

COAL GASIFICATION WITH INTERNAL RECIRCULATION CATALYSTS

by

A. H. Hill, G. L. Anderson
Institute of Gas Technology
3424 S. State Street
Chicago, IL 60616

and

M. R. Ghate, W. Liou
U.S. Department of Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, WV 26507

One of the primary economic penalties of many catalytic coal gasification processes is recovery of the added catalysts from the spent char. For example, the EXXON catalytic coal gasification process as presently conceived, requires several stages of digestion with calcium hydroxide to recover potassium from the converted char and then the digestion only recovers between 65 and 85% of the potassium.¹

Recently, IGT has been exploring a process concept that might avoid this complex and costly situation. In the IGT process concept, a coal gasification process with an inherent thermal gradient (e.g., Lurgi, staged fluidized-bed processes, etc.) and a catalyst that is semivolatile under gasification conditions are used. The semivolatile catalyst is sufficiently volatile at the highest temperature encountered in the lower section of the gasifier, that it is completely vaporized from the char before the char is discharged. The catalyst, however, is nonvolatile at the lowest temperature encountered in the upper section of the gasifier so that it precipitates on the cold, feed coal. The catalyst, therefore, is automatically recycled from the product char to the fresh coal and the need for catalyst recovery is eliminated.

Three different materials have been undergoing testing by IGT as semivolatile catalysts. These materials were selected based on an examination of their vapor pressures and the following process assumptions. It was assumed that a catalyst loading of approximately 5 wt % is sufficient for catalyzing the gasification reactions, that the temperatures in the gasifier vary from 600° to 1600°F, that the gasifier operates at 1000 psig with a product gas/coal feed ratio of 15 SCF/lb, and that a rate of loss of catalyst in the product gas of less than 1% of the circulation rate of the catalyst in the gasifier is acceptable. With these assumptions, the requisite vapor pressure of the "semivolatile" catalyst in the hottest section and the coldest section of the gasifier was calculated to be greater than 1.0 atmosphere at 1600°F (870°C) but less than 10 mm Hg at 600°F (315°C).

The materials identified to have the proper physical properties are shown in Table 1. Arsenic in its elemental form is relatively stable under reducing conditions. Some arsine, AsH₃, formation is expected; but at high total arsenic partial pressures and moderate temperatures, more than 99% of the gas phase arsenic is expected to be present as As₂ and As₄. Although less is known about the behavior of cadmium, studies have shown that fines generated in coal gasification are highly enriched in cadmium, indicating "semivolatile"

Table 1. MATERIALS WITH VAPOR PRESSURES IN THE DESIRED RANGE FOR A "SEMIVOLATILE" CATALYTIC COAL GASIFICATION PROCESS

Element	Temperature (°F) for a Vapor Pressure of:	
	10 mm HG	1 atm
Arsenic	819	1130
Cadmium	903	1403
Cesium Hydroxide	1160	1790

behavior in the gasifier. Cesium hydroxide, on the other hand, is known to enhance the reactivity of carbon towards steam.² Studies have also presented evidence for the volatility of cesium hydroxide under gasification conditions.³

This paper summarizes the results of 1) laboratory-scale batch reactor screening tests conducted to evaluate the performance of arsenic, cadmium and cesium hydroxide as catalysts for coal gasification and 2) continuous bench-scale tests with cesium hydroxide, the most effective catalyst tested in the initial screening tests, to determine the volatility of cesium hydroxide, i.e., its release from the char before discharge, under continuous gasification conditions.

EXPERIMENTAL

Laboratory-Scale Screening Tests. During the catalyst screening portion of the project, 49 char gasification tests were conducted in the laboratory-scale batch reactor catalyst testing unit pictured in Figure 1. The reactor is constructed of Rene 41 steel and is 12-inches high with a 0.05-inch I.D., a 2-inch O.D., and a 28-cm³ capacity. The high temperature valve (Figure 1) has an extended stuffing box which allows the body of the valve to be located in the furnace with the reactor. This is necessary to avoid condensation of both the steam and semivolatile catalyst during the test. Tests were conducted with devolatilized North Dakota lignite and Illinois No. 6 bituminous coal chars. The chars were prepared in a separate 1-inch-diameter fluidized-bed reactor with nitrogen as the fluidizing gas. Analyses of the chars used in the study are presented in Table 2.

The batch reactor char gasification tests were conducted under the following conditions:

Temperature:	1200°, 1300°, 1400°F
Initial Pressure:	~160 psig
Gasifying Medium:	Steam, Hydrogen
Char Particle Size:	~200 Mesh
Char Residence Time:	3, 6 h
Catalyst Loading:	10 Wt %
Char Sample Weight:	~200 mg

The experimental procedure was as follows. With arsenic or cadmium, the char and the appropriate amount of powdered metal were thoroughly mixed in a high-speed pulverizing shaker. About 220 milligrams of the mixture was then weighed out and placed in a small quartz test tube. A sufficient amount of water (~240µl) was then added to the mixture with a volumetric syringe such that the resultant water-to-carbon molar ratio was 1. In tests with cesium hydroxide, a 50 wt % solution of cesium hydroxide in water was added to the char in the test tube. Additional water was then added to give the required water/carbon molar ratio of 1.

Table 2. ANALYSIS OF THE CHARS USED IN THE LABORATORY-SCALE BATCH REACTOR GASIFICATION TESTS

<u>Elemental Analysis*</u>	North Dakota	Illinois No. 6
	<u>Lignite</u>	<u>Bituminous</u>
	-----wt % dry-----	
Carbon	75.88	80.90
Hydrogen	0.65	0.58
Nitrogen	0.86	1.21
Ash	20.86	14.16
Total	98.25	96.85

* Carbon, hydrogen and nitrogen determined by ERBA analyzer (Automated Elemental Analyzer) which was used to analyze residues of all batch reactor tests.

The test tube containing the char/catalyst/water mixture was placed into the reactor, the reactor was reconnected to the system, and the system and reactor were then evacuated. To prevent losing the added water during evacuation, the reactor was placed in a dry-ice bath to freeze the water in the test tube. After evacuating the reactor, the dry-ice bath was removed, and the reactor was allowed to come to ambient temperature. The reactor was then placed into the furnace and was charged with sufficient hydrogen (~160 psig) such that the resultant hydrogen-to-carbon molar ratio is 1. After the reactor was charged with hydrogen, the high-temperature valve was closed, the remainder of the system was evacuated, and the furnace was allowed to heat up to the desired operating temperature. When the desired time had elapsed, the furnace was turned off and opened, allowing the reactor to cool to ambient temperature.

The reactor valve was then opened and the total system pressure was measured. This allowed the total moles of non-condensable gas in the system at the end of the test to be calculated. A sample of the product gas was then taken for analysis, and reactor was depressurized and opened. The test tube containing the mixture was removed from the reactor, and the residue was submitted for chemical analysis.

Bench-Scale Tests. Cesium hydroxide catalyzed and uncatalyzed char gasification tests were conducted in a 2-inch I.D. bench-scale unit (BSU). Nine tests were conducted in the BSU with North Dakota lignite and Illinois No. 6 bituminous chars. The chars used in the BSU gasification tests were prepared in an IGT 4-inch I.D. fluidized-bed reactor. Analyses of the chars used in the gasification tests are given in Table 3. The cesium hydroxide catalyst (Alfa Products®) was obtained as a hydrated solid containing about 85 wt % cesium hydroxide. It was deposited on the char by evaporation from solution under vacuum at 105°C.

The BSU is shown in Figure 2. It consists of a reactor (2-inch I.D., 39.125-inches long) and associated equipment for feeding and measuring the flow rates of char, steam, reference/purge gas (argon); for collecting and/or measuring the flow rates of residue char, liquid product, and product gas; and for collecting representative samples of the product gas.

In this unit char is fed to the top of the reactor by a calibrated screw feeder from a pressurized feed hopper, while the residue char is discharged from the bottom of the reactor into a pressurized residue receiver by a discharge screw. A piston-type metering pump is used to pump water from a reservoir into a steam generator that provides steam for the reactor.

Table 3. ANALYSES OF CHARs USED IN THE BSU GASIFICATION TESTS

Char Type	North Dakota Lignite	Illinois No. 6 Bituminous
Proximate Analysis, wt %		
Moisture	6.06	0.00
Volatile Matter	14.38	2.34
Fixed Carbon	64.69	81.59
Ash	14.87	16.07
	<u>100.00</u>	<u>100.00</u>
Ultimate Analysis, wt %		
Ash	15.83	16.07
Carbon	71.25	77.63
Hydrogen	1.87	0.91
Sulfur	1.54	2.58
Nitrogen	0.79	1.11
Oxygen	8.72	1.70
	<u>100.00</u>	<u>100.00</u>

The reactor steam enters the bottom of the reactor above the discharge screw through a dip tube. Metered and preheated argon is added as an internal reference and carrier gas and enters the bottom of the reactor between discharge screw and the exit of the steam dip tube.

Effluent gases from the top of the reactor pass through two water-cooled condensers in series. The condensed liquids are drained into separate vessels and weighed. An "aliquot" sample of the product gas is taken for componential analysis by feeding a portion of it into a water-sealed gas holder during selected periods of each test. "Spot" gas samples are also taken throughout the test period for componential analysis.

In a typical run, the reactor was initially filled with char and/or a char/catalyst mixture. After charging the reactor the system was flushed with argon. The temperatures of the reactor, steam pre-heater, super-heater and line heaters were then brought to operating temperatures in 1 to 2 hours and (except for Test 9) were maintained at these values for the duration of the test.

Gasification data were collected beginning immediately after the reactor furnace heaters were turned on and continued to be collected for 3 hours after the introduction of the steam to the reactor (fixed-bed operating period). Steam was fed after the lower zones of the reactor reached 1400°F.

Gasification data were also collected for an additional 5 hours after the 3-hour fixed-bed operating period under moving-bed conditions. Steady-state conditions were attained during the last two hours of the moving-bed operating period of Tests 2 and 3. "Steady-state" is defined as a condition wherein the reactor pressure is stable, the temperature profile in the bed, char feed rate and bed height are essentially constant.

In this study product gas compositions were determined by gas chromatography. Feed and residue char compositions and the carbon content of the condensate samples were determined by standard ASTM methods. The cesium content of the catalyzed feed and residue chars, steam condensate and the water used to rinse the reactor and product gas exit lines were determined by atomic absorption spectroscopy.

After each test was completed, the weight of the char fed was determined by weighing the char initially charged to the feed hopper and the char remaining in the feed hopper at the end of the test. The residue char was

also weighed after the test. Feed and residue char rates were calculated by dividing these weights by the measured char feeding time.

Results and Discussion. Figures 3 and 4 compare the measured effects of arsenic, cadmium and cesium hydroxide on the rate of gasification of lignite and bituminous char in the laboratory-scale batch reactor char gasification tests. The relative rate of gasification of the uncatalyzed and catalyzed chars are expressed in Figures 3 and 4 as reactivity ratios, i.e., the ratio of carbon conversions (X_c) obtained in the catalyzed tests and the average of all the carbon conversions (X_c) in the uncatalyzed tests at each temperature. A reactivity ratio value of one (shown by the horizontal line in each figure) indicates no effect of the catalyst on the char reactivity by the catalyst.

Although a great deal of scatter remains in the data shown in Figures 3 and 4, it is apparent that cesium hydroxide is more effective than arsenic or cadmium for char gasification. Increasing the reaction temperature strongly increases the catalytic effect of cesium hydroxide on the bituminous char reactivity, but has little effect on the lignite char reactivity.

A summary of the BSU gasification tests is given in Table 4. A number of operational problems prevented all but Tests 2 and 3 from being conducted under continuous moving-bed conditions. In Tests 4 and 5 (in which the catalyst was placed in reactor Zones 2 and 3 only), the formation of a clinker-like mass blocked the downward movement of the bed and, therefore, prevented residue discharge. In Tests 6, 7 and 9, moving-bed conditions could not be attained because the catalyzed char adhered to the reactor walls and prevented residue discharge.

The dry gas production rates for the tests with uncatalyzed and catalyzed bituminous char during the reactor heat-up and the fixed-bed operating periods are shown in Figure 5. The addition of catalyst to the bituminous char increased the gas production rate by as much as 72%.

The tests with catalyzed lignite char also showed consistently higher gas production rates than the tests without catalyst. In Tests 4 and 5, the catalyst was placed in the hottest zone of the reactor. The gasification rate with this distribution of catalyst quickly increased to very high values but then decreased rapidly as gasification proceeded, to the rates obtained with the uncatalyzed char. Distributing the catalyst evenly throughout the reactor, as was done in Tests 6 and 7, resulted in gasification rates that were initially slightly higher than in the tests with the uncatalyzed chars but the rate of gasification tended to decrease less rapidly with time. Although the lignite char showed higher overall gasification reactivity, the catalyst is 33% more effective in catalyzing the gasification of the less reactive bituminous as compared to the lignite char.

The dry gas constituent production rates during the reactor heat-up and fixed-bed operating periods for the uncatalyzed and catalyzed bituminous char are shown in Figure 6. Hydrogen and carbon dioxide account for most of the increases in the catalyzed dry gas production rates in both the bituminous and lignite char gasification tests. In the two lignite gasification tests, where the catalyst was concentrated in the two hottest zones of the reactor (Tests 4 and 5), a small increase in the production rate of carbon monoxide and methane relative to the hydrogen was observed.

Figures 7 and 8 compare the cumulative carbon gasified as a function of time for both char types during the fixed-bed operating period. A significant increase in the total amount of carbon gasified is shown in the catalyzed char tests. The extent of the increase is highly dependent on where the catalyzed char was initially placed in the reactor before heating.

The disposition of the cesium catalyst in the various solid and liquid product streams from the bench-scale reactor has been investigated. The results have thus far indicated minimal movement of the cesium from its initial position under the applied test conditions. This suggests that either higher temperatures or lower pressures might be required to effect cesium volatilization from the char.

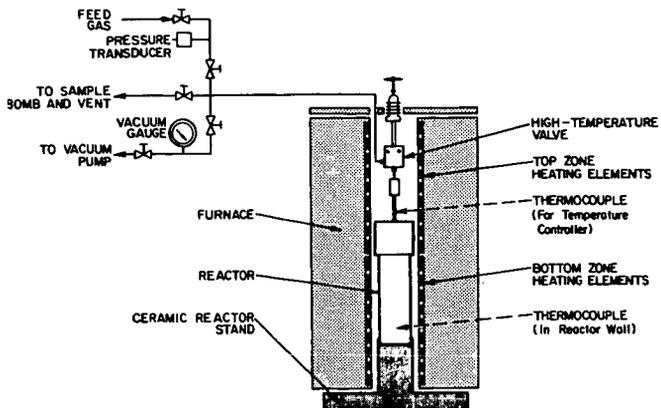
Plans are to conduct larger-scale BSU tests, wherein the operating problems encountered in the 2-inch BSU might be avoided, to answer this question.

ACKNOWLEDGEMENT

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3. Kosky, P. G. et al., "Coal Gasification Catalysis Mechanisms," Final Report to DOE for the period September 29, 1980-November 29, 1982. DOE/MC/14591-1397 (DE83011051), by General Electric Company, September 1982.



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Figure 1. LABORATORY-SCALE BATCH REACTOR CATALYST TESTING UNIT

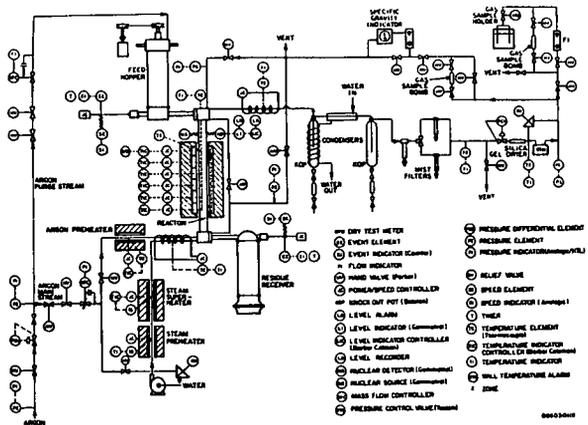


Figure 2. BENCH-SCALE REACTOR UNIT

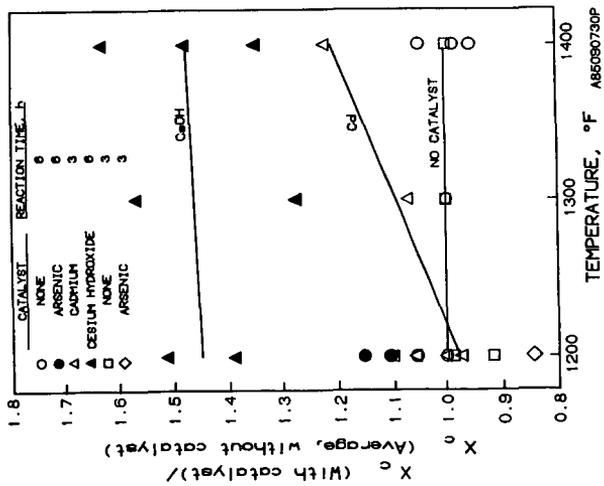


Figure 3. COMPARISON OF THE EFFECT OF ARSENIC, CADMIUM AND CESIUM HYDROXIDE ON THE REACTIVITY OF LIGNITE CHAR

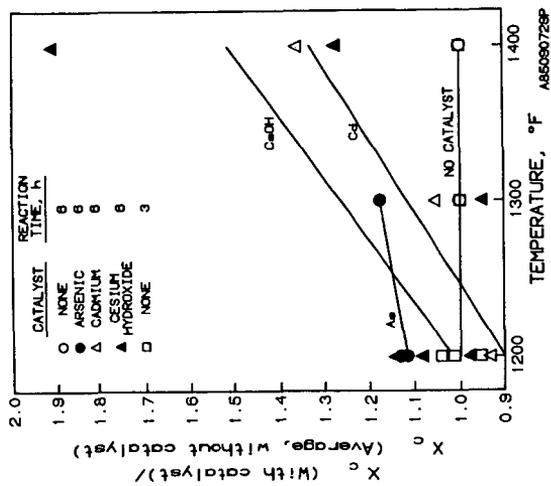


Figure 4. COMPARISON OF THE EFFECT OF ARSENIC, CADMIUM AND CESIUM HYDROXIDE ON THE REACTIVITY OF BITUMINOUS CHAR

Table 4. SUMMARY OF THE NORTH DAKOTA LIGNITE AND ILLINOIS NO. 6 BITUMINOUS CHAR BSU GASIFICATION TESTS

Test No.	Operating Period, min												
	1	2	3	4	5	6	7	8	9	10			
Char Particle Size (U.S. Sieve)	None												
Catalyst	None												
Fixed-Bed Operation	None												
Steam-Bed Operation	None												
Operating Pressure, psia	None												
Reactor Temperature, °F	None												
Average Reactor Temperature, °F	None												
Zone 7 (top)	None												
Zone 8 (bottom)	None												
Initial Reactor Char Charge, g ^b	825	777	892	892	675	518	518	741	761	665	676	578	709
Below Steam Injection Point, uncatalyzed	1244	8	8	8	888	888	888	1277	1277	1277	487	532	535
Above Steam Injection Point, uncatalyzed	0	0	0	0	0	0	0	0	191	255	775	508	0
Cesium Hydroxide, g	0	0	0	0	0	0	0	0	85	87	88	170	0
Char Feed Rate, g/min ^a	201	217	287	287	287	287	287	287	194	132	169	112	177
Char Feed Rate, g/min ^b	0	0	8.23	7.87	0	7.84	7.87	0	0	0	0	0	0
Char Residence, g/min ^a	907	0	1705 ^d	383	0	221 ^d	593	939	938	906	1055 ^e	846 ^c	935 ^{c,1}
Char Residence, g/min ^b	0	0	5.68 ^d	3.19	0	7.39 ^d	4.94	0	0	0	0	0	0
Carbon In Condensate, g	4.4	0	12.6 ^e	0	1.9	10.3 ^e	3.4	3.0	3.6	3.5	3.4	1.3	1.1(1.1) ^h
Steam Feed Rate, g/min	6.70	6.38	6.91	6.91	6.60	6.85	6.85	6.63	5.88	6.84	5.92	8.34	8.41
Argon Reference Gas Rate, SLPM	4.96	4.96	4.96	4.96	4.96	4.96	4.96	4.96	4.96	4.96	4.96	4.96	4.96
Argon Feed Hopper Charge, g ^{100%} SLPM	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Average Gas Composition, %													
H ₂	63.3	64.2	53.5	52.2	66.1	57.0	56.2	63.6	65.2	59.1	60.6	62.0	
CO ₂	27.6	26.6	23.9	22.5	27.3	25.7	25.0	23.9	23.9	26.8	26.2	30.4	33.0
CO	5.7	4.5	14.3	16.5	4.3	9.7	10.7	8.3	8.6	4.6	9.0	5.7	2.5
CH ₄	3.2	4.5	8.1	8.6	2.3	7.6	8.1	4.0	3.8	3.3	5.6	3.3	2.5
C ₂ H ₆	0.2	0.2	0.2	0.2	0.2	0.001	0.001	0.2	0.1	0.1	0.1	0.001	0.001
C ₂ H ₄	0.02	0.02	0.03	0.03	0.001	0.001	0.001	0.004	0.007	0.003	0.004	0.001	0.001
C ₂ H ₂	0.03	0.03	0.03	0.03	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
C ₂ H	0.03	0.03	0.03	0.03	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
H ₂ O	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

^aRise from when steam was first fed to reactor until beginning of moving-bed operating period or end of test.
^bBased on an as-received basis.
^cBased on a moisture-free basis.
^dAlso includes fixed-bed operating period.
^eAlso includes reactor heat-up and fixed bed operating periods.
^fIncludes gas produced during reactor heat-up for fixed-bed operating periods only.
^gReactor volume filled with gravel
^hProduced after fixed-bed operating period, when the temperatures of all reactor zones were raised to 1400°F.
¹Includes 44 minutes when all reactor zones were at 1400°F.

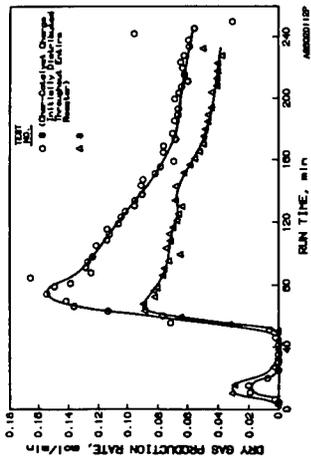


Figure 5. GASIFICATION RATES FOR UNCATALYZED AND CATALYZED BITUMINOUS CHAR

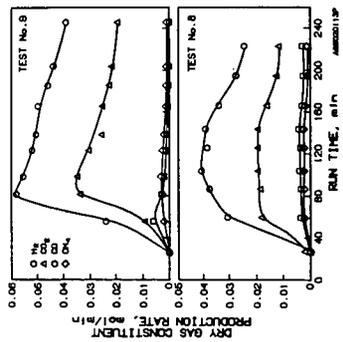


Figure 6. DRY GAS PRODUCTION RATES OF H_2 , CO_2 , CO AND CH_4 FOR THE UNCATALYZED AND CATALYZED BITUMINOUS CHAR

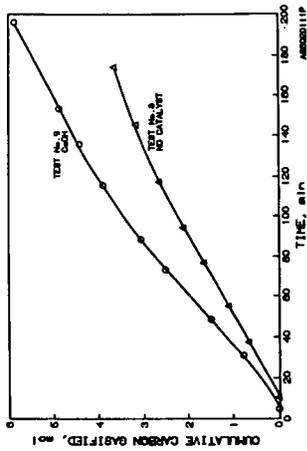


Figure 7. EFFECT OF CATALYST ON THE CUMULATIVE CARBON GASIFIED FOR THE BITUMINOUS CHAR

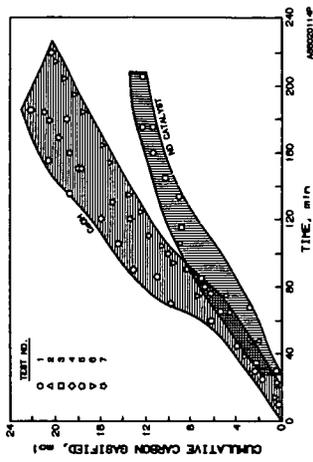


Figure 8. EFFECT OF CATALYST ON THE CUMULATIVE CARBON GASIFIED FOR THE LIGNITE CHAR