

CATALYTIC GASIFICATION OF SHALE OIL

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INTRODUCTION

Although the United States has large proven reserves of natural gas, our annual marketed production increased from less than 4 trillion cubic feet in 1945 to nearly 16 trillion cubic feet in 1964 (9). This increase, coupled with our decreasing ratio of reserves to production, has stimulated interest in possible methods for supplementing our future natural gas supply. The large quantities of oil shale in the western United States suggest the use of oil shale or shale oil for such supplemental purposes. Various authors have reported on the thermal gasification of these materials (5,6,7,8). The present study is concerned with catalytic hydrogasification of crude shale oil, using as catalysts depleted uranium and cobalt molybdate on alumina supports.

Previous experiments in catalytic hydrogenation of crude shale oil at the Laramie Petroleum Research Center of the Bureau of Mines (3,4) showed that pressures in excess of 2,000 pounds per square inch greatly suppressed the formation of methane, ethane, and catalyst deposits. At 500 pounds pressure, catalyst deposits became excessive. The gasification experiments were, therefore, made at 1,000 pounds pressure as a means of obtaining high gas yields with moderate catalyst deposits.

APPARATUS AND PROCEDURE

A simplified flow diagram of the apparatus used for the gasification study is shown in figure 1. The reactor was a vertical 2-9/16-inch-I.D. by 32-inch-long stainless steel vessel; it was modified for these experiments by a stainless steel sleeve that was inserted to reduce the internal diameter to 1 inch. This modification effected improved temperature control. The reactor contained 18 inches of alundum granules at the top to serve as a preheater, 12-1/2 inches of catalyst, and 1-1/2 inches of alundum granules at the bottom. Catalyst temperatures were determined by five thermocouples spaced at 2-1/4-inch intervals in a central thermowell in the catalyst bed.

Hydrogen and oil were mixed at the inlet to the reactor and passed downward through the catalyst. Liquid products were separated in two high-pressure separators operated in series at 350°F. and 40°F. Gas from the cold receiver was metered and stored until it could be sampled for mass spectrometer analysis.

Each gasification experiment was run for 6 hours with 12,000 cubic feet of hydrogen per barrel. At the end of an experiment, liquid products were distilled into a light-ends fraction collected in a dry-ice trap, a naphtha fraction boiling up to 400°F., and a recycle fraction containing everything boiling above 400°F. The light ends from the cold trap were analyzed by the mass spectrometer and appropriate weights were added to the gaseous and liquid products. Carbon deposits in the reactor were determined by measuring the carbon dioxide obtained when passing air through the reactor to regenerate the catalyst.

CATALYSTS

The catalysts used were commercial cobalt molybdate and a laboratory-prepared depleted uranium catalyst. The cobalt molybdate is a rugged catalyst, able to stand repeated regenerations and exposure to high temperatures such as those used in gasification work. It consisted of cobalt and molybdenum oxides on 6- to 8-mesh alumina

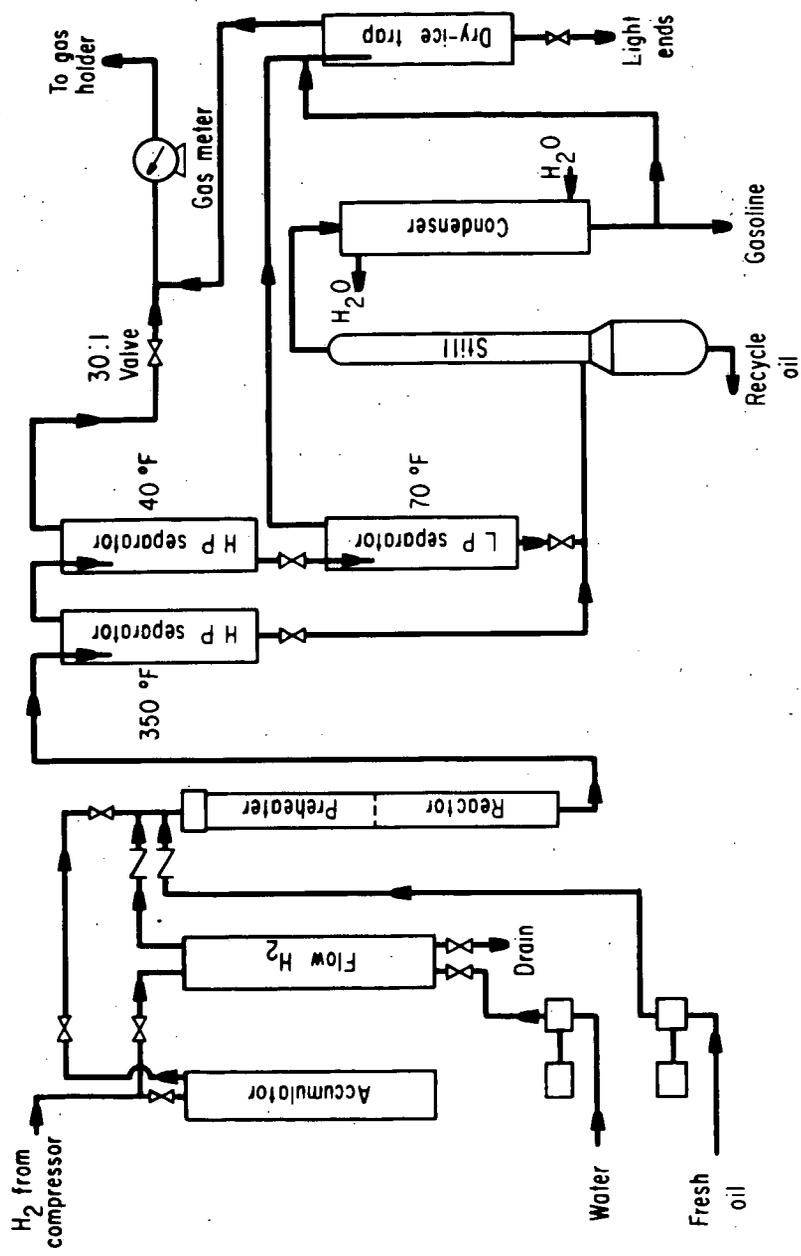


FIGURE 1 - Hydrogenation unit

granules. The uranium catalyst consisted of 7.7 percent depleted uranium (uranium from which the U-235 has been removed) in the oxide form on 1/8-inch H-151 alumina balls. This catalyst had produced high gas yields in previous hydrogenation experiments with shale oil at the Laramie Petroleum Research Center, and these results suggested its possible use as a hydrogasification catalyst. Both catalysts were maintained under a hydrogen atmosphere at approximate reaction temperature and pressure for about 12 hours before each experiment.

FEEDSTOCK

The crude shale oil used for these studies was prepared in the Bureau of Mines gas-combustion retort at Rifle, Colorado. It was filtered before use to reduce the ash content to a few hundredths of 1 percent. Properties are shown in table 1. The

TABLE 1. - Properties of crude shale oil

Specific gravity at 60°/60°F.		0.9408
Elemental analysis:		
Sulfur	wt. %	0.68
Nitrogen	wt. %	2.18
Carbon	wt. %	83.96
Oxygen (by diff.)	wt. %	11.40
Hydrogen/carbon atomic ratio		1.61
Carbon residue	wt. %	3.5
Iron	p.p.m.	40
Zinc and arsenic		Present
Viscosity at 140°F.	cs.	28.30
Viscosity at 210°F.	cs.	8.23
ASTM gas-oil dist'n at 760 mm.:		
I.B.P.	°F.	407
Max. (cracking)	°F.	695
Recovery	vol. %	37.5
Residue	vol. %	62.5

oil contains a large amount of sulfur-, nitrogen-, and oxygen-containing compounds, and more than half of it may consist of non-hydrocarbons (2). It has a high viscosity and contains no gasoline-boiling-range material. The hydrogen-carbon mole ratio of 1.61 shows that additional hydrogen must be added to the oil in order to convert it to pipeline gas.

CALCULATIONS

All gas measurements are reported at 60°F. and 760 mm. mercury pressure. The hydrogen feed rate of 12,000 cubic feet per barrel at these conditions was 1.1 times the stoichiometric amount of about 10,890 cubic feet needed to convert the crude oil completely to methane, hydrogen sulfide, ammonia, and water. The yield of methane as percent of stoichiometric was calculated by dividing the volume in cubic feet per barrel by 8,740, which was the stoichiometric yield at the given conditions.

Conversion of feedstock was defined to be that portion of the feed converted to materials other than liquid oil and gas heavier than propane. It would include water, hydrogen sulfide, ammonia, coke, and gas. Weight percent conversion was defined as 100 minus the weight percent liquid and gaseous products heavier than propane. Yields of methane as percent of conversion were obtained by dividing the weight percent methane by the weight percent conversion and multiplying by 100.

Gross heating values were calculated from component heating values used by the Bureau of Mines in reporting the analyses of natural gases (1). The values were calculated at 760 mm. mercury pressure to agree with the volume measurements.

RESULTS WITH DEPLETED URANIUM CATALYST

Table 2 shows the results from five experiments in hydrogasifying crude shale oil over depleted uranium catalyst at a space velocity of 0.5 volumes of oil per volume of catalyst per hour. Average reaction temperatures for the different experiments were from 880° to 1,102°F.

Total gas volumes increased from 762 cubic feet per barrel at 880°F. to 3,303 cubic feet at 1,102°F.; at the same time, the methane content of the gas increased from 47.9 to 53.5 volume percent, resulting in a change in the volume of methane from 365 to 1,767 cubic feet. A corresponding decrease in the heating values of the gas occurred, from 1,589 to 1,481 Btu per cubic foot, as the heating values tended to approach that of methane.

Expressed on the weight basis, the yield of methane increased from 4.7 percent at 880°F. to 22.6 percent at 1,102°F., and total conversion increased from 23.6 to 69.4 percent; the corresponding change in methane yield expressed as weight percent of conversion was from 19.9 to 32.6 percent.

RESULTS WITH COBALT MOLYBDATE CATALYST

Table 3 shows results from hydrogasifying crude shale oil over cobalt molybdate catalyst at a space velocity of 1.0 volume of oil per volume of catalyst per hour. The average reaction temperatures from 974° to 1,183°F. were higher than those used with depleted uranium catalyst. Consequently, greater gas yields were obtained with the cobalt molybdate. However, similar trends were shown by the results obtained with both catalysts.

Conversion increased from 34.1 to 85.1 percent as the average temperature was increased from 974° to 1,183°F., and, at the same time, methane yield, as weight percent of conversion, increased from 24.6 to 46.6 percent. Also, the methane content of the gas increased from 45.8 to 63.0 volume percent. The increased percentage of methane in the gas at the higher temperature and conversion levels was reflected in the heat content of the gas, which decreased from 1,601 Btu per cubic foot for the gas obtained at 974°F. to 1,315 Btu per cubic foot for the gas obtained at 1,183°F.

Table 4 shows results from hydrogasifying crude shale oil over cobalt molybdate at space velocities of 0.50 and 0.25. Results of two experiments at different temperatures are shown for each space velocity.

Decreasing the space velocity had much the same effect as increasing the reaction temperature. Comparing results obtained at 1,106°F. average temperature and 0.25 space velocity with those obtained at 1,114°F. and 0.50 space velocity shows that greater methane yield, greater total gas yield, greater conversion, and higher methane yields expressed either as percent of conversion or percent of total gas were obtained at the lower space velocity. Heating value of the gas is lower for the gas produced at the lower space velocity because of the higher methane content. These comparisons can be extended to the results shown in table 3 for the experiment at 1,106°F. and 1.0 space velocity.

The highest methane yield, of 4,341 cubic feet per barrel, and highest gas yield, of 5,725 cubic feet per barrel, were obtained at the highest temperature (1,196°F. average or 1,208°F. maximum) and lowest space velocity (0.25) that were used. The greatest conversion of feedstock, 88.1 weight percent, and greatest yield of methane as percent of conversion, 63.3 percent, also were obtained at these conditions. Methane content of the gas was 75.8 volume percent, or 49.7 percent of stoichiometric. Heating value of the gas was 1,202 Btu per cubic foot.

TABLE 2. - Gasification of crude shale oil over depleted uranium catalyst

Space velocity	(Pressure 1,000 p.s.i.g.; hydrogen feed 12,000 scf/bbl)							
	0.5 V ₀ /V _c /hr.				0.5 V ₀ /V _c /hr.			
Temp. (average)	880	954	1010	1053	1102			
Temp. (maximum)	906	979	1035	1074	1125			
H ₂ consumed	1340	1840	3080	3980	4170			
Methane	365	598	1152	1507	1767			
Ethane	200	387	693	971	1059			
Propane	146	247	441	536	459			
Ethylene	18	4	29	18	18			
Propylene	33	0	44	40	0			
Total	762	1236	2359	3072	3303			
Heat value, gross	1589	1570	1565	1550	1481			
C ₄ + liquid	wt. %	76.4	67.5	44.9	32.9	30.6		
Conversion	wt. %	23.6	32.5	55.1	67.1	69.4		
Catalyst deposit	wt. %	5.1	4.7	4.9	4.0	5.5		
Water	wt. %	2.0	2.0	2.0	2.0	2.0		
Hydrogen sulfide	wt. %	0.6	0.7	0.7	0.7	0.7		
Ammonia	wt. %	1.6	2.0	2.1	2.5	2.4		
Methane	wt. %	4.7	7.7	14.8	19.3	22.6		
Methane	wt. % of conv.	19.9	23.7	26.9	28.8	32.6		
Methane	vol. % of gas	47.9	48.4	48.8	49.0	53.5		
Methane	vol. % of stoich.	4.2	6.8	13.2	17.2	20.2		

TABLE 3. - Gasification of crude shale oil over cobalt molybdate catalyst

(Pressure 1,000 p.s.i.g.; hydrogen feed 12,000 scf/bbl)

Space velocity		1.0 V_0/V_C /hr.			
Temp. (avg.)	°F.	974	1004	1106	1183
Temp. (max.)	°F.	1018	1049	1172	1226
H ₂ consumed	scf/bbl	2680	3210	4850	5980
Methane	scf/bbl	652	972	1945	3090
Ethane.	scf/bbl	427	663	1292	1699
Propane	scf/bbl	288	435	504	109
Ethylene	scf/bbl	27	48	5	0
Propylene	scf/bbl	30	57	0	5
Total	scf/bbl	1424	2175	3746	4903
Heat value, gross	Btu/cu.ft.	1601	1611	1490	1315
C ₄ + liquid	wt. %	65.9	50.5	24.9	14.9
Conversion	wt. %	34.1	49.5	75.1	85.1
Catalyst deposit	wt. %	2.4	2.0	2.4	4.2
Water	wt. %	2.0	2.0	2.0	2.0
Hydrogen sulfide	wt. %	0.7	0.7	0.7	0.7
Ammonia	wt. %	2.6	2.6	2.6	2.6
Methane	wt. %	8.4	12.5	25.0	39.7
Methane	wt. % of conv.	24.6	25.3	33.3	46.6
Methane	vol. % of gas	45.8	44.7	51.9	63.0
Methane	vol. % of stoich.	7.5	11.1	22.2	35.4

Conditions used with the cobalt molybdate were not generally the same as those used with the depleted uranium catalyst. However, the gas yields obtained at 1,062°F. and 0.50 space velocity over cobalt molybdate were similar to those obtained at 1,053°F. and 0.50 space velocity over depleted uranium. Better elimination of nitrogen from the liquid products was achieved with the cobalt molybdate, as shown by the higher yield of ammonia obtained. No special advantages were found for the depleted uranium, but further research would be needed to fully evaluate it over the entire range of conditions investigated with the cobalt molybdate.

SUMMARY

Cobalt molybdate on alumina and depleted uranium on alumina were tested as catalysts for hydrogasifying crude shale oil at 1,000 pounds pressure with a hydrogen feed rate of 1.1 times the stoichiometric, with on-stream periods of 6 hours for each experiment. Temperatures used were in the range 880° to 1,102°F. with depleted uranium and 974° to 1,196°F. with cobalt molybdate. With both catalysts, the higher reaction temperatures produced greater gas yields, greater percentages of methane in the gas, and greater methane yields expressed as percentage of conversion of feedstock. The high heating values of the gases decreased at the higher reaction temperatures and more nearly approached that of methane. Lowering the space velocity through the range 1.0 to 0.25 with cobalt molybdate produced effects similar to those obtained when raising the temperature. Further research would be necessary to adequately evaluate the process variables when using depleted uranium catalyst.

pressure regulator (P). The unit pressure is indicated by a precision pressure gage, the pressure drop across the catalyst bed by a differential pressure gage. The reactor temperatures and the feed-vaporizer temperatures are controlled by a six-point potentiometric-type on-off temperature controller.

The reactor used in the first series of tests with *n*-hexane, *n*-octane, and kerosene was simpler in construction than that used in the remainder of the test program. The major reactor and furnace dimensions are shown schematically in Fig. 2. The reactor had been designed and used for operation at high temperatures and pressures and is described fully elsewhere.¹¹ Because of its large diameter, the reactor was provided with a thick insert to reduce the internal diameter as well as to contain the catalyst and provide for complete and easy catalyst removal. The entire reactor was heated by a single-zoned electric furnace. The temperatures within the reactor were measured by a single traveling thermocouple made of Chromel-Alumel and insulated with magnesium oxide. It has a 0.040-inch-OD swaged stainless steel sheath. The thermocouple was mounted within an 1/8-inch-OD stainless steel thermowell which was mounted in the top cover of the reactor. Feed vapors entered the top of the reactor, flowed downward through the catalyst bed, and returned to the top of the reactor through a 3/16-inch-OD dip tube sealed into the top cover of the reactor by a compression-type fitting.

The major reactor and electric furnace dimensions for the second reactor are shown schematically in Fig. 3. The furnace has four heating zones; two are on the catalyst bed which is supported and contained by two beds of alumina inerts. Two separate heaters were used in the catalyst zone to provide better temperature control. A thermocouple rake assembly, which contained seven Chromel-Alumel thermocouples was used to measure reactor temperatures. The thermocouples are insulated with magnesium oxide and have 0.025-inch-OD swaged stainless steel sheaths. To minimize possible temperature-measurement errors due to axial heat conduction along the thermocouples assembly, each thermocouple extends perpendicularly from the axial thermowell. To follow the progress of the reaction through the catalyst bed and the deactivation of the catalyst with time, four sampling probes were inserted at the same levels as thermocouples 3, 4, 5, and 6. The probes were located approximately 1/4 inch, 1-1/2 inches, 2-3/4 inches, and 4 inches below the top of the bed.

Methods were developed for collecting and analyzing the gas and liquid samples taken with the probes. These methods allow continuous samples to be withdrawn simultaneously at all four points within the catalyst bed. The bed ranged from 25 to 200 cc in volume. Since the total flow rate of the probe samples is only a few percent of the total exit stream flow rate, the stability of reactor operation is not impaired, and the flow rate in the bed does not vary appreciably. A Precision Scientific Co. Chronofrac gas chromatograph was installed for analyzing probe and product gas samples.

A special feed system was devised for high-vapor-pressure light hydrocarbons such as propane and butane. The light hydrocarbons were fed through a high-pressure rotameter from pressurized stainless steel cylinders. Two cylinders were used so that one cylinder could be used to feed the hydrocarbon while the other was being weighed. The cylinders were switched and weighed at the beginning and end of each steady-state period so that the hydrocarbon feed rate could be

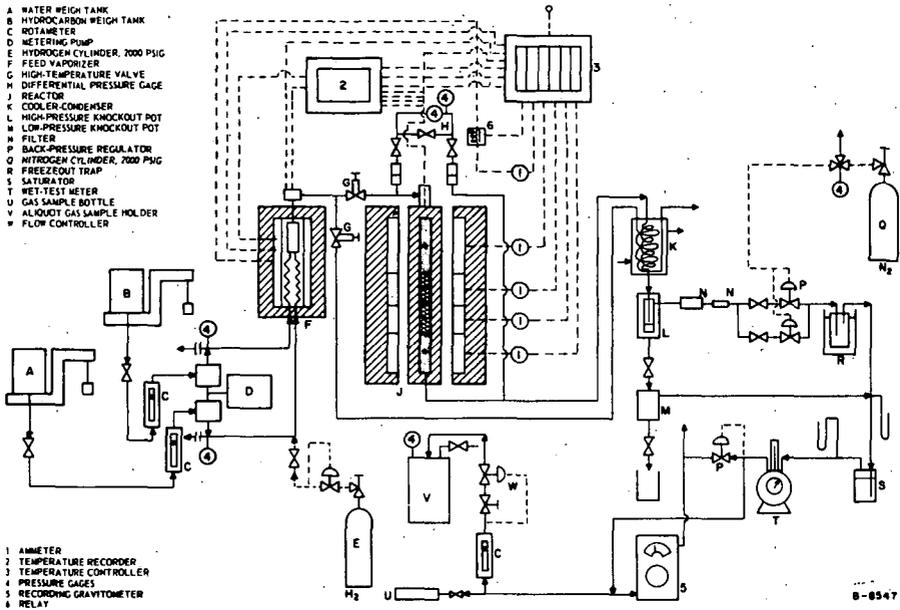


Fig. 1. -CATALYST TESTING UNIT

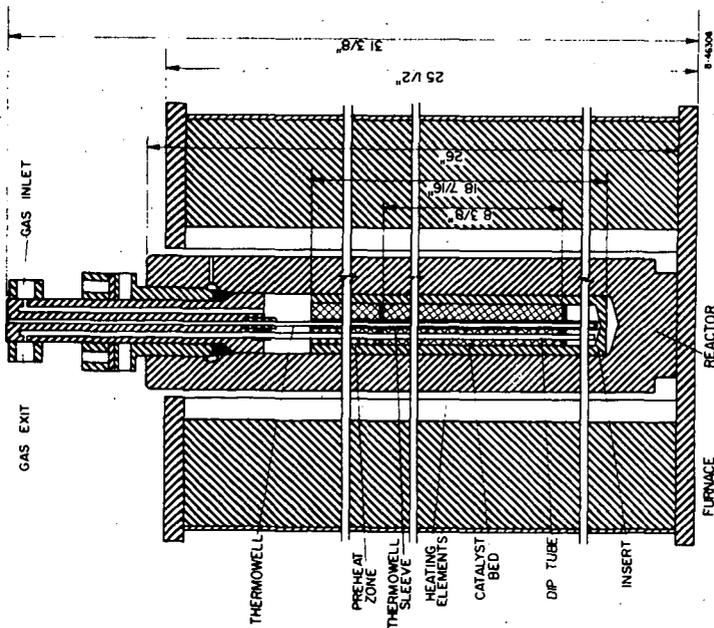


Fig. 2. -FIRST REACTOR AND FURNACE

measured more accurately. The tanks were provided with quick-disconnect couplings at each end. These couplings contained double, integral check valves to reduce loss of hydrocarbon during the switching operation to a minimum.

Feedstocks were obtained from several sources. Pure hydrocarbons were obtained from Phillips Petroleum Company. The *n*-hexane and benzene were pure grade (99.0 mole percent minimum purity). The *n*-octane was technical grade (95.0 mole percent minimum purity).

The propane used was a commercially available feed supplied by Pyrofax Corporation. The light kerosene, supplied by Universal Oil Products Company, had been partially desulfurized. The light fuel naphtha was obtained from Industrial Solvents Corporation. The jet fuel was obtained from Humble Oil and Refining Company. The properties of the commercial feeds are presented in Table 1.

Chemical and physical analyses of liquid feeds were performed by A.S.T.M. standard methods where applicable.¹ Gaseous feeds and product gases were analyzed by a method which is based largely on that given by Hoggan and Battles¹⁰ and Bertolacini and Barney.⁹ The liquid feeds, having low sulfur contents, were analyzed for sulfur by a method given by Attari.²

RESULTS

Thermodynamic Equilibrium Studies

A detailed thermodynamic equilibrium study was made for a number of pure hydrocarbon feedstocks to calculate the effects of operating variables on the heat of reaction and product gas composition. These calculations were made because experimental work done elsewhere had shown that product gas compositions approached equilibrium quite closely with active catalysts.⁵ It was thus expected that not only would these calculations be a guide for conducting experimental work, but also would minimize the amount of experimental work required.

Equilibrium gas compositions, heats of reaction, and adiabatic temperature changes were calculated for each initial reaction temperature. The variables studied were temperature, pressure, feed steam/carbon ratio, and feedstock.

Equilibrium gas compositions (on a dry basis) for steam reforming of *n*-hexane are given as a function of temperature, pressure, and feed steam/carbon ratio in Fig. 4. In the range of variables studied, the carbon dioxide content is almost independent of temperature, pressure, and feed steam/carbon ratio above a pressure of 10 atm and below 750°K. The carbon monoxide content is affected by temperature and pressure, but is not present in substantial concentrations. Increasing the pressure and decreasing the temperature results in increases in raw gas heating value, since methane content increases and hydrogen content decreases. The high hydrogen contents shown at 1 atm, 800°K, and high steam/carbon ratios suggest the possibility of using this process for hydrogen production in some systems, such as fuel cells, where a pure hydrogen stream is not required.

The effect of paraffin carbon number on the equilibrium methane concentration is shown for three feed steam/carbon ratios in Fig. 5. These results indicate that a higher methane content gas can

Table 1.-COMMERCIAL FEEDSTOCK PROPERTIES

<u>Liquid Feeds</u>			
Feedstock	Light Naphtha	Jet Fuel	Light Kerosene
Source	Industrial Solvents Corp.	Humble Oil & Refining Co.	Universal Oil Products Co.
Specific Gravity, °API (60°/60°)	70.3	56.5	48.8
ASTM Distillation, °F			
I.B.P.	167	194	361
5%	171	238	371
10%	171	253	374
20%	173	268	378
30%	174	280	384
40%	176	293	388
50%	177	308	394
60%	180	323	400
70%	183	350	408
80%	187	385	416
90%	194	430	430
End Point	203	478	445
Recovery, %	99	95	98
Residue, %	1	3	2
Ultimate Analysis, wt %			
Carbon	84.42	84.84	85.41
Hydrogen	15.58	14.56	14.58
Total	100.00	99.40	100.00
C/H Ratio	5.42	5.83	5.85
Sulfur, ppm	28.9	80.5	32.4
Hydrocarbon Type A Analysis, vol %			
Aromatics	2.0	10.6	5.3
Olefins	0.0	4.6	1.1
Saturates	98.0	84.8	93.6
Total	100.0	100.0	100.0
<u>Gaseous Feed</u>			
Feedstock	Propane		
Source	Pyrofax Corp.		
Composition, mole %			
Propane	94.5		
Propylene	2.5		
Ethane	1.5		
i-Butane	1.0		
n-Butane	0.5		
Total	100.0		
Sulfur Content, ppm	16.8		

TABLE 4. - Gasification of crude shale oil over cobalt molybdate catalyst

(Pressure 1,000 p.s.i.g.; hydrogen feed 12,000 scf/bbl)					
Space velocity		0.50 V_0/V_C /hr.		0.25 V_0/V_C /hr.	
Temp. (avg.)	°F.	1062	1114	1106	1196
Temp. (max.)	°F.	1089	1141	1129	1208
H ₂ consumed	scf/bbl	3803	4985	5460	6852
Methane	scf/bbl	1465	2141	2485	4341
Ethane	scf/bbl	995	1379	1683	1357
Propane	scf/bbl	461	407	231	25
Ethylene	scf/bbl	9	23	0	1
Propylene	scf/bbl	24	18	18	1
Total	scf/bbl	2954	3968	4417	5725
Heat value, gross	Btu/cu.ft.	1530	1451	1393	1202
C ₄ + liquid	wt. %	35.5	23.2	20.2	11.9
Conversion	wt. %	64.5	76.8	79.8	88.1
Catalyst deposit	wt. %	4.7	2.6	1.4	4.1
Water	wt. %	2.0	2.0	2.0	2.0
Hydrogen sulfide	wt. %	0.7	0.7	0.7	0.7
Ammonia	wt. %	2.6	2.6	2.6	2.6
Methane	wt. %	18.8	27.5	31.9	55.8
Methane	wt. % of conv.	29.1	35.8	40.0	63.3
Methane	vol. % of gas	49.6	54.0	56.2	75.8
Methane	vol. % of stoich.	16.8	24.5	28.4	49.7

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PRODUCTION OF HIGH-METHANE-CONTENT GAS BY
STEAM REFORMING OF LIGHT DISTILLATES

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INTRODUCTION

A novel approach to gasification of light distillate oils, developed by the British Gas Council, was first reported in 1957^{4,7,8} and was subsequently discussed in later publications.^{6,9} The process entails reducing the sulfur content of the feed by a hydrodesulfurization step with subsequent steam reforming in the presence of a nickel catalyst. Because of the low temperature at which reforming is conducted - in the range of 400° to 550°C - the product gas contains 60 to 80 mole percent methane (dry basis). Data reported by the Gas Council^{5,6} show product gas heating values of 626 to 704 Btu/SCF in operation over a pressure range of 1 to 25 atm. There was no carbon deposition at fairly low steam/hydrocarbon ratios, and the reaction was either thermally balanced or slightly exothermic. The catalyst is reported to be extremely sulfur-sensitive and is also subject to poisoning by olefins.

When a high-Btu gas is not the desired final product, the process includes a further stage in which the high-methane-content gas is further reformed to a low-Btu gas. This process is now used in Great Britain for baseload town gas production.⁹

A study of this process was begun under an IGT-supported basic research project. After a detailed study of the thermodynamics of the process, experiments were conducted with high-purity *n*-hexane, *n*-octane, and benzene, as well as commercial propane, naphtha, kerosene, and jet fuel.

The objectives of this study were to determine whether a catalyst could be developed that would be capable of reforming a variety of feedstocks that include paraffinic, olefinic, and aromatic materials with a wide range of molecular weights. Once a catalyst was developed, it was necessary to determine minimum steam/hydrocarbon ratios for operation without carbon deposition, the activity of the catalyst, and the effects of various operating variables on the gas yield and composition.

EXPERIMENTAL EQUIPMENT AND PROCEDURES

A schematic diagram of the reaction system is shown in Fig. 1. Weighed amounts of the hydrocarbon feedstock (A) and water (B) flow through rotameters (C), and are charged by a duplex metering pump (D) to the feed vaporizer (F). The vaporized feeds are thoroughly mixed in a chamber above the vaporizer. The mixed feed flows down through the catalyst bed in the reactor (J). The product gas is cooled, and liquids are condensed in a cooler-condenser (K). Condensate is knocked out and drained from the system (L,M). The gas flows through filters (N) into a freezeout trap (R). After saturation with water vapor, the product gas (S) is metered by a wet-test meter (T) and sampled (U). The specific gravity is monitored by a recording gravitometer (5). The unit pressure is controlled by a dome-loaded back-

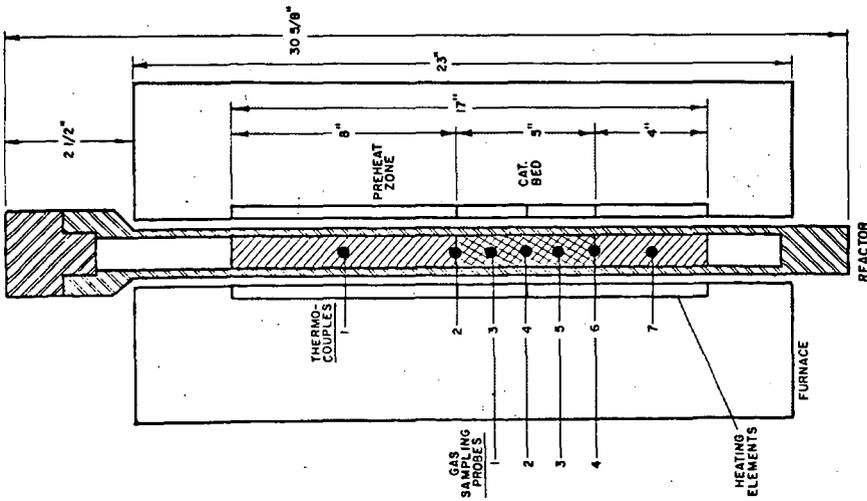


Fig. 3. - SECOND REACTOR AND FURNACE

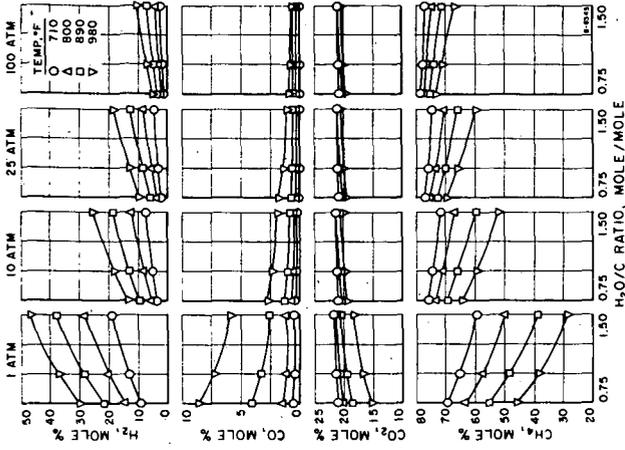


FIG. 4. - IDEAL GAS EQUILIBRIUM COMPOSITION (water-free) FOR STEAM REFORMING OF n-HEXANE

be produced from low molecular weight paraffins than from high molecular weight paraffins.

The reforming reaction can be either exothermic or endothermic depending on the temperature and pressure. Increases in pressure cause the reaction to become more exothermic, whereas increases in temperature cause the opposite effect. The reaction becomes progressively less exothermic as the feed steam/carbon ratio is increased. The degree of exothermicity increases with increases in molecular weight.

Reforming Studies with n-Hexane Feedstock

Space Velocity

Initial studies were made with pure grade n-hexane to determine the reaction stoichiometry, approach to equilibrium, and the catalyst behavior without complicating factors such as catalyst poisons. The feedstock space velocity was the first process variable studied to measure the maximum catalyst activity under the most ideal conditions. The effect of space velocity on product gas composition was also noted. At space-time yields over 50,000 SCF/cubic foot catalyst per hour, 98 percent of the hexane could be converted to gaseous products. When conversions dropped below 100 percent, the major effect of an increase in space velocity on gas composition was a decreased methane content and an increased hydrogen content of the product gas (Fig. 6). The carbon dioxide content of the gas remained essentially constant. Carbon monoxide remained negligible over the entire range of space velocity. Even at the highest space velocity used, the heating value of the product gas could be raised to about 850 Btu/SCF by simply scrubbing out carbon dioxide to a final content of 2 mole percent. This could be satisfactory for peakshaving.

Because the carbon monoxide content of the gas was so low, approaches to equilibrium could not be calculated accurately for runs at nearly complete conversion and low space velocity. One other factor that also makes it difficult to calculate approaches to equilibrium is the presence of a hot spot within the catalyst bed, which indicates that the reaction may occur in a very narrow zone. Temperature profiles were measured in three runs (Fig. 7). The gas compositions for these runs correspond to equilibrium at the temperatures measured near the bottom (exit) of the catalyst bed, which is what would be expected.

Steam/Hydrocarbon Ratio

The next series of tests was made to show the effect of the steam/hydrocarbon ratio on gas composition (Fig. 8) and to determine the minimum practical steam/hydrocarbon ratio. The trends shown are approximately the same as predicted by equilibrium calculations. The lack of complete temperature profile data makes it difficult to show how closely the trends agree with equilibrium predictions. Steam/hydrocarbon weight ratios as low as 1.6 (molar ratio of 7.7) were shown to be adequate to prevent carbon deposition. The product gas heating value at this low ratio was about 774 Btu/SCF. It could be raised to 957 Btu/SCF if the exit gas carbon dioxide were reduced to 2.0 mole percent by scrubbing.

Reforming of Various Feedstocks

When the catalyst developed proved to be capable of reforming pure n-hexane successfully at low steam/hydrocarbon ratios, we decided to test a variety of feedstocks having a wide range of molecular weight:

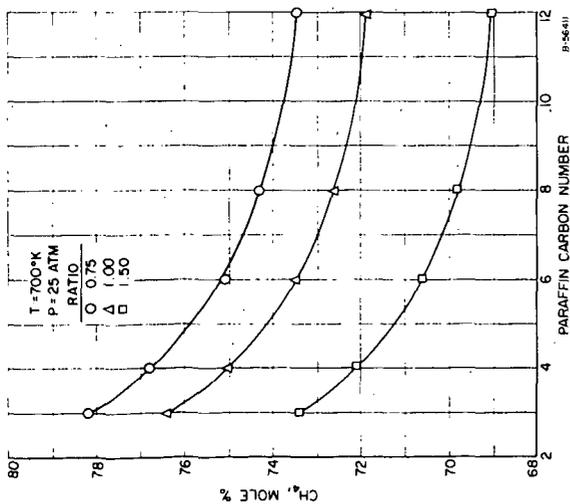


Fig. 5. - IDEAL GAS EQUILIBRIUM METHANE CONTENTS (Water-Free) FOR STEAM REFORMING OF VARIOUS PARAFFINIC HYDROCARBONS

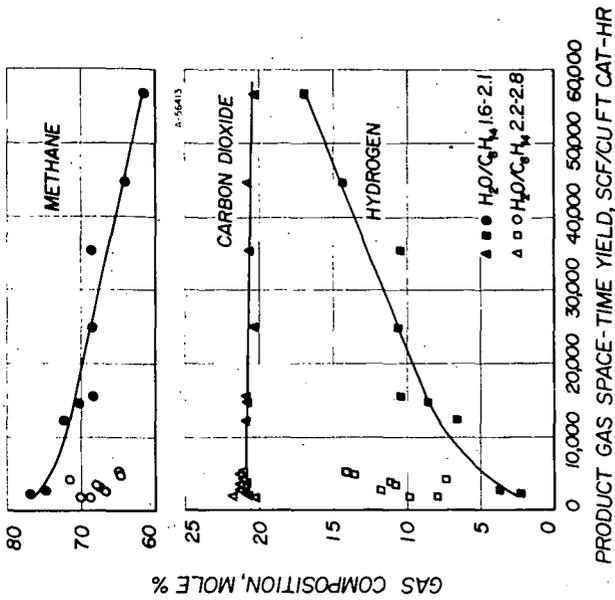


Fig. 6. - GAS COMPOSITION AS A FUNCTION OF SPACE-TIME YIELD AND STEAM/HYDROCARBON RATIO

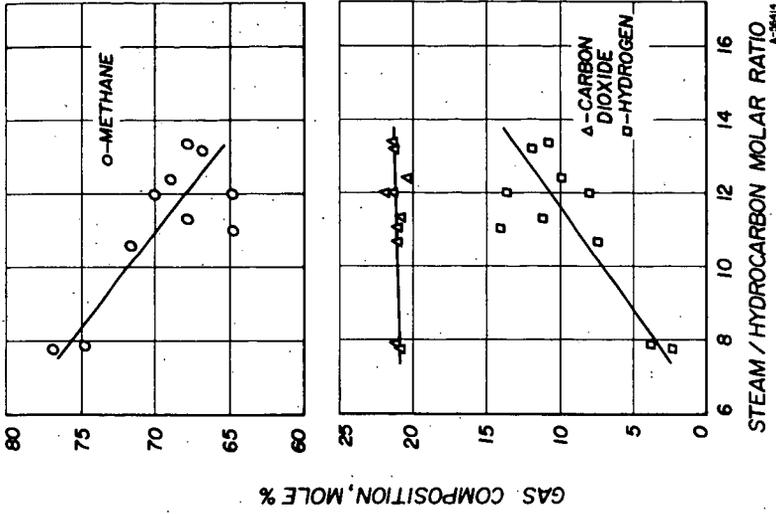


Fig. 8.-EFFECT OF STEAM/HYDROCARBON RATIO ON GAS COMPOSITION

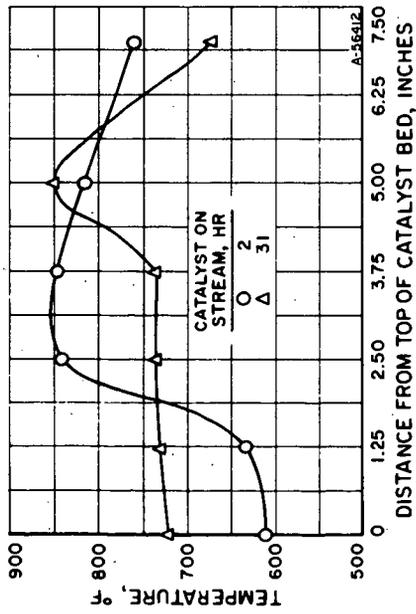


Fig. 7.-BED CATALYST TEMPERATURE PROFILES

and various types of hydrocarbons. The first tests were conducted with n-octane and benzene to show whether heavier paraffins and aromatics could be reformed and whether the gases produced could be predicted by equilibrium calculations.

Test results for n-octane and benzene reforming are summarized in Table 2. The steam/hydrocarbon ratios were deliberately set high to avoid possible carbon formation with these heavier or aromatic feedstocks.

Table 2.-TEST RESULTS FOR STEAM REFORMING
OF n-OCTANE AND BENZENE

<u>Feedstock</u>	<u>n-Octane</u>	<u>Benzene</u>
Pressure, psig	375	353
Temperature at Center of Bed, °F	768	905
Steam/Hydrocarbon Weight Ratio	2.07	4.42
Hydrocarbon Space Velocity, lb/hr-cu ft catalyst	300	324
Product Gas Composition, mole % (water-free)		
N ₂ + CO	0.4	0.9
CO ₂	21.7	30.7
H ₂	11.3	31.3
CH ₄	66.4	36.7
C ₃ H ₈	0.2	--
C ₆ H ₆	--	0.4
Total	100.0	100.0
Scrubbed Gas Composition, mole % (water-free)		
+ CO	0.5	1.3
CO ₂	2.0	2.0
H ₂	14.2	44.3
CH ₄	83.1	52.4
C ₃ H ₈	0.2	--
C ₆ H ₆	--	--
Total	100.0	100.0
Scrubbed Gas Heating Value, Btu/SCF	879	675

The remaining commercial feedstocks studied were propane, light naphtha, light kerosene, and JP-4 jet fuel. The results with these feedstocks are given in Table 3. As can be seen, a higher methane content gas can be produced from the lighter hydrocarbons. This result agrees with results of equilibrium calculations shown in Fig. 5. These feedstocks were all highly paraffinic, of course, but as can be seen from Table 1, the kerosene contained 1.1 volume percent olefins and 5.3 volume percent aromatics; the naphtha contained 2.0 volume percent aromatics, and the jet fuel contained 4.6 volume percent olefins and 10.6 volume percent aromatics. This indicates that over short time periods, aromatics and olefins are not likely to be a problem. However, earlier studies on the methanation process have shown that sulfur compounds may react with the nickel in nickel catalysts almost quantitatively, resulting in catalyst poisoning. Therefore, for commercial operation, low-sulfur-content feedstocks would be preferred.

Table 3. -TEST RESULTS FOR STEAM REFORMING OF SEVERAL COMMERCIAL FEEDSTOCKS

Feedstock	Propane	Naptha	Jet Fuel	Kerosene
Pressure, psig	355	355	350	375
Temperature at Center of Bed, °F	890	935	900	832
Steam/Hydrocarbon Weight Ratio	1.26	2.16	2.36	2.03
Hydrocarbon Space Velocity, lb/hr-cu ft catalyst	834	328	254	226
Product Gas Composition, mole % (water-free)				
N ₂ + CO	0.1	0.2	0.2	1.1
CO ₂	16.8	21.5	22.5	23.6
H ₂	1.9	12.1	14.5	18.1
CH ₄	80.1	66.2	62.6	57.2
C ₂ H ₆	0.1	--	--	--
C ₃ H ₈	1.0	--	--	--
C ₆ H ₁₄	--	--	0.2	--
Total	100.0	100.0	100.0	100.0
Scrubbed Gas Composition, mole % (water-free)				
N ₂ + CO	0.1	0.3	0.3	1.4
CO ₂	2.0	2.0	2.0	2.0
H ₂	2.2	15.1	18.3	23.2
CH ₄	94.4	82.6	79.1	73.4
C ₂ H ₆	0.1	--	--	--
C ₃ H ₈	1.2	--	--	--
C ₆ H ₁₄	--	--	0.3	--
Total	100.0	100.0	100.0	100.0
Scrubbed Gas Heating Value, Btu/SCF	980	883	860	809

ACKNOWLEDGMENT

This work was conducted as part of the Institute of Gas Technology's Basic Research program with funds provided by Institute members and contributors. The guidance and counsel of H. R. Linden, J. Huebler, and H. A. Dirksen is gratefully acknowledged. Tests were conducted by F. Todesca, R. F. Johnson, P. Cameron, and A. S. Lane.

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A REACTION WHICH PERMITS THE CYCLIC USE OF CALCINED DOLOMITE
TO DESULFURIZE FUELS UNDERGOING GASIFICATION

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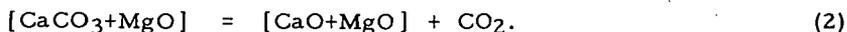
Raw fluid fuels, derived for instance from coal and heavy residual oils by a variety of processes such as gasification, carbonization, or cracking, may be substantially desulfurized by reaction at high temperature with calcined dolomite. This solid can also remove CO₂ from a gas stream; it has the power to convert CO and steam to H₂; and it may participate in the gasification of carbon by steam under a condition of thermal neutrality.

The cyclic use of calcined dolomite for these purposes has previously been hampered by lack of means to recover elemental sulfur from sulfurized calcined dolomite, containing CaS, while at the same time recovering solid in a form suitable for reuse.

The reaction of steam and CO₂ at high pressure with sulfurized calcined dolomite,



can be used to generate a gas stream containing H₂S at a concentration well above the minimum concentration which can be used by a Claus sulfur recovery system. Later, the solid product can be calcined at high temperature to provide a solid containing CaO:



The latter solid can be used to remove H₂S from a fuel gas:



Reactions (1), (2), and (3) can be combined in a cyclic process to desulfurize a fuel undergoing gasification. Heat developed by reaction (1) is at a level suitable for raising or superheating high-pressure steam.

Alternatively, the solid product of reaction (1) can be used directly to remove H₂S from a fuel gas at high temperature by the reverse of reaction (1). The temperature should preferably be just a little below the equilibrium decomposition temperature of CaCO₃ at the prevailing partial pressure of CO₂.

The solid product of reaction (2) can be used to promote CO-shift:



This reaction is the basis of the CO-shift process developed by Gesellschaft für Kohlentechnik during the 1920's (24). The process was conducted in fixed beds, had poor thermal efficiency, and never caught on. An improved version of the process which uses fluidized beds may find modern applications. In this version,

reaction (4) may be combined with reactions (1), (2), and (3) in a cyclic process in which elemental sulfur is recovered.

The solid product of reaction (2) can also participate in the gasification of carbon by steam:



This reaction is the basis of Consolidation Coal Company's Carbon Dioxide Acceptor Gasification Process (16, 18, 19), which eliminates need for oxygen to provide heat to the steam-carbon reaction. The process could be modified for recovery of elemental sulfur by incorporating a step using reaction (1).

Residual oils may be gasified or cracked over calcined dolomite with recovery of elemental sulfur in a cyclic process incorporating reaction (1). A version of this process may find a use in providing sulfur-free fuel to existing power-station boilers in communities which impose restrictions on SO₂ content of flue gases.

These new fuel-desulfurization processes reject very little heat at low temperatures. If a fuel gas is to be used in a combustion, or if the gas is to be subjected to further processing at high temperature -- CO-shift, for example -- the new desulfurization processes have the advantage that the heat exchange required to cool the gases to a low-temperature sulfur-removal step is eliminated. The processes are well suited for use in schemes to produce a clean fuel gas to be burned at high pressure in an advanced power cycle. Indeed, the conception of the new processes was a result of a search for a combination incorporating fuel-gasification at high pressure, fuel-gas cleanup, and an advanced power cycle which could provide electricity at lower cost. Such a combination would be adopted by the power industry as much for reasons of economy as for the advantage that the combination would provide dust-free and sulfur-free effluent. Power cycles which offer the prospect of significant improvement in efficiency are the supercharged-boiler cycle, a cycle incorporating a magnetohydrodynamic device which "tops" the steam cycle, and a top heat power cycle, in which the temperature of steam is raised by direct addition of the products of combustion of a clean fuel with oxygen or air (63, 64).

Dolomite is cheap and widely available, and the solids produced by reactions (1), (2), and (3) are rugged and suitable for use in fluidized beds.

This paper discusses the thermodynamic equilibria which govern the proposed new desulfurization processes; gives results of exploratory bench-scale studies; reviews the relevant dolomite chemistry; and briefly indicates some of the potential applications.

1.0 Discussion of Process Thermodynamics

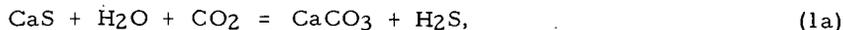
1.01 Review of Thermodynamic Equilibria

Figure 1 gives the equilibrium constant for the reaction



CaO is seen to be an effective desulfurization agent at temperatures as high as 2000° F.

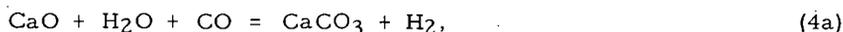
Figure 2, showing the equilibrium constant for the reaction



illustrates the basis for the proposed new desulfurization processes. At temperatures below about 1100° F and at pressures above about 4 atmospheres, say, reaction (1) can be used to derive a gas containing H₂S at a concentration which permits the recovery of elemental sulfur in a Claus system.

The curve of Figure 2 is so steep that the reverse of reaction (1) can be used to desulfurize a gas at temperatures above about 1600° F.

Figure 3 gives the equilibrium constant for the reaction



which must often be considered in finding the composition of gas desulfurized by the new process.

The upper curve of Figure 4 gives an estimate of the equilibrium constant for the reaction



A key to the success of Consolidation's CO₂ Acceptor Process is control of conditions for the calcination of [CaCO₃+MgO] so that sulfur is expelled as SO₂. By using fuel-rich combustion which provides a calciner offgas containing H₂ in an amount greater than called for by the upper curve of Figure 4, one can prevent the oxidation of CaS to CaSO₄ and the "fixing" of sulfur in the latter form. Sulfur is then rejected as SO₂ by reaction between CaS and CaSO₄ (19, 74).

In contrast to Consolidation's procedure, one wishes to preserve CaS unchanged during a calcination step in the new desulfurization process. The lower curve of Figure 4 gives an extremely rough estimate of the equilibrium constant for the reaction



Since CaSO₃ disproportionates to CaS and CaSO₄ at temperatures above about 930° F (46, 70), it would appear that calciner offgas should contain hydrogen in an amount greater than called for by the lower curve of Figure 4 if one wishes to avoid rejecting any sulfur as SO₂. This has been arranged for in studies of the new desulfurization process. If the reaction rejecting SO₂ is slow by comparison with the rate of reduction of CaSO₄ by H₂, less hydrogen may be required to prevent significant loss of sulfur as SO₂.

Since CaSO₄ is readily reduced by H₂ to CaS at 930° F (51), it would appear desirable that H₂ be present during reaction (1) to avoid oxidation of CaS by steam. Presence of H₂ in excess of the amount called for by the lower curve of Figure 4 has been assumed in studies of the new desulfurization process. Because

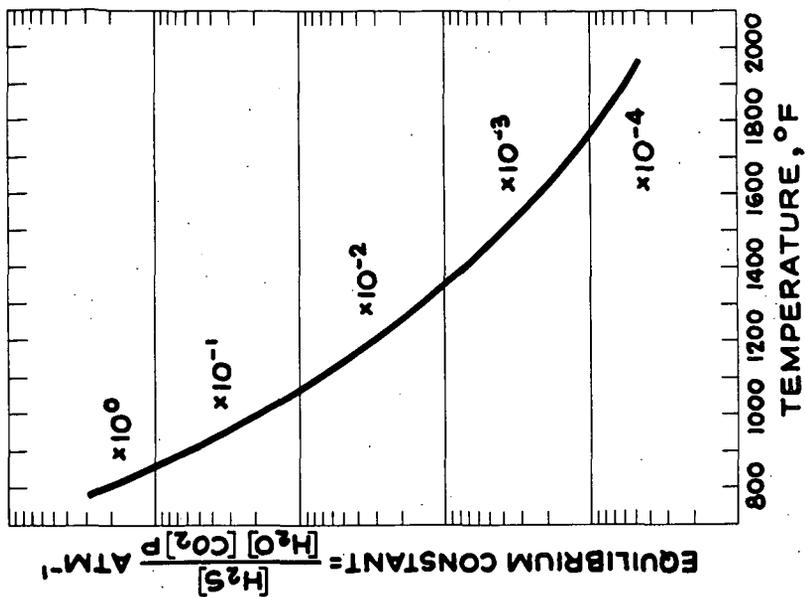


Figure 2. EQUILIBRIUM CONSTANT FOR:
 $\text{CaS} + \text{H}_2\text{O} + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{S}$

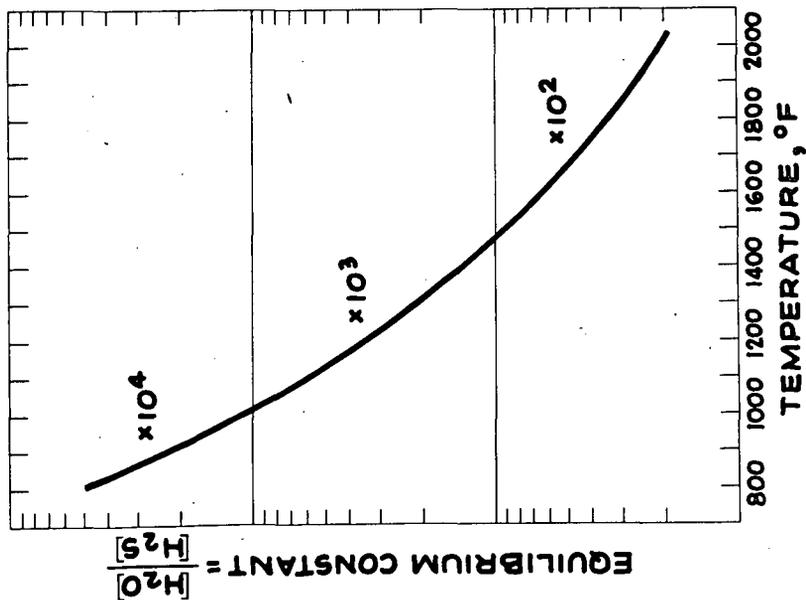


Figure 1. EQUILIBRIUM CONSTANT FOR:
 $\text{CaO} + \text{H}_2\text{S} = \text{CaS} + \text{H}_2\text{O}$

of the tendency of CaSO_3 to disproportionate, less H_2 may in fact be needed to prevent a significant degree of reaction between steam and CaS .

If CaO is present, the steam partial pressure should not exceed the equilibrium decomposition pressure of $\text{Ca}(\text{OH})_2$. As Curran, Rice, and Gorin (19) pointed out, the steam partial pressure should not exceed 13 atmospheres if both CaO and CaCO_3 are present at a temperature around 1650°F ; at higher steam pressures, a melt is formed.

Equilibrium is against the formation of MgS under all conditions encountered in the new desulfurization process.

1.02 Sources of Thermodynamic Data

The curve of Figure 1 is based upon the equation: $\log [\text{H}_2\text{O}] / [\text{H}_2\text{S}] = (3421.5/T) - 0.190$, where p [...] signifies mole fraction and $T = ^\circ\text{K}$. The equation is derived from Rosenqvist (52), who studied the equilibrium over the range 1396° to 2597°F . Uno (69) gave an equation, based upon data between 1652° and 2012°F , which agrees well with Rosenqvist over the range of Uno's data, but which extrapolates to lower values at lower temperatures. Data by Curran et al (19) between 1310° and 1660°F fall above the curve in Figure 1. Additional measurements would be desirable in the low-temperature range, and equilibria for reaction (3a) might well be derived from careful measurements of equilibria for reaction (1a).

Determination of equilibrium decomposition pressures of calcite has proved a durable problem, and dubious values have appeared recently (33, 45). Following Hill and Winter (35), Kubaschewski and Evans (42) adopted the equation: $\log P_{\text{CO}_2} = -(8799.7/T) + 7.521$, where P_{CO_2} = equilibrium decomposition pressure in atmospheres; this equation is used here. Hill and Winter's data were between 840° and 1659°F ; no one else has made such careful measurements at such low temperatures. Their data agree well with Southard and Royster (62) between 1427° and 1652°F , and with Smyth and Adams (61) between 1567° and 1664°F . Smyth and Adams' data extended to 2266°F , and data obtained by Consolidation Coal Company between 1472° and 1895°F agree well with Smyth and Adams' data at higher temperatures (17). Consolidation's measurements were conducted on a dolomite having a Ca/Mg atomic ratio of about 1.03. An ingenious new technique was used: a bed of the solid was fluidized with N_2 and CO_2 , and the temperature of the bed was cycled a few degrees above and a few degrees below the equilibrium decomposition temperature, which was identified by a thermal conductivity cell capable of precisely determining the instant at which the exit gas showed zero change in composition.

In obtaining the curves of Figure 4, the free energy of CaS was deduced from Uno's data (69) in order to provide estimates which are probably on the low side. Free energies of CaO , CaSO_4 , H_2 , and H_2O were derived from heats of formation and entropies at 298°K found in Kubaschewski and Evans (42) and from increments in these functions at higher temperatures found in Kelley (38). The heat of formation of CaSO_3 was estimated roughly to be 298,100 calories at 18°C from the heat of formation of $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$ given in International Critical Tables, vol. V, p. 196. The entropy of CaSO_3 was given by Kelley and Moore (39) to be 24.2 entropy units at 298°K . The heat capacities of CaSO_3 and CaCO_3 are within 0.5% of each other at 298°K , and so Kelley's increments (38) for the heat

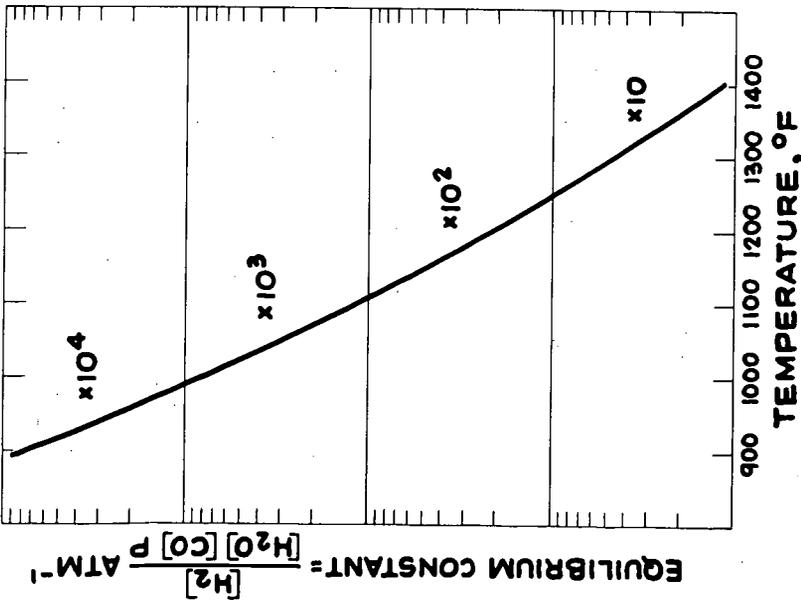


Figure 3. EQUILIBRIUM CONSTANT FOR:
 $\text{CaO} + \text{H}_2\text{O} + \text{CO} = \text{CaCO}_3 + \text{H}_2$

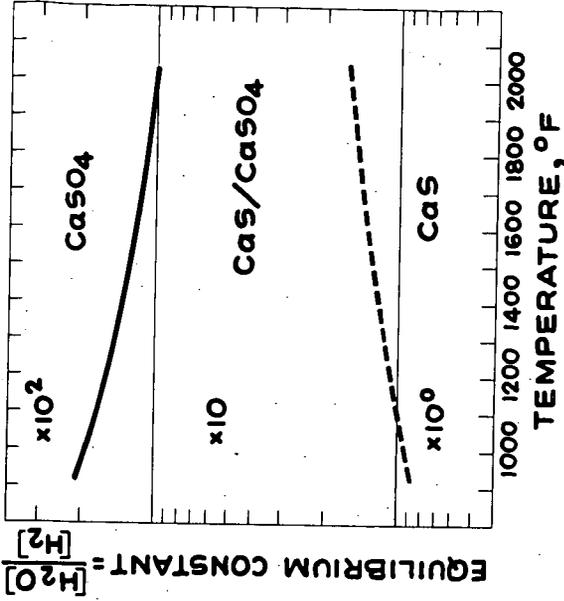
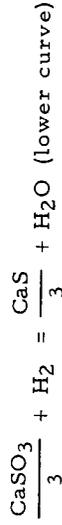
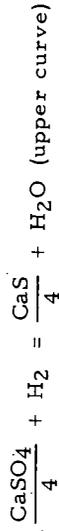


Figure 4. ROUGH ESTIMATES OF
 EQUILIBRIUM CONSTANTS FOR:



content and entropy of CaCO_3 were used to obtain a rough estimate of the free energy of CaSO_3 at higher temperatures.

The equilibrium decomposition pressure of Ca(OH)_2 may be estimated from an equation based upon data by Tamaru and Siomi (66): $\log P_{\text{H}_2\text{O}} = - (5464.5/T) + 6.949$. These authors measured decomposition pressures over the range 760° to 930° F. Their equation agrees well with data by Halstead and Moore (32) at 950° F, and with data by Dräger between 570° and 830° F (36). Berg and Rassonskaya's data (7) are probably faulty.

2.0 Experimental Studies

Exploratory bench-scale experimental studies were undertaken by Walter C. McCrone Associates of Chicago, Illinois, primarily to demonstrate (a) that reaction (1) is capable of producing a gas containing H_2S at a concentration sufficient for the Claus process, and (b) that the solid does not undergo chemically-induced decrepitation during an operation which includes reactions (1), (2), and (3). This was to be done at the minimum possible cost, and no effort was to be made to determine reaction kinetics or to confirm chemical equilibria.

2.01 Summary of Experimental Results

Dolomite was supplied by Dolese & Shepard Co. of LaGrange, Illinois. This is a typical dolomite of the Chicago area, and has a Ca/Mg atomic ratio of 1.10. Reactions were conducted in a fixed bed of particles of 16 to 30 mesh (NBS sieves).

Reaction (4) was conducted over calcined dolomite at about 1250° F and between about 140 and 315 psia. Two initial gas mixtures were used, containing H_2/CO in ratios 1.0 and 1.6 respectively. The gas mixtures were humidified with steam to afford $\text{H}_2\text{O}/\text{CO}$ ratios between about 1.2 and 1.8. Effluent contained no CO or CO_2 detectable by gas-chromatographic analysis sensitive to less than 0.01% of either constituent. No hydrocarbon synthesis occurred.

Reactions (3) and (4) were conducted simultaneously over calcined dolomite at about 1200° F and between about 140 and 215 psia. The initial gas mixture contained about 1% H_2S , the balance consisting of equal quantities of H_2 and CO. Concentrations of H_2S in effluent ranged from 2 to 140 ppm, and depended upon the quantity of steam in effluent.

Reaction (3) was conducted over calcined dolomite at about 1100° F and atmospheric pressure until the material was substantially all converted to $[\text{CaS}+\text{MgO}]$. The inlet gas mixture contained about 85% N_2 , 10% H_2S , and 5% H_2 . During this operation, effluent contained about 10 ppm of H_2S .

Reaction (1) was conducted over the resulting solid $[\text{CaS}+\text{MgO}]$ at about 1000° to 1100° F and at about 220 psia. The initial gas mixture contained about 82% CO_2 and about 9% each of H_2 and CO. The gas mixture was humidified with steam to afford a $\text{CO}_2/\text{H}_2\text{O}$ ratio of about 1.75. Dry effluent contained 20 to 24% H_2S , levels which are satisfactory for feed gas to a Claus system. It is reasonably certain that a much higher concentration of H_2S could have been obtained by using a lower $\text{CO}_2/\text{H}_2\text{O}$ ratio, since effluent appeared to be substantially at chemical equilibrium for reaction (1).

None of the foregoing chemical manipulations of calcined dolomite produced a decrepitation of the solid, or any evident change in the shape of particles viewed under a microscope; sharp edges and points were still to be seen.

2.02 Experimental Procedures

The reaction system used components supplied by Autoclave Engineers, Inc. of Erie, Pennsylvania. The reactor was 1" I. D. x 36" inside depth, and was fitted with a 5/16" thermowell containing 5 chromel-P-alumel thermocouples. An active dolomite bed between 8" and 12" in depth was used, the remainder of the reactor being packed with alumina chips. The reactor was situated within two Hoskins furnaces, each affording a heating length of 12". Tanks containing various mixtures of gases at high pressure were obtained from Matheson Company of Joliet. Gases were metered through a rotameter, and were passed through a pool of water in a saturator immersed in a heated oil bath. Gas from the saturator passed upward through the reactor, from the reactor through a filter, thence through a cooling coil, and into a chamber collecting water. Dry gas was let down in pressure across a needle valve, and sent to analysis. Most constituents were analyzed by a gas chromatograph (Perkin-Elmer Model 154) having a column of 1/4" O. D. copper tubing, 5' long, packed with 28-200 mesh silica gel, held at 125°C and swept with helium. Known gas mixtures, analyzed by Matheson, were used to calibrate the chromatograph for CO₂, CO, and H₂. Kitagawa H₂S-Low-Range Detector Tubes were used to analyze for H₂S at low concentrations. The Kitagawa "pump" was not used; a tube was placed in the gas-sampling line, and by trial and error the flow through the tube was adjusted to about 100 ml in 3 minutes. A modification of the Tutwiler method was used to determine H₂S at high concentrations (57). The method was calibrated against a gas mixture analyzed by Matheson and stated by Matheson to contain 10.9% H₂S.

Calcinations were conducted at atmospheric pressure with either N₂ or 90/10 N₂/H₂ flowing through the reactor.

2.03 Selected Results

Figure 5 illustrates the breakthrough of CO and CO₂ at the conclusion of a run using an initial gas mixture containing H₂/CO in the ratio 1.62. Flow of the initial gas at breakthrough was about 250 ml (70°F, 1 atm)/min; pressure was 315 psia; and temperature in the active bed ranged from 1217° to 1290°F. The gas was humidified to a H₂O/CO ratio of 1.83. Neither CO nor CO₂ could be detected in effluent prior to breakthrough. The rise in CO occurred a little earlier than the rise in CO₂. The width of the temperature peak was approximately the same as the time interval during which CO and CO₂ rose to their final steady values. This time interval can be interpreted as the time required for the reaction front to pass any given point in the active bed. The catalytic effect of MgO for the CO-shift reaction is indicated by presence of CO₂ in the gas following breakthrough, for the initial gas mixture contained no CO₂.

Data like those in Figure 5 were presented by Glud et al (24) for operations at atmospheric pressure and about 930°F.

Reaction (3) was conducted at atmospheric pressure with gas containing 85% N₂, 10% H₂S, and 5% H₂, humidified at 79°F. Temperatures in the active bed ranged from 976° to 1138°F, the temperature sharply dropping toward the

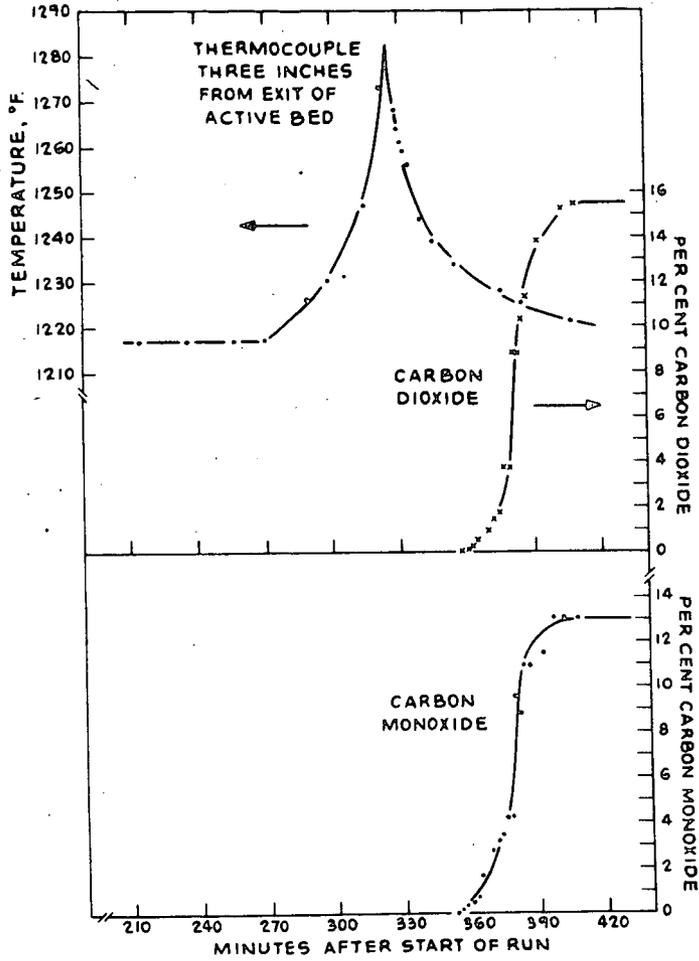


Figure 5. BREAKTHROUGH OF CARBON OXIDES WHEN SOLID IS USED UP BY REACTION (4) IN A FIXED BED AT 315 PSIA

outlet end. The ratio of H_2O/H_2S leaving the bed prior to breakthrough of H_2S was approximately 14,000, a value in close agreement with Figure 1 for the temperature at the outlet of the bed.

After reaction (3), reaction (1) was conducted at atmospheric pressure with gas humidified at 75°F. The initial gas mixture contained 81.7% CO_2 , 9.3% H_2 , and 9.0% CO . Dry gas effluent contained 1.1% H_2S . The active bed temperature ranged from 976° to 1138°F, the temperature sharply dropping toward the outlet end. The value of $[H_2S]/[H_2O][CO_2]P$ in reactor effluent was 0.21, which corresponds to 990°F at equilibrium, according to Figure 2. The purpose of this atmospheric-pressure, low-humidity step was to assure that no CaO remained in the active bed. If this step had been omitted, $Ca(OH)_2$ might have formed at steam partial pressures to which the solid was later subjected.

Later, the pressure was raised to 220 psia, and the saturator temperature was raised to 302°F, providing a CO_2/H_2O ratio of 1.79. The active bed temperature remained as before. Dry gas effluent contained 20.2% H_2S , and corresponded to equilibrium for reaction (1) at about 1040°F. The temperature of the bed was lowered to the range 891° to 1040°F, and the pressure fell to 215 psia, reducing the CO_2/H_2O ratio to 1.73. The H_2S content of dry gas increased to 24.0%, which corresponded to equilibrium at about 1010°F. [Most of the bed was at about 1000°F, and CaS may have been gone from solid near the exit of the bed by this time, for conditions had favored production of H_2S near the exit throughout the experiment.]

These results demonstrated the ability of reaction (1) to provide a dry gas containing H_2S in a concentration adequate for the Claus process. The results provide an indication that H_2S concentrations approaching thermodynamic equilibrium may be achieved, and it is practically certain that much higher concentrations of H_2S could have been reached by working at lower CO_2/H_2O ratio.

3.0 Review of Relevant Dolomite Chemistry

Primary sources of information are: (a) the series of papers from the Gesellschaft für Kohlentechnik (24), reporting in 1930 on studies of a process to manufacture H_2 by reforming coke-oven gas with steam and thereafter shifting the reformed gas with steam over calcined dolomite; and (b) the series of reports from Consolidation Coal Company on the CO_2 Acceptor Process (16, 18, 19). The latter reports are particularly valuable for the evidence that the solids [$CaO+MgO$], [$CaCO_3+MgO$], and [$CaS+MgO$] are rugged materials which stand up under fluidization, and do not decrepitate under various chemical reactions which convert the solids from one to another.

Dolomite is the mixed carbonate of Ca and Mg , "normal" dolomite being written $CaCO_3 \cdot MgCO_3$. It is a common rock, of wide geographical distribution, and often occurs in a state of high purity. Analyses of typical dolomites were given, for example, in Sikabonyi (59) and Willman (71). Dolomite is a member of a large class of rhombohedral carbonates, which includes calcite and magnesite. These carbonates are built of alternating layers of carbonate ions and cations. In dolomite, ideally, cation planes populated entirely by Mg^{++} alternate with planes populated entirely by Ca^{++} (13). Natural dolomite often diverges from the ideal of one atom of Mg for each Ca , the latter usually being present in excess. True dolomites richer in Mg are seldom encountered (24, 26).

3.01 Formation of [CaO+MgO]

If dolomite is heated in a vacuum, it decomposes in one step, with evolution of CO_2 and formation of a solid comprising an intimate intermingling of tiny crystallites of CaO and MgO. Britton et al (14) studied this process between 640° and 720°C , and believed the decomposition to occur with formation of a transient species $(\text{Ca, Mg})\text{O}$, which quickly breaks up into crystallites of CaO and MgO. The product may be written [CaO+MgO] as a reminder that it is not a true chemical species. Decomposition proceeds from the outside surface inward.

In an atmosphere of CO_2 , dolomite decomposes in two steps (6, 23, 34). Wilsdorf and Haul (72) followed the first step with X-ray diffraction techniques. Decomposition proceeds from the surface inward, and the state of order in the kernel of undecomposed dolomite remains perfect. At around 600°C and 100 mm Hg of CO_2 , predominantly single-crystal patterns for calcite are found, the CaCO_3 crystallites apparently being oriented as in the original lattice. At 800°C and 650 mm Hg of CO_2 , powder calcite patterns are obtained, randomization of the CaCO_3 crystallites having occurred. If dolomite is decomposed at moderate CO_2 pressures, as in a calcination process, the calcite produced is essentially pure CaCO_3 (27), and the product may be written [CaCO_3 +MgO]. At extremely high CO_2 pressures, the product is a mixture of crystallites of MgO and of a magnesian calcite, i. e., a calcite containing MgCO_3 in solid solution (29, 33).

Bischoff (10) and MacIntire and Stansel (43) found that both stages in the decomposition of dolomite are catalyzed by steam. Schwob (56) and Graf (28) reported a catalytic effect of alkali. There is evidence that the decomposition of [CaCO_3 +MgO] is faster than that of CaCO_3 (34).

From the foregoing, it will be recognized that the intimate mixture of CaO and MgO crystallites which result from the total calcination of dolomite retain no "memory" of the original dolomite structure. Goldsmith (26) believed that this solid would be indistinguishable from one which could be prepared by calcining a mixed precipitate of CaCO_3 and MgCO_3 . Such a precipitate never shows signs of dolomitic order if prepared in the laboratory from solutions at room temperature (27). Artificially-made dolomites are known (29, 30, 33) but these materials and the extensive literature on the problem of the formation of dolomite in nature are not particularly relevant to the new desulfurization process, since [CaO+MgO] can be prepared artificially for use in the process without the material's having passed through the dolomitic state.

Clark et al (15) studied the sintering of MgO at high temperatures. They found a sudden increase in strength to occur at a temperature well below that at which sintering proper with densification sets in, and they interpreted this increase in strength to be a result of destruction of adsorbed moisture films on the surfaces of the particles, i. e., the replacement of hydrogen or hydroxyl bonding between particles by primary ionic bonds.

3.02 Recarbonation of [CaO+MgO] to Form [CaCO_3 +MgO]

Glud et al (24) studied the recarbonation, at about 1050°F , of samples of [CaO+MgO] prepared from a wide variety of dolomitic rocks. Uniformly, the initial reaction with CO_2 was extremely rapid. The course of later stages of the reaction was found to depend upon the Ca/Mg atomic ratio of the starting material.

Glud et al recommended that a dolomite be selected having a Ca/Mg ratio as close to unity as could be found. The later stages of recarbonation of $[\text{CaO}+\text{MgO}]$ from a stone having a high Ca/Mg ratio were slow, and the reaction ceased for all practicable purposes far short of complete conversion of CaO to CaCO_3 . Moreover, stones having a high Ca/Mg ratio displayed poor resistance to deactivation when calcined. Working with dolomites having Ca/Mg ratios below about 1.2, Glud et al were able to achieve 90% recarbonation of CaO at good rates, provided the solid had not been exposed to a temperature above about 1920°F . If a dolomite was calcined at 2190°F , its reactivity was drastically reduced. Other workers (9, 14, 49) confirmed that recarbