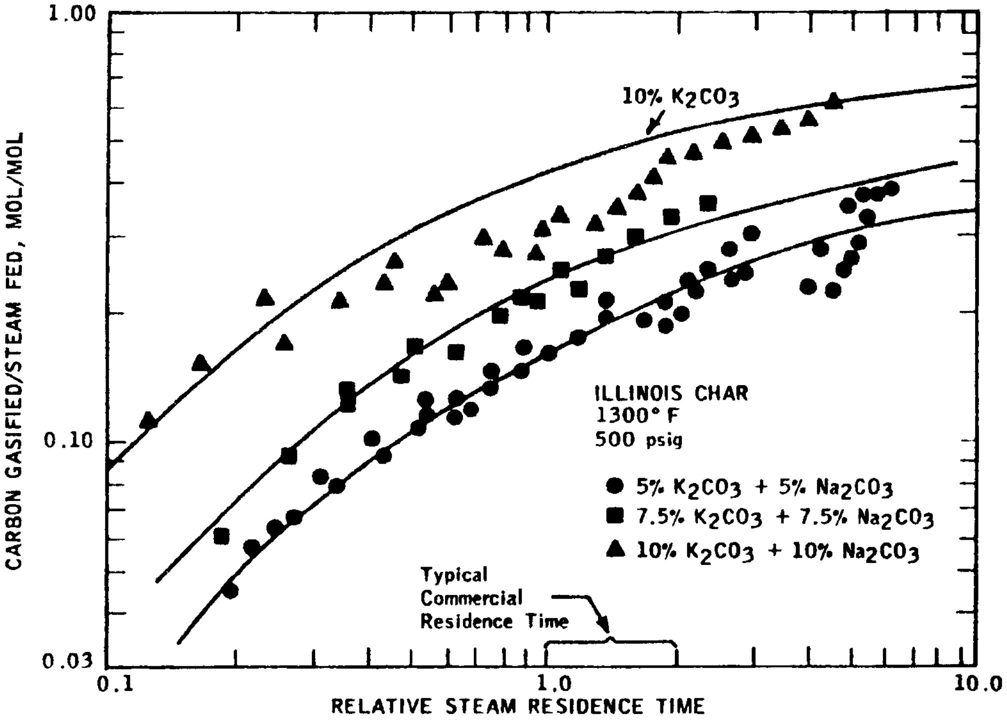

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FIGURE 2.2-9

CATALYST RECOVERY IN 20 WT.% MIXED CATALYST SYSTEM

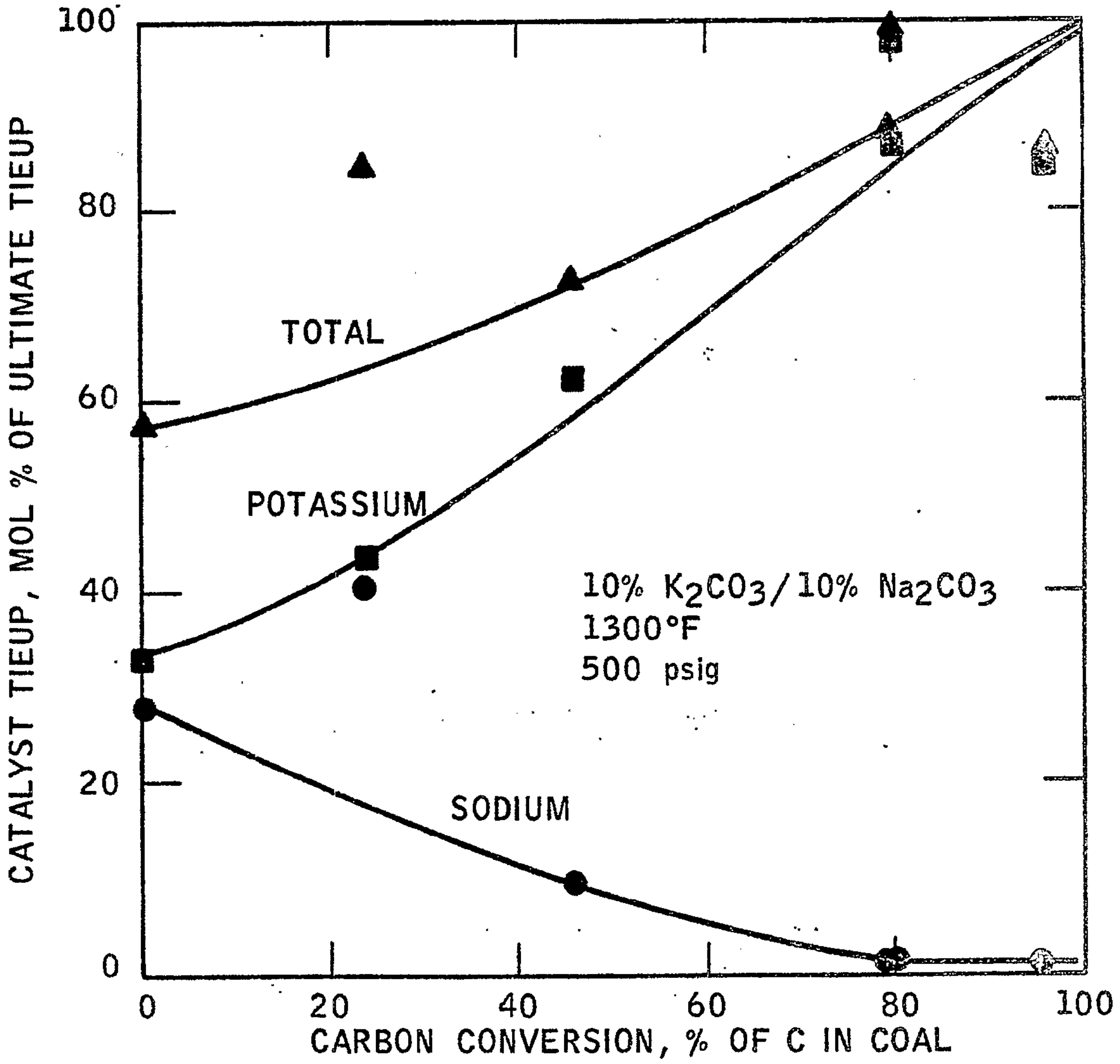

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FIGURE 2.2-10

CATALYST RECOVERY IN 15 WT.% MIXED CATALYST SYSTEM

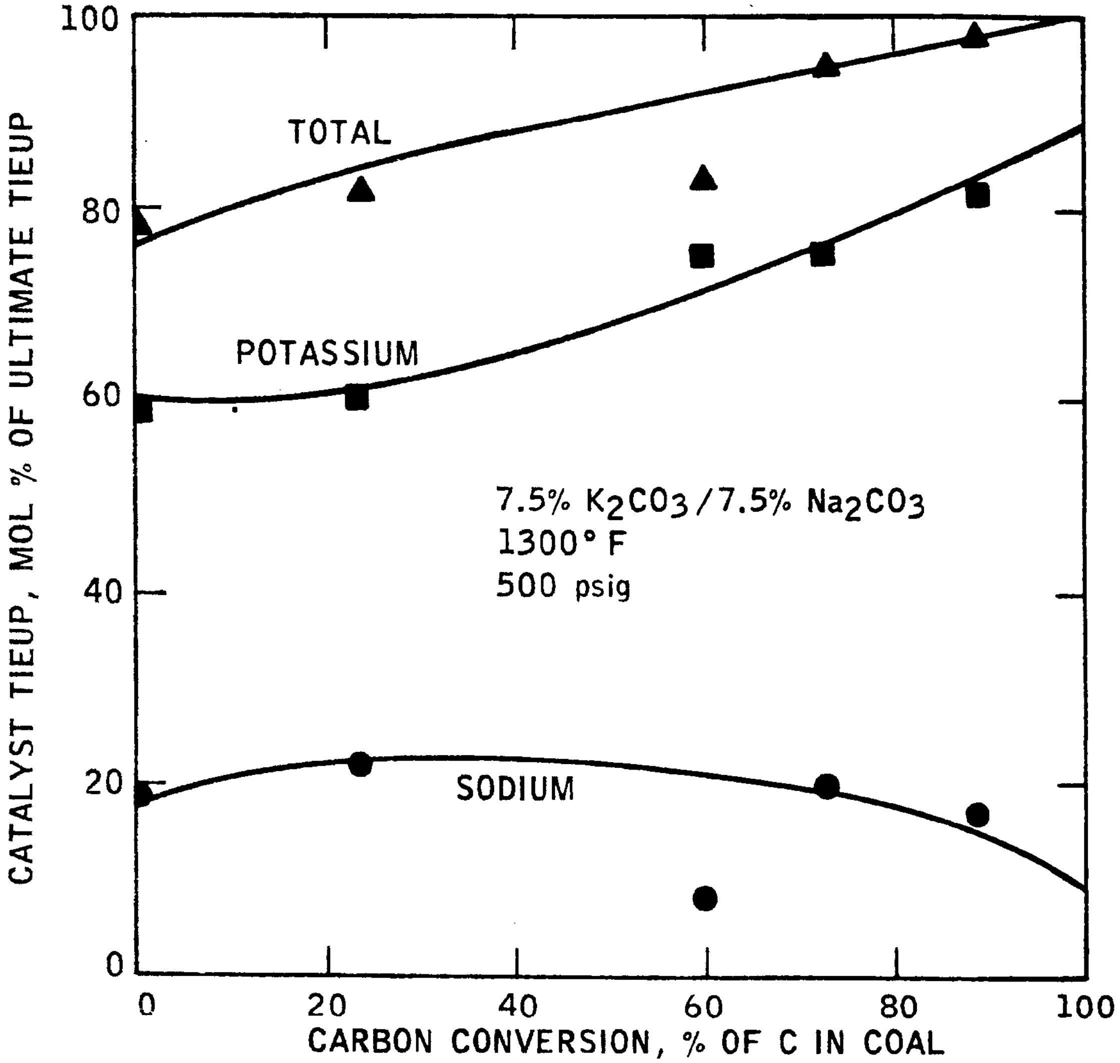

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FIGURE 2.2-11

CATALYST RECOVERY IN 10 WT.% MIXED CATALYST SYSTEM

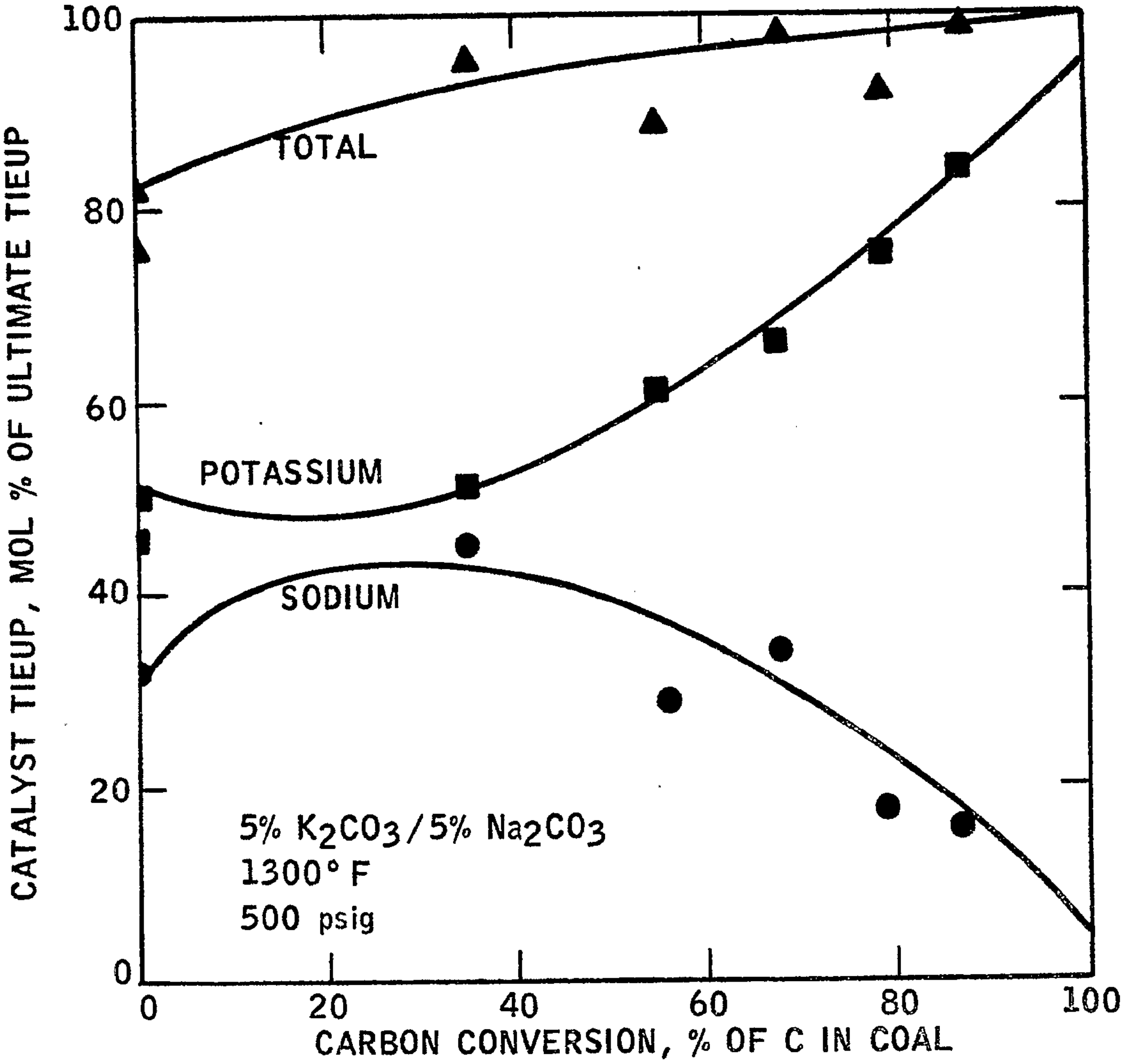

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Figure 2.2-12 shows the gasification rates of Illinois coal impregnated with 16% K_2CO_3, 10% KOH (12% K_2CO_3 equivalent), and 12% K_2S (15% K_2CO_3 equivalent) as obtained in the fixed bed reactor at 1300°F and 500 psig. The plot represents conversion expressed as moles of carbon gasified per mole of steam fed versus residence time expressed as moles carbon in the bed divided by moles steam fed per hour. Also shown on the plot are correlation lines for 12% and 16% K_2CO_3 which have been estimated from the fixed bed kinetic model. The data obtained with 16% K_2CO_3 closely approximates the predicted reactivity of Illinois coal with this catalyst level. The 10% KOH loading yielded reactivities which are similar to those predicted for a 12% K_2CO_3 (this K_2CO_3 loading represents equivalent moles of alkali per coal feed). The reactivity of Illinois coal impregnated with 12% K_2S (15% K_2CO_3 equivalent) yielded significantly lower reactivity than an equivalent amount of K_2CO_3. Two possibilities for this behavior exist: either K_2S is a poor catalyst or the pure steam atmosphere oxidizes the K_2S to an inactive sulfate form. Future work should focus on possible forms of K_2S in the gasifier under reducing conditions.

In Figure 2.2-13, the reactivities of Wyodak coal impregnated with 15% K_2CO_3 and 12% KOH are shown. As the plot indicates, these catalyst loadings on Wyodak coal are essentially equivalent. In addition, 15% K_2CO_3 on Wyodak is essentially equivalent to 15% K_2CO_3 on Illinois. The scatter in the KOH data is most likely due to uneven impregnation of the sample.

2.3 RECOVERY OF WATER SOLUBLE CATALYST

Bench scale studies on water soluble catalyst recovery focused on the following objectives: (1) to identify the chemical forms of potassium present in the recovered catalyst solution, (2) to determine how recovery of water soluble potassium in the Catalyst Recovery Unit (CRU) could be improved, and (3) to learn more about the physical and chemical effects occurring in catalyst leaching. Also, the effect of residence time on water soluble catalyst recovery was investigated for use in the Catalytic Coal Gasification Study Design.

2.3.1 Chemical Forms of Water Soluble Potassium

Initial investigations revealed that water soluble potassium is present in solution as K_2CO_3, KOH, and potassium-sulfur compounds. Although the proportions of K_2CO_3 and KOH vary with pH, these two compounds together constitute 75-85% of the water soluble potassium in solution. The interconversion of these two compounds is not important, as both are active gasification catalysts.

The remaining 15-25% of the water soluble potassium is present in solution as sulfur compounds. Current evidence indicates that K_2S is the predominant potassium-sulfur compound on fresh gasifier char, but this compound is readily oxidized in air to $K_2S_2O_3$ and K_2SO_4. This oxidation was demonstrated in an experiment in which char samples were withdrawn from the FBG under a nitrogen blanket and then leached with water, again under an inert atmosphere. The results were then compared with samples withdrawn under partial blanketing. The table below summarizes the leaching results. The hydroxide analyses were obtained by difference.

FIGURE 2.2-12

CATALYTIC GASIFICATION OF ILLINOIS COAL

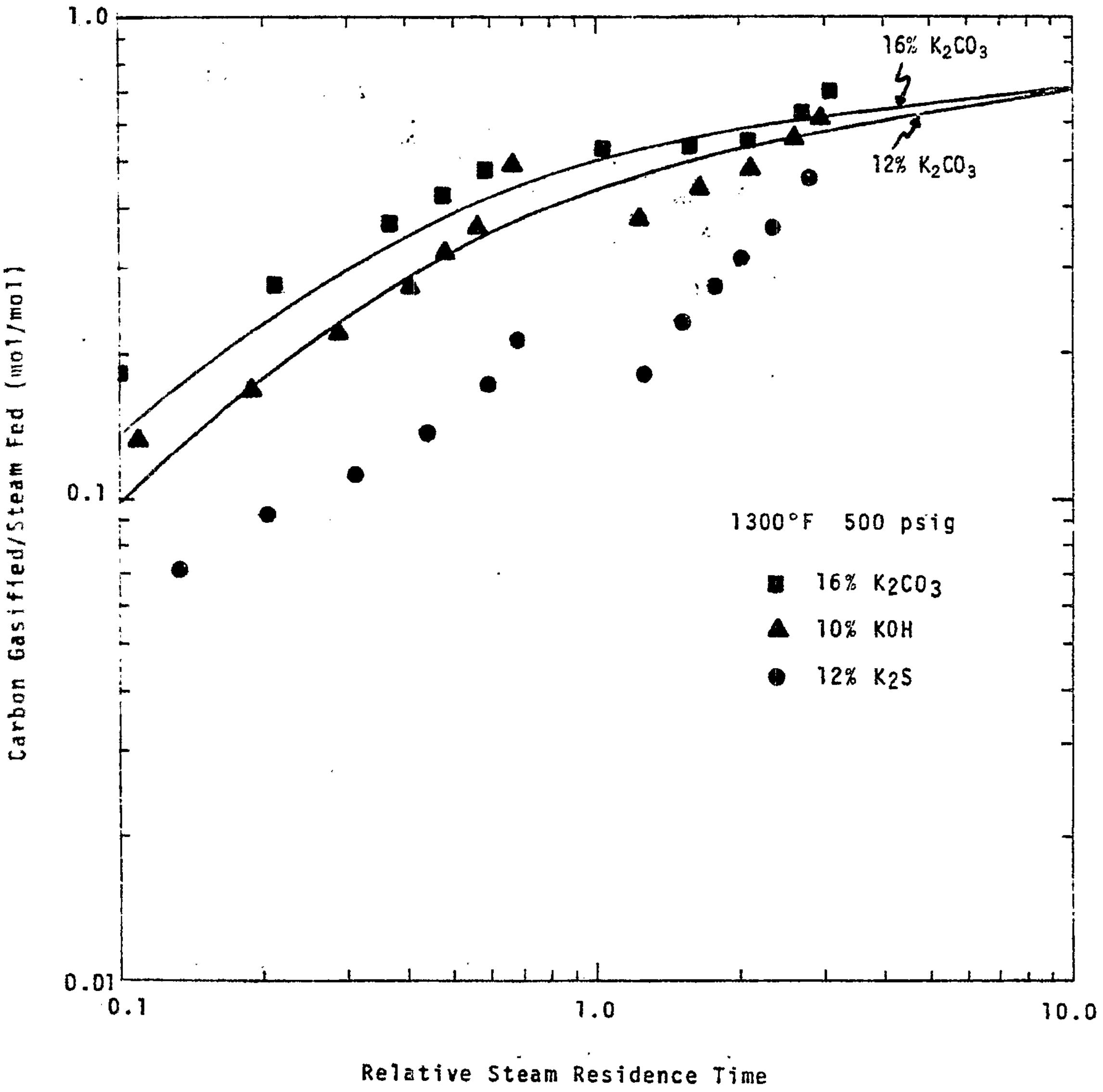

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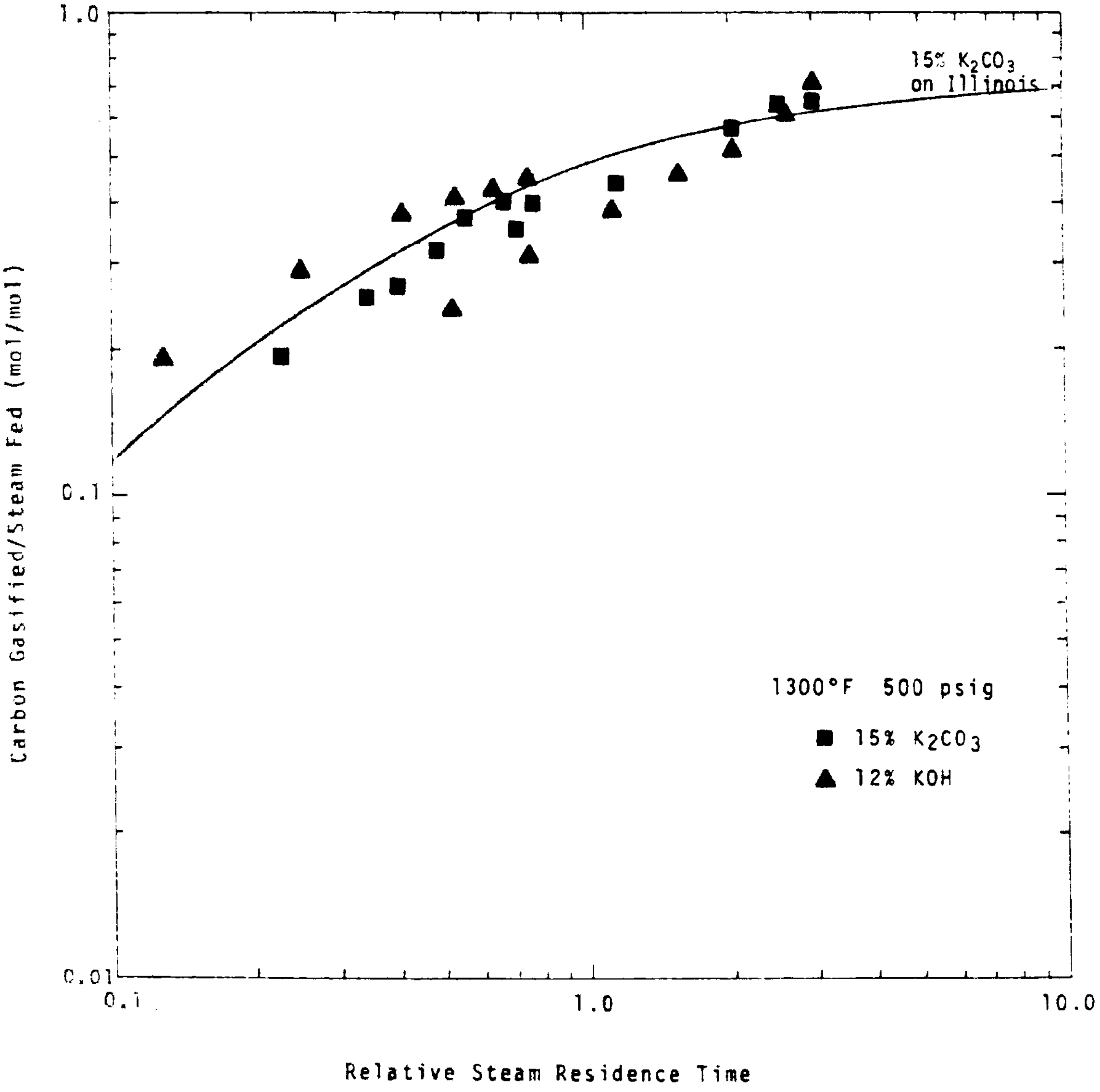
FIGURE 2.2-13

CATALYTIC GASIFICATION OF WYODAK



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Percent of K^+ Tied up with Various Sulfur Forms
Species in Leaching Solution

	Partial Blanketing						Complete Blanketing	
Sample No.	1	2	3	4	5	6	7	8
Sulfate Sulfur	4.7	3.3	3.8	4.0	2.8	5.7	1.0	0.2
Sulfide Sulfur	2.9	7.9	7.1	6.7	5.6	8.8	12.0	15.7
Thiosulfate Sulfur	15.5	3.5	9.9	9.1	9.5	11.5	3.0	0.9
Carbonate	47.6	45.8	53.1	53.8	60.4	31.7	65.0	39.3
Hydroxide	29.3	39.5	26.1	26.4	21.7	42.3	19.0	43.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

In order to qualitatively assess the rate at which the oxidation occurs, another brief study was performed. Samples of residue which had been withdrawn from the gasifier in an inert atmosphere were exposed to air for varying periods of time by spreading the samples on a flat pan. The samples were then washed with a large excess of water (20-fold) and the concentrations of sulfur compounds in solution were determined. These data are shown below.

Time of Air Exposure Before Leaching	Concentration, ppm		
	Sulfide Sulfur	Thiosulfate Sulfur	Sulfate Sulfur
None	1050	125	15
10 Min.	230	680	375
3 hrs.	50	1240	500

It is evident that, relative to a sample which had not been exposed to air, even a ten minute exposure resulted in a substantial reduction in the level of sulfide sulfur and an accompanying increase in the concentrations of the thiosulfate and sulfate forms. After three hours of exposure, 95% of the sulfide sulfur was converted to oxidized sulfur forms. However, fresh char withdrawn without contacting air produced little sulfate and thiosulfate sulfur; most of the sulfur in solution was in the sulfide form. Thus, K_2S would be the predominant sulfur form in a commercial unit where ash-char residue would be withdrawn from the gasifier and leached without exposure to air. Also, depending on the type of coal drier employed, the sulfide form could be converted to K_2SO_4, a significantly less active form than K_2S. More data are needed to fully assess these effects.

One alternative to the recyle of K_2S is the stripping of the recovered catalyst solution with CO_2 to convert K_2S from the sulfide form to the carbonate form:

$$K_2S + CO_2 + H_2O \rightarrow K_2CO_3 + H_2S$$

The effect of CO_2 acidification on the water washing of ash/char residue was examined for a residue obtained from a Fluid Bed Gasifier run with 15 wt.%

K_2CO_3 on Illinois coal. Care was taken to prevent air exposure and oxidation of the residue. Ten grams of the residue were added to 250 ml of H_2O and the slurries were exposed to either a CO_2 or N_2 atmosphere at 100°C for three hours. Analysis of the solution and residual char are shown below.

Atmosphere	N_2	CO_2
	- - Millimoles	- -
Solution		
Sulfide	5.0	<0.1
Total Sulfur	5.9	1.2
K	54	51
Si	6	0.7
Char		
Residual Potassium	23	25
Total Sulfur	10	11

Acidification with CO_2 removed essentially all of the sulfide sulfur and reduced the total sulfur in solution by at least a factor of five. The CO_2 treatment also reduced the silica in solution by a factor of ten. The treatment had no effect on the potassium or sulfur remaining on the char. Thus, it would appear that CO_2 stripping will be effective in converting recovered K_2S to K_2CO_3. As a result of this finding, the FBG pilot plant Catalyst Recovery Unit was modified to allow for CO_2 stripping of the recycle solution.

2.3.2 Improvement of Catalyst Recovery from the CRU

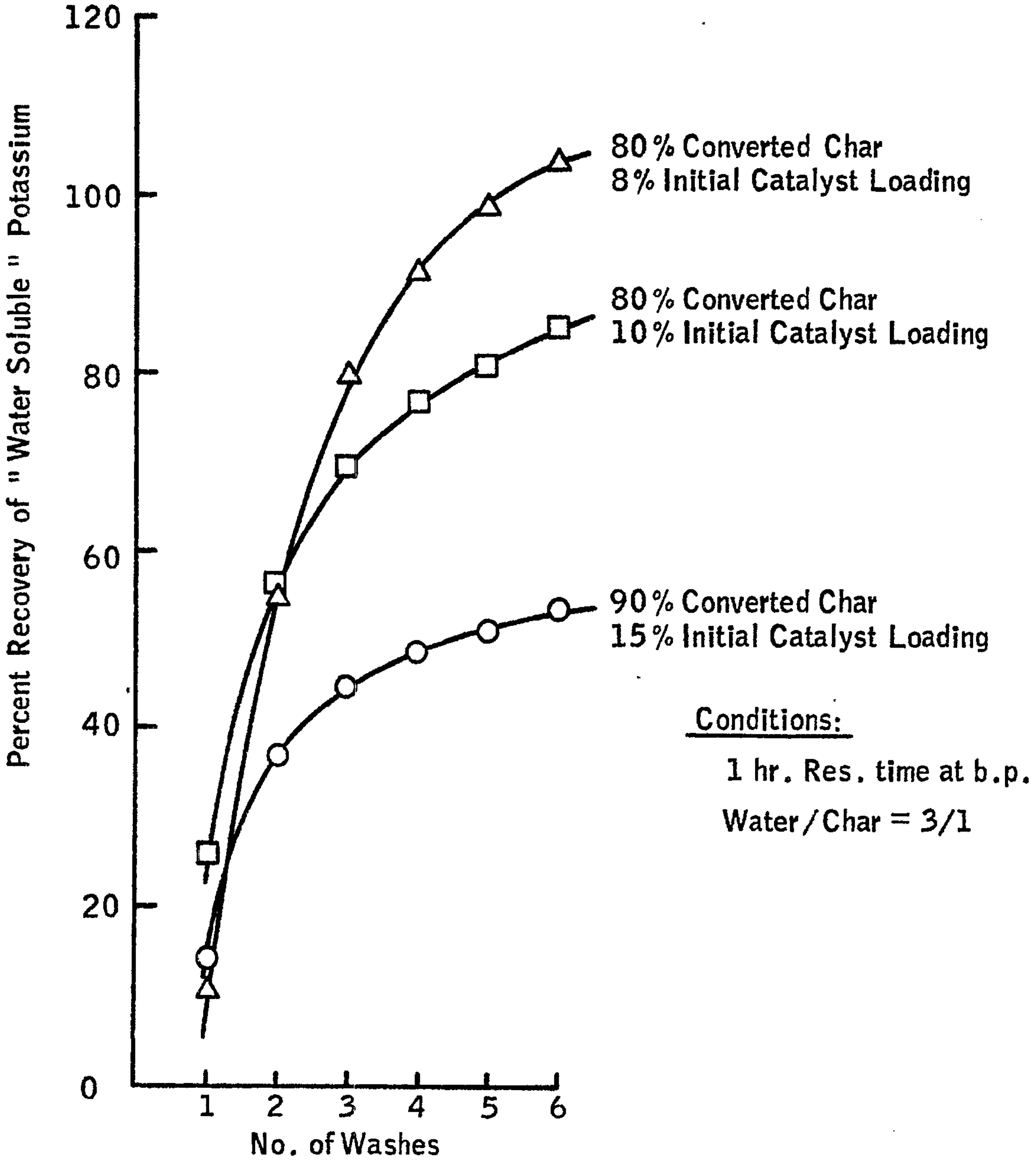
Additional catalyst recovery studies were initiated to investigate lower-than-expected recoveries of water soluble catalyst obtained in the CRU during catalyst recycle operations. In order to determine how recovery could be improved, several runs were conducted in which FBG char was serially boiled with portions of distilled water. Fresh distilled water was used for each wash (i.e., a cross-current extraction), and the water/char ratio was 3:1 on a weight basis.

Figure 2.3-1 shows the recoveries of water-soluble potassium achieved for 80% and 90% converted chars. Apparently, it is more difficult to remove the "water soluble" potassium from the more highly converted char. It was postulated that this behavior is due to exposure of the char to air. Highly converted chars are very reactive due to the high effective catalyst loading on the remaining carbon residue. When exposed to air, these chars react with oxygen and/or water vapor in the air, become quite hot, and occasionally ignite spontaneously. Although some precautions are taken to prevent exposure of the char to air, it is possible that sufficient air may leak into the char storage containers over a period of time to react with the char and significantly alter the behavior of the char during water washing.

In order to test this theory, a sample of highly converted (90%) char was withdrawn from the FBG. Particular care was taken to cool the char and keep

FIGURE 2.3-1

POTASSIUM RECOVERY BY CROSS-CURRENT WATER WASHING AT LOW WATER/CHAR RATIOS



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it under inert conditions. The char was then washed three times with low water/char ratios in a nitrogen atmosphere. Then, in order to determine the effect of air exposure on recovery, the procedure was repeated with samples of the same char that had been exposed to air for specific lengths of time. The results are shown in Figure 2.3-2 and compared to the results obtained for an older, unblanketed char with a catalyst loading and conversion similar to the fresh char. The unexposed char showed more than twice the potassium recovery of the older char after three washes, indicating that air exposure is a critical factor in the recovery of water-soluble catalyst.

The fresh char which was exposed to air for 30 minutes also showed a lower potassium recovery than the unexposed char. In addition, even after 30 minutes exposure, the char was still quite warm. This indicated that a reaction was still occurring. The data for the sample with 24 hour air exposure are very significant since both the location of the recovery curve and its shape are intermediate between the 30 minutes and 3 month curves. These findings indicate that the reaction responsible for reduced recovery does not reach completion rapidly, but continues to occur for several hours, if not longer, after initial exposure.

It is clear that the oxidation of sulfide cannot explain the reduced recoveries obtained after air exposure since both potassium thiosulfate and potassium sulfate are soluble in hot water. Also, since sulfur compounds constitute only 15-25% of the water soluble potassium, it would be impossible to attribute a 50% reduction in catalyst recovery to sulfur conversion. Therefore, investigations were undertaken to find another mechanism by which air exposure affects recovery. Investigations were made into the "fundamentals" of water washing. Several runs were conducted in which FBG char was serially washed at a water/char ratio of 50:1. Although this ratio is not commercially viable, the results obtained are very interesting. The results of one series of washes are shown in Figure 2.3-3. Notice that the first wash removes slightly more potassium than the amount analyzed as "water-soluble". This is expected since "water-soluble" potassium is determined by a separate analysis in which one gram of char is washed with 250 grams of distilled water, and the extracted potassium measured. The "water-soluble" analysis and the amount of potassium removed in our laboratory test agree within 10 percent.

The surprising fact about the data shown in Figure 2.3-3, however, is that an amount of potassium far exceeding the "water-soluble" limits can indeed be removed by water washing. Unfortunately, such recovery of "water soluble" potassium is only possible with large amounts of water and long contact times between the water and char. One possible explanation for this behavior is that the "insoluble" potassium remaining on the char (principally in the form of aluminosilicates) really has a small finite solubility, and thus, can be removed by water washing. Another explanation is that some of the residual potassium is held on active char sites by ion-exchange. The displacement of this potassium by hydrogen ions in the water wash is difficult, especially in the basic potassium solution.

As a test of this ion-exchange hypothesis, one series of cross-current washes was carried out using a saturated calcium hydroxide solution instead of distilled water. The results of this test are shown in Figure 2.3-4

FIGURE 2.3-2

EFFECT OF AIR EXPOSURE ON POTASSIUM RECOVERY BY WATER WASHING

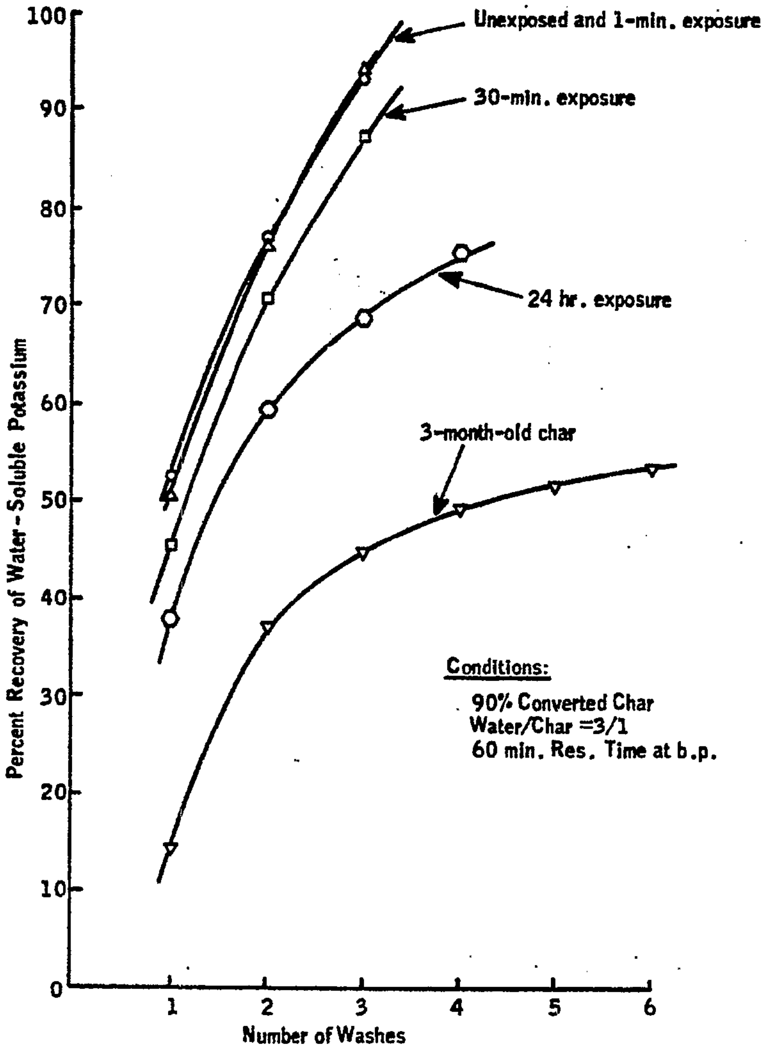

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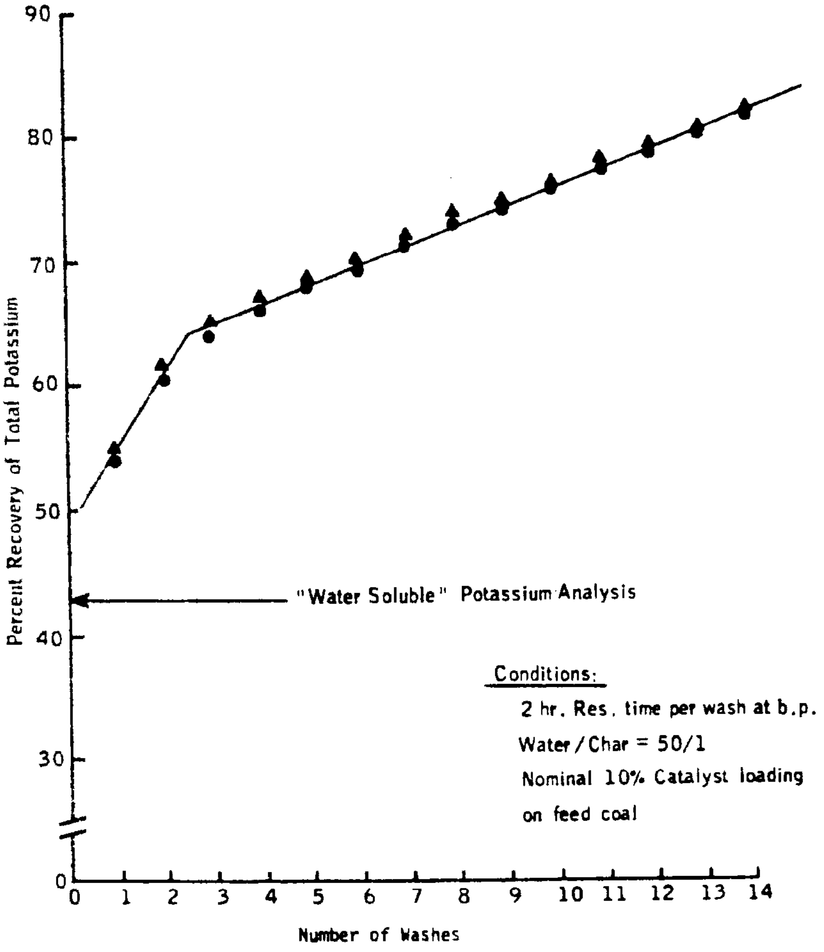
FIGURE 2.3-3

POTASSIUM RECOVERY BY CROSS-CURRENT WATER WASHING AT HIGH WATER/CHAR RATIO



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and compared to the results obtained using distilled water. A significant improvement in potassium recovery was observed when limewater was used. Nevertheless, it is uncertain whether this improvement is due to ion-exchange or to another effect (possibly chemical).

Two possible mechanisms could be involved if ion exchange is responsible for the observed behavior. Either ion exchange sites are created by oxidation of the char, or simple moistening of the char allows potassium ions to migrate to existing ion exchange sites within the char. Experimental results indicate that both mechanisms may be involved.

In order to identify whether the char reacts with oxygen or with water vapor in the air, identical portions of char were exposed to streams of wet air, dry air, wet nitrogen, and dry nitrogen for a 24 hour period. At the end of the reaction period, the weight change of each char sample was noted, and two samples of that char were analyzed for water soluble and total potassium. The ratio of water soluble to total potassium was used as an indicator to determine how each gas affects the leachability of the char. The char initially had a water soluble to total potassium ratio of 0.71. The results of the experiments are as follows:

Reactant Gas	Weight Change	Water Soluble K (% of Total K)
Dry Air	+1%	77
Dry N_2	0	74
Wet Air	+18	66
Wet N_2	-	73

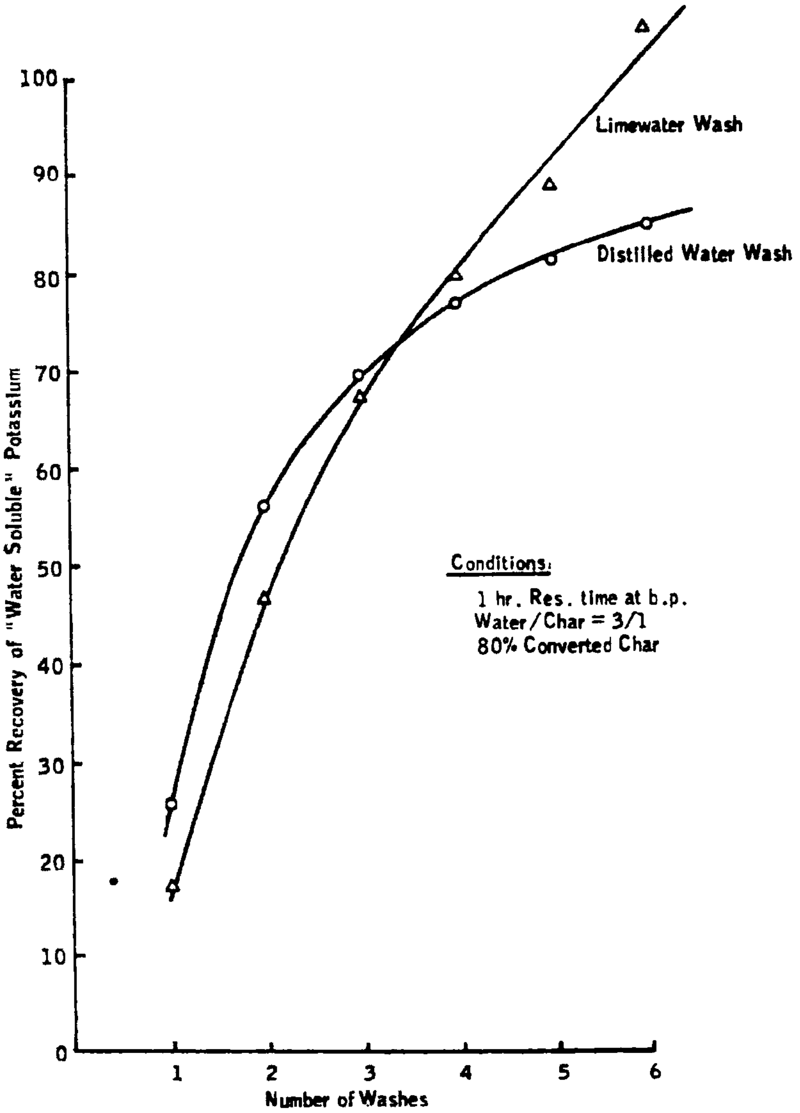
The data clearly indicate that there is a reaction between char and wet air, and that this reaction reduces the fraction of potassium which is water soluble. This supports previous observations in the laboratory that exposure of char to humid air significantly decreases catalyst recovery by cross-current water washing.

Any reaction between char and the other gas mixtures, however, is not as obvious. On the basis of the consistently higher ratios of water soluble to total potassium, it appears that char leachability might actually be improved by treatment with the appropriate gases. The usefulness of these data, however, are somewhat limited by the analytical technique used for determination of water soluble potassium.

As a more direct test of ion exchange effects, the ion exchange capacity of FBG char was measured both before and after exposure of the char to air. To determine ion exchange capacity, samples of the char were washed with a hydrochloric acid solution to remove all the potassium. The char was then oxidized in a fluidized bed at 400°F for 15 minutes. The results, shown below, reveal that while unexposed char has only negligible ion-exchange capacity, air exposure of the char increases this capacity by an order of magnitude.

FIGURE 2.3-4

EFFECT OF LIMEWATER WASHING ON POTASSIUM RECOVERY



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FBG Char Sample	Ion Exchange Capacity (Milliequiv./g)
Unexposed	0.013
Exposed to air overnight	0.162
Oxidized in fluidized bed at 400°F	0.113

A second experiment revealed that oxidation increases the ion exchange capacity of the organic portion of char, but does not significantly alter the ion exchange capacity of the mineral matter. In this experiment, fresh Illinois coal was divided into mineral-rich and organic-rich fractions via a sink/float separation in perchlorethylene. Both fractions were impregnated with potassium carbonate, dried, and devolatilized under nitrogen at 1200°F for 30 minutes. ~~Each fraction~~ was then split into two portions, one portion being stored under nitrogen, while the other was oxidized in a fluidized bed at 400°F for 15 minutes. The ion exchange capacity of all four portions was then measured. The results show that oxidation creates ion exchange sites in the organic portions of the char, while not significantly affecting the ion exchange capacity of the mineral portion.

	Ion Exchange Capacity (Milliequiv./g)	
	Unexposed Char	Oxidized Char
Organic-rich fraction (float) (25.6% Ash)	0.013	0.274
Mineral-rich fraction (sink) (79.5% Ash)	0.176	0.136

Based on these experiments, it appears that creation of ion exchange sites in the organic portion of the char is responsible for the reduced recoveries obtained from air-exposed char. Moistening of the char (by exposure to humid air or by mixing with water in a recovery process) allows water-soluble potassium ions to migrate to these ion exchange sites and become ion exchanged and insoluble.

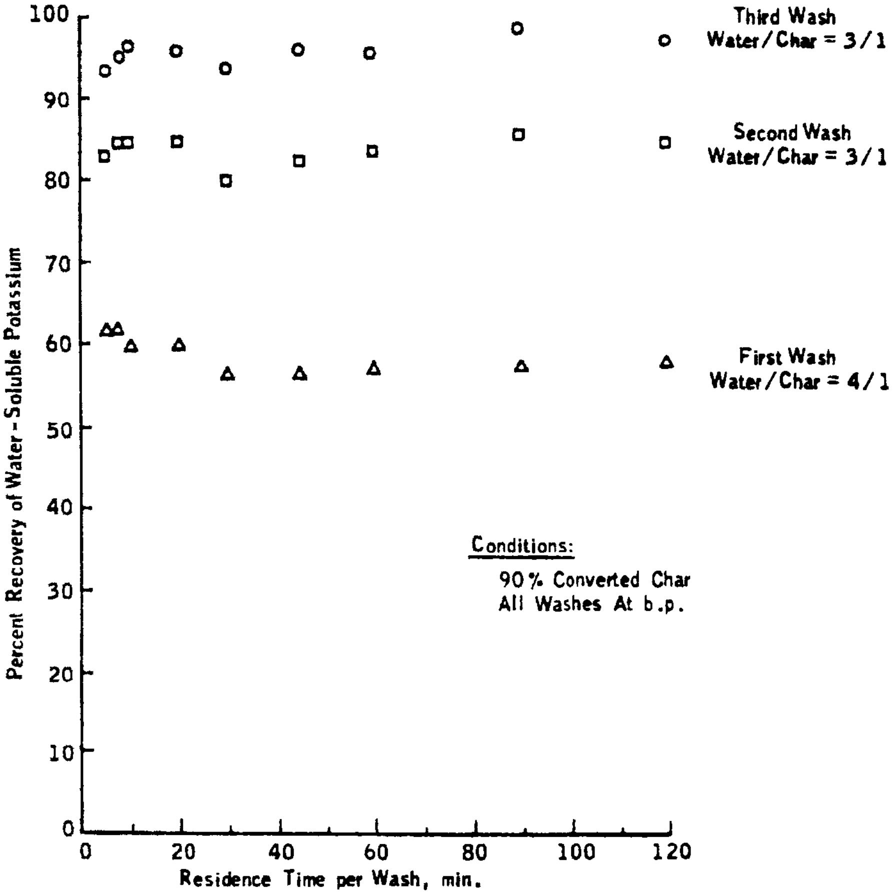
The effect of residence time on catalyst recovery by water washing was also investigated. Again, a cross-current extraction was used, with a 4:1 water/char ratio being used for the first wash, and ratios of 3:1 being used for subsequent washes. The char used in all runs was kept under inert conditions before the washes. The residence times were varied from 5 minutes to 2 hours. The results of these experiments are shown in Figure 2.3-5. Over the range of conditions investigated, recovery of water-soluble catalyst is independent of residence time. This result implies that mixing vessels in the catalyst recovery section of the Catalytic Gasification Study Design can be sized to provide good operability, without having to provide extended residence time.

2.4 RECOVERY OF WATER INSOLUBLE CATALYST

During gasification, 3-5 wt.% K_2CO_3 catalyst on Illinois coal reacts with minerals in the coal to form water insoluble potassium compounds, mainly

FIGURE 2.3-5

EFFECT OF CONTACT TIME ON POTASSIUM RECOVERY WITH LOW WATER/CHAR RATIO



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kaliophilite ($KAlSiO_4$). Recovery of this water insoluble catalyst results in a substantial reduction in catalyst makeup cost. Bench scale studies of water insoluble catalyst recovery have focused on recovery of this water insoluble catalyst from gasifier char by aqueous digestion with calcium hydroxide. Results of the studies show that recoveries of about 90% can be achieved. Also, parameter studies of catalyst recovery were used to identify optimum reaction conditions and develop equations to predict recovery at those conditions. Additional work served to better define the chemistry involved, and to investigate recovery of water insoluble compounds from ashed gasifier char.

2.4.1 Mineral Matter Reactions

The major constituent of the water insoluble potassium in the gasifier char is kaliophilite ($KAlSiO_4$). This compound is produced in the gasifier by the reaction of clay minerals (e.g., kaolinite) originally in the coal with the added K_2CO_3 catalyst:

$$\underset{\text{kaolinite}}{\underline{Al_2Si_2O_5(OH)_4}} + K_2CO_3 \xrightarrow{1300^\circ F} \underset{\text{kaliophilite}}{\underline{2KAlSiO_4}} + CO_2 + 2H_2O \qquad (2.4\text{-}1)$$

The aqueous digestion of the gasifier char residue with $Ca(OH)_2$ at 300°- 400°F results in a variety of solid products. Two major components have been identified and studied by x-ray diffraction techniques. These two compounds are hydrogarnet, a calcium aluminum silicate hydrate, and tobermorite, a hydrated calcium silicate. The hydrogarnet formation is represented by the following reaction:

$$2H_2O + 3Ca(OH)_2 + 2KAlSiO_4 \xrightarrow[\text{2 Hours}]{300^\circ F} \underset{\text{hydrogarnet}}{\underline{Ca_3Al_2SiO_4(OH)_8}} + SiO_2 + 2KOH \qquad (2.4\text{-}2)$$

The hydrogarnet species formed has a 3:1 Ca/Si ratio as determined by the x-ray diffraction results. The excess silica produced in reaction (2.4-2) along with free silica already present in the char reacts directly with $Ca(OH)_2$ to form a poorly crystallized tobermorite:

$$6SiO_2 + 5Ca(OH)_2 \xrightarrow[\text{2 Hours}]{300^\circ F} \underset{\text{tobermorite}}{\underline{(CaO)_5(SiO_2)_6(H_2O)_5}} \qquad (2.4\text{-}3)$$

In Illinois coal, the Si/Al molar ratio is approximately 2:1. Assuming that virtually all of the aluminum is in the form of kaliophilite (which has 1:1 Si/Al ratio), then there is about a 50/50 distribution of silica as kaliophilite and as free silica. Taking into account this silica stoichiometry, an overall reaction can be represented by combining reactions (2.4-2) and (2.4-3) as follows:

$$4KAlSiO_4 + 11Ca(OH)_2 + 4SiO_2 + 4H_2O \xrightarrow[0.1\ M\ KOH]{300^\circ F}$$

$$\underbrace{2Ca_3Al_2(SiO_4)(OH)_8}_{\text{hydrogarnet}} + \underbrace{(CaO)_5(SiO_2)_6(H_2O)_5}_{\text{tobermorite}} + 4KOH \qquad (2.4\text{-}4)$$

2.4.2 Experimental Procedure

A bench scale "tubing bomb" reactor used for the experimental program is shown schematically in Figure 2.4-1. The standard procedure is to load the tubing bomb with 20 gms char, $Ca(OH)_2$, water or a solution of KOH, and several steel balls to provide mixing. The bomb is pressure tested with an inert gas at 500 psig, and then rotated in a furnace. After the run, the bomb is cooled before opening. The contents are separated by filtration, and approximately 300 ml distilled water is used to rinse out the tubing bomb. Several runs were made to determine if additional rinsing of the filter cake with 400 ml distilled water would result in further recovery. This additional rinsing was found to have very little effect on recovery, but was continued to assure that the char pores were flushed with distilled water as completely as possible.

The char is analyzed before and after treatment to determine water soluble and total potassium. For both tests, 0.2 gram portions of char are combined with 50 ml of liquid and refluxed for 2 hours. Distilled water is used to determine water soluble potassium, and 2M HCl is used to determine total potassium. The resulting supernatants are analyzed by atomic absorption to determine the weight percent water soluble and total potassium present on the original char. The difference between these two values is defined as the "water insoluble" potassium.

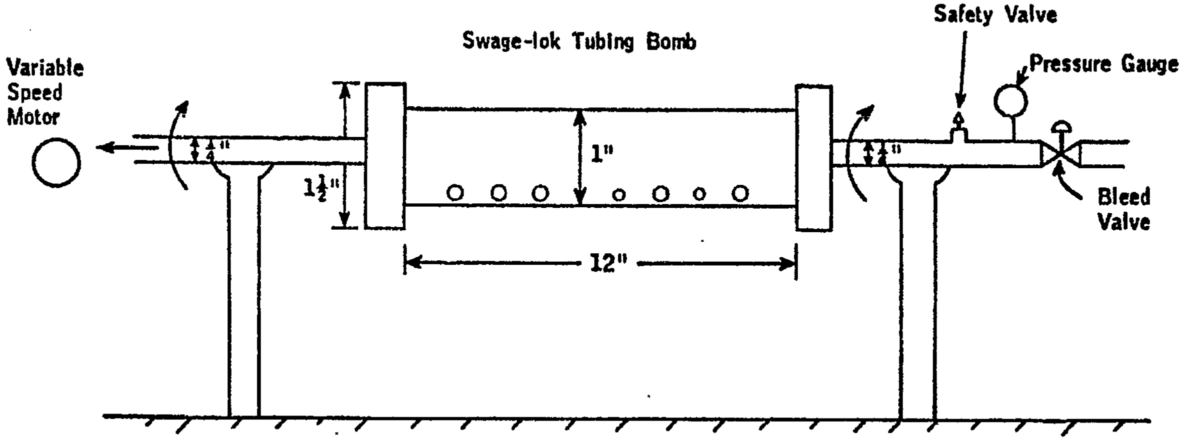
2.4.3 Effect of Washing Solutions

Initially, experiments were carried out on char which had been washed to remove the water soluble potassium. However, the recoveries for these runs were low, and a second series of experiments were conducted with char which had not been water washed. The recoveries of water-insoluble potassium greatly increased when unwashed char was used. Apparently the pH was elevated by the presence of water soluble potassium compounds on the char, which promoted the breakup of the $KAlSiO_4$. Further experiments in which pH was raised by addition of NaOH confirmed that high pH favors the recovery of water insoluble potassium.

The results of these experiments led to several runs with different potassium solutions. In a commercial countercurrent catalyst recovery system, the ash/char residue would be combined with K_2CO_3/KOH solution from the downstream water washing steps. Thus, runs were made with water, 15% KOH and 20% K_2CO_3 to assess the impact of these solutions on the recovery of water insoluble potassium. As expected from previous runs with NaOH solution, the runs made with KOH gave good recoveries; however, very poor recoveries were achieved with K_2CO_3 solution.

FIGURE 2.4-1

BENCH SCALE TUBING BOMB REACTOR



CHARGE: 20 GMS CHAR, 80 ML 15% KOH, $Ca(OH)_2$

CONDITIONS: 400°F, 250 PSIA

Most of the initial experiments were carried out at conditions of 400°F, 4 hours residence time, and a liquid to char ratio of 10:1. However, in a commercial catalyst recovery system there is an incentive to operate the digestion step with a more concentrated slurry. Therefore, several bench scale runs were made with a liquid:char ratio of 4:1. The runs were made using a 15% wt.% KOH solution and various amounts of $Ca(OH)_2$ at 400°F for 4 hours. The recoveries from these runs have been compared to the recoveries for runs made with 10:1 15% KOH char in Figure 2.4-2. The calcium to potassium mole ratio shown in the x-axis is based on the amount of calcium loaded and the total potassium present on the undigested char fed. Recoveries of water insoluble potassium from unwashed char decreased with a decrease in liquid:char ratio. Two factors which could contribute to this decrease in recovery with decrease in liquid:char ratio are solubility limits or mixing effects.

The procedure used for most runs has included rinsing the treated char with an excess of distilled water to remove potassium solution held in the moist char. In order to estimate possible recoveries with minimal water rinsing, the usual procedure was slightly modified for several runs. Temperature and residence time were maintained at 400°F and 4 hours, respectively. To avoid the use of excess water, the treated slurry was removed from the tubing bomb and separated by filtration, without adding water, and the filtrate was used to rinse the bomb. The moist char was washed three times with distilled water added at a liquid:char ratio of about 3.0. In each wash, the mixture was held at its boiling point for 15 minutes. This washing procedure is similar to that used to determine the recovery of water soluble potassium by water washing. The data for the runs made with this modified procedure and various calcium loadings are shown below:

Molar Ratio Ca/K	Total K Recovered
0.85	83%
0.73	87%
0.65	84%
0.48	85%

The recoveries for all of these runs are approximately 85%. This recovery is similar to that attained for runs made under the same process conditions and washed with an excess of water. A commercial countercurrent catalyst recovery system would use a KOH/K_2CO_3 solution from downstream water washing steps as a source of liquid for the digestion process. For this reason, recycle of solution to the digestion process was simulated on the bench scale. Portions of solutions resulting from runs made with 15% KOH were concentrated and used instead of 15% KOH for the first recycle runs. The recycle solutions were made up to contain an amount of potassium equivalent to the amount which would be found in an equal volume of 15% KOH. The solutions resulting from runs were subsequently reused through two or three cycles as shown by the flow diagram presented in Figure 2.4-3. The data from two series of runs conducted with 4:1 liquid:char ratios are shown below:

FIGURE 2.4-2

EFFECT OF SLURRY CONCENTRATION ON POTASSIUM RECOVERY

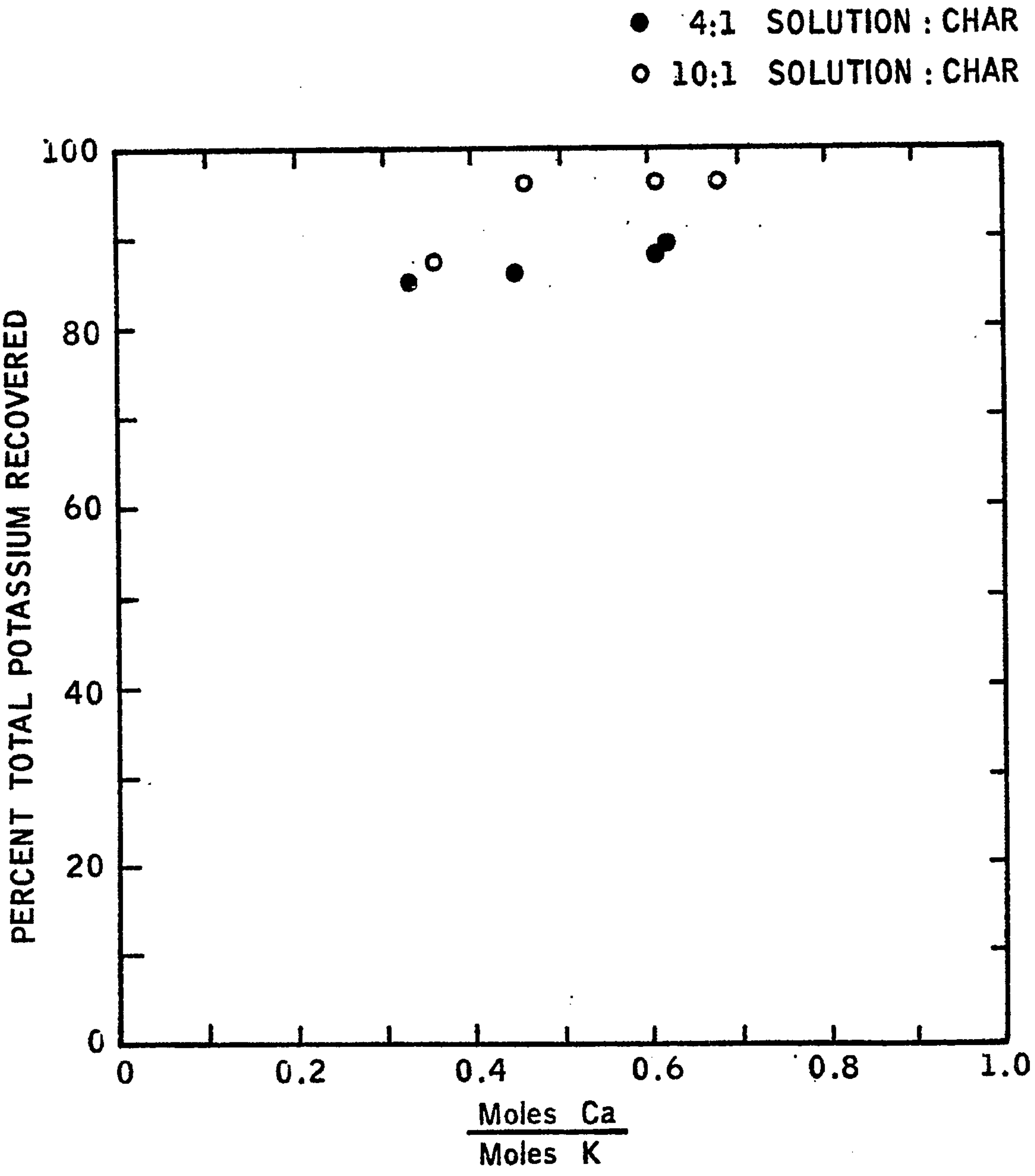
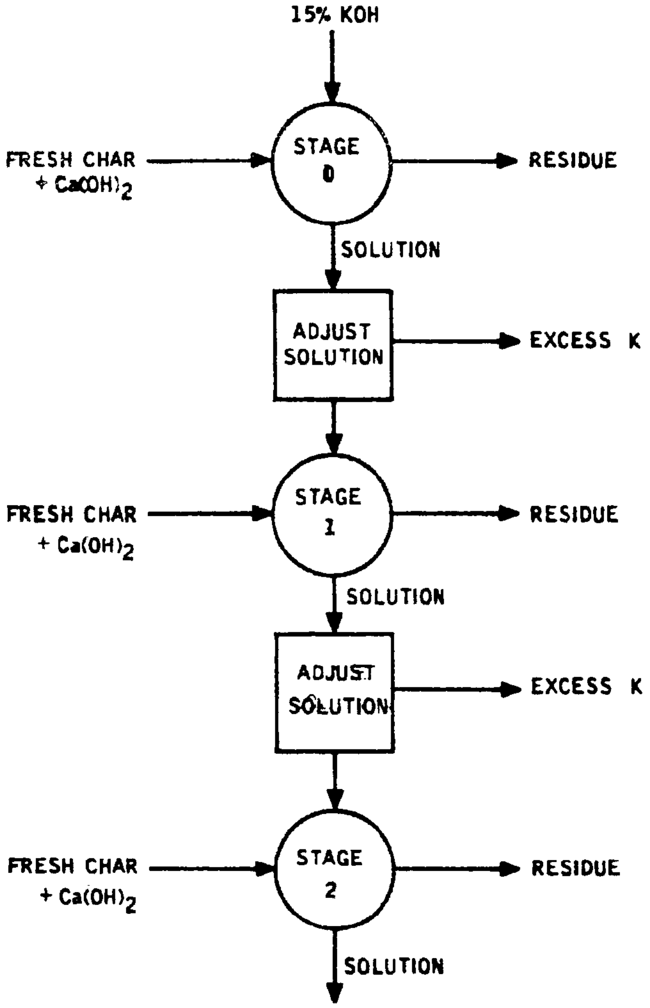


FIGURE 2.4-3

SIMULATION OF DIGESTION WITH DOWNSTREAM SOLUTION COMPOSITIONS



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Ca/K	Cycle No.	Total K Recovered
0.62	0	89%
0.68	1	88%
0.62	2	85%
0.62	3	85%
0.61	0	88%
0.65	1	87%
0.61	2	85%

Recoveries in these cyclic runs are in the same range as recoveries obtained in runs made under the same conditions with fresh 15% KOH solution. These data indicate that the results obtained with KOH solution are representative of what should be achieved with a recycle solution in the commercial countercurrent process.

2.4.4 Effects of Temperature, Residence Time, and Calcium Loading

A series of experiments to investigate the effect of temperature on potassium recoveries were initiated in August, 1977. The runs were made according to usual procedure. This process included an excess of water to rinse the treated char. Data from these runs are summarized below.

Run Temperature	Molar Ratio Ca/K	Total K Recovered
200°F	0.78	74%
300°F	0.81	87%
350°F	0.80	86%
400°F	0.68	89%
450°F	0.84	90%

These results show that acceptable recoveries are possible at a temperature as low as 300°F.

Several experiments were then made to investigate the effect of residence time on potassium recoveries. Runs were made at 300°F and at several residence times. The results from these runs are summarized below.

Residence Time	Molar Ratio Ca/K	Total K Recovered
2 hours	0.63	82%
3 hours	0.67	86%
4 hours	0.81	87%
5 hours	0.66	86%

These data show that essentially the same potassium recovery was achieved at residence times of 3, 4, and 5 hours. Therefore, a 3 hour residence time may be adequate for the digestion reaction. However, in a bench scale apparatus, part of the residence time is required to heat the contents of the tubing bomb to the required temperature. In a commercial process, this heatup time would be minimized, and a residence time of less than 3 hours might be adequate.*

A series of experiments to investigate the effect of calcium loading on potassium recoveries was initiated in September, 1977. Several runs were made at 400°F and 4 hours, and are summarized below.

Mole Ratio Ca/K	Total K Recovered
0.00	71%
0.29	74%
0.49	79%
0.68	89%
0.87	82%
1.04	90%

From these data, a stoichiometric Ca/K ratio of 0.7-0.8 appears to be the minimum necessary for good potassium recoveries.

Additional tubing bomb runs at various Ca/K mole ratios and a residence time of 2 hours were made at temperatures of 300°, 350°, and 400°F. The usual procedure, including an excess of water to rinse the treated char, was employed. The data from these runs are shown below.

Temperature	Molar Ratio Ca/K	Total K Recovered
400°F	0.63	82%
400°F	0.74	84%
350°F	0.72	78%
350°F	0.79	80%
350°F	0.89	85%
300°F	0.79	82%
300°F	0.89	83%

---

*Pilot scale studies of secondary catalyst recovery show that residence times as low as 1 hour are adequate (See Section 1.5).

Two of the runs shown here gave potassium recoveries of 84 and 85%. However, similar runs made in September 1977, at 400°F and 4 hours gave recoveries as high as 89-90%, indicating that shorter residence times may result in slightly lower recoveries. Higher temperatures, longer residence times, and greater amounts of calcium all favor better recovery, and an analysis of the tradeoffs between greater recovery and increased cost may be necessary to determine the optimum commercial conditions.

2.4.5 Catalyst Recovery from Combusted Char

Most of the water insoluble catalyst work involved recovery from FBG char as it comes from the gasifier. During November 1977, brief experiments were made to investigate water insoluble catalyst recovery from ashed FBG char. The char removed from the FBG is not completely converted and still contains some carbon. It may be possible to make use of this energy remaining in the char by burning the char after the gasification step. The calcium digestion process could then be used on the residual ash.

To test this possibility, FBG char was finely ground and combusted at about 2500°F in a pilot scale solid fuel test furnace. This char was produced from coal which originally contained about 15% K_2CO_3. Several ash samples were collected, including fly ash from the cyclone, slag, and ash screened from the slag. These ash samples were used as feed for several tubing bomb runs. The liquid: char ratio was increased to 5:1 for these runs to reduce handling problems resulting from the "stickiness" of the ash slurry. The results from these tubing bomb runs are summarized below:

Sample Type	Temperature	Residence Time	Mole Ratio Ca/K	Total K Recovered
Fly ash	300°F	2 hours	0.95	89%
Fly ash	400°F	4 hours	0.94	97%
Ash from slag	300°F	2 hours	0.94	84%
Ash from slag	400°F	4 hours	0.94	96%
Slag	300°F	2 hours	1.53	75%
Slag	400°F	4 hours	1.53	80%

The calcium to potassium mole ratio is based on the amount of calcium loaded and the total potassium present on the undigested ash fed. These data indicate that excellent recoveries can be obtained from char fly ash, particularly at conditions of high temperature (400°F) and long residence time (4 hours). If the char were to be burned in a furnace after gasification, the furnace could be operated to produce a minimum amount of slag and a maximum amount of fly ash, which gave the best recoveries in these tests.

A previous Exxon study indicated that solid state combustion of pure $KAlSiO_4$ with $Ca(OH)_2$ could produce water soluble potassium compounds. If the solid state reaction could be carried out in the combustion stage, no treatment step would be required. For this reason, it was suggested that water insoluble potassium might be recovered by burning char mixed with $Ca(OH)_2$. A sample of the char which was used to produce the ash samples described above was obtained and combined with $Ca(OH)_2$ to give a Ca/K mole ratio of about 1.25. The mixture was burned in a small laboratory furnace at about 1750°F for several hours.

Analysis of the resulting ash indicated that much of the water insoluble potassium originally present on the char had remained water insoluble. Previous work and information from the literature indicate that 100% conversion of alkali metal aluminosilicates should occur by reaction with calcium. However, a temperature higher than the 1750°F used for this experiment may be required.

2.4.6 Data Analysis

Experiments on the recovery of water insoluble catalyst from FBG char were completed in November, 1977. Correlation analysis of the data from about 40 tubing bomb runs was initiated at this point. The data included in the correlation analysis were from runs made with nitrogen blanketed char. The emphasis in this analysis was on determining the effect of four parameters: temperature, residence time, calcium loading, and liquid/char ratio. A stepwise linear regression analysis was used to generate an equation for predicting total potassium recovery from the char. The correlation shown below was developed using only the four parameters, their inverses, and their squares.

$$\%\text{ K Recovered} = C_1 - C_2\,(\text{Temperature}) - C_3\,(\text{K/Ca}) + C_4\,(\text{Liquid/Char}) + C_5\,(\text{Time}) - C_6\,(1/\text{Temperature})$$

Use of a stepwise linear regression program allows the selection of independent variables in the order in which they explain the variation of the data. For example, in the first correlation, temperature was selected as the variable which explained most of the variation in the data. The second variable selected explained most of the variation remaining in the data after the addition of the first variable, and so on. This equation has a correlation coefficient of 0.90.

A second correlation equation was developed using a similar procedure as the first. Now, however, cross products of the parameters, in addition to the parameters, their inverses, and their squares were considered. The resulting equation is:

$$\%\text{ K Recovered} = C_1 - C_2\,(\text{Temperature}) + C_3\,(\text{Ca/K})(\text{Liquid/Char}) + C_4\,(\text{Ca/K})\,(\text{Time}) - C_5\,(1/\text{Temperature}) + C_6\,(\text{Ca/K})^2$$

This equation has a correlation coefficient of 0.89.

Since the procedure for making runs is not the same on both bench and pilot scale, an accurate prediction of pilot scale results from an equation developed from bench scale data was not expected. However, the recoveries predicted by this equation can be compared to actual results achieved on the pilot scale Secondary Catalyst Recovery Unit (SCRU). Using parameter values from actual runs made on the SCRU, the predicted recoveries were always less than those actually obtained. However, as can be observed from the SCRU data in Table 1.5-1, cumulative recoveries were determined for each step in a series of washes. Recoveries predicted by the correlation equation consistently fell between the recoveries achieved in the second and third washes of a SCRU run. This is reasonable since the correlation was developed from runs made with a minimum of washing of the digested char. The data from the SCRU, therefore, show that a fifth parameter, i.e., degree of washing, is also important in catalyst recovery. This parameter, however, was not investigated in the bench scale program.

2.5 CATALYST RECOVERY VIA THE FORMATE PROCESS

Investigations were made concerning the use of the formate process for recovery of water insoluble catalyst. Originally developed for the manufacture of potassium carbonate, the formate process involves the reaction of potassium sulfate with lime and carbon monoxide at 200°C and 440-470 psia:

$$K_2SO_4 + Ca(OH)_2 + 2CO \rightarrow 2KHCO_2 + CaSO_4\downarrow$$

In the original process, this was followed by a calcining reaction to convert the formate to carbonate:

$$2KHCO + O_2 \rightarrow K_2CO_3 + CO_2 + H_2O$$

For enhanced catalyst recovery, the insoluble potassium species is substituted for potassium sulfate in the formate reaction. The calcining reaction is not necessary since potassium formate is believed to be equivalent to potassium carbonate as a gasification catalyst.

The formate process was tested as an alternative to the calcium digestion process for recovery of water insoluble potassium. Unfortunately, the formate process was not as effective. One benefit of the formate process, however, is that any sulfate present on the char is converted to catalytically active potassium formate. Another possible benefit is that makeup potassium in the form of sulfate could be added directly to the char slurry, eliminating the need for separate catalyst manufacture facilities.

As a preliminary test of the viability of the formate process for enhanced recovery, a series of tubing bomb experiments was conducted in which FBG char, water, calcium hydroxide and carbon monoxide were reacted for 3 hours at 200°C. The initial bomb pressure was 450 psig, but the pressure dropped as CO was consumed by reaction. At the end of the reaction period, the mixture was rapidly cooled and the solid residue separated by filtration. The solids were then water-washed twice and potassium recovery calculated using analyses of the recovered liquid and the starting char material. The results are as follows:

	Initial Charge to Bomb			Recovery
Ca/K Insol (Mol/Mol)	Total K (Millimoles)	$Ca(OH)_2$ (Millimoles)	CO (Millimoles)	Total K (%)
0.6	85	27	41	63
1.3	85	54	41	85
2.6	85	108	41	74
3.9	85	162	29	85

Clearly, the formate reaction results in total potassium recoveries significantly in excess of those attainable by water-washing alone. However, in these preliminary runs, the potassium recoveries are not as high as those attained in the calcium hydroxide digestion experiments described above.

Additional studies were carried out in a stirred autoclave, in which CO pressure can be maintained constant throughout a run, providing a closer approximation to potential commercial conditions. The results obtained in the autoclave studies confirm the tubing bomb data, showing that the formate process is not as effective as calcium hydroxide digestion for potassium recovery.

The autoclave experiments were conducted with unwashed FBG char slurried with four times its weight of water. Calcium hydroxide was added such that the molar ratio of calcium to total potassium was 0.8. The mixture was reacted at 200°C and 450 psig for 3 hours. Two runs were made: a blank run under argon (i.e., calcium hydroxide digestion reaction conditions), and a formate run under carbon monoxide pressure.

The blank run gave essentially identical results to previous investigations. Total potassium recovery was 95.6% after three water washes. The solid residue remaining after digestion was analyzed by x-ray diffraction and found to contain hydrogarnet and tobermorite, the same calcium-silicon compounds found in the residue from tubing bomb runs. There was no evidence of $KAlSiO_4$, indicating that this insoluble compound was consumed by the reaction.

The formate run gave a substantially lower potassium recovery than the blank run. Total potassium recovery after three washes was only 74%. This confirms low recoveries obtained in tubing bomb investigations of catalyst recovery by the formate process. In this run, the solid residue remaining after digestion contained $KAlSiO_4$, indicating that this compound was not destroyed by the formate reaction. Thus, the formate reaction is not an attractive alternative for achieving high potassium recoveries.

Nevertheless, the formate process still has the advantage of converting sulfate to formate - a feature not shared by the calcium hydroxide digestion process. As a test of this reaction, several additional tubing bomb runs were conducted using the procedure outlined above, with potassium sulfate being used as the potassium source. Pressure above the reaction mixture was monitored to follow the course of the reaction, and the reaction was judged complete when the pressure fell to the vapor pressure of water at 200°C (about 240 psia). The results show that CO uptake occurs readily, driving the reaction to completion in a relatively short time.

Initial Charge to Bomb				
K_2SO_4 (Millimoles)	$Ca(OH)_2$ (Millimoles)	CO (Millimoles)	H_2O (Ml)	Time Required For all CO to be Consumed, Min.
29	54	40	30	110
29	27	40	30	100
57	108	29	60	50
29	27	29	60	60

In addition, analysis of the rich solutions recovered from the autoclave runs revealed that substantially lower amounts of sulfate and thiosulfate were present in the solution recovered from the formate run, indicating that the formate reaction is effective in destroying these species. The following data show that CO treatment reduced sulfate content by more than 50% and thiosulfate by 85%.

	Blank Run (Argon)	Formate Run (CO)
Sulfate Sulfur, Millimoles	10.8	4.4
Thiosulfate Sulfur, Millimoles	43.7	6.4

Addition of CO to the digestion mixture results in acidification of the solution and formation of calcium formate, $Ca(HCO)_2$, a very soluble compound. The low pH of the solution hinders the decomposition of $KAlSiO_4$. Destruction of this compound has been shown to decrease with decreasing pH. However, the high concentration of calcium in solution releases any potassium ion-exchanged onto the char surface, resulting in a recovery slightly above that achievable by water washing alone.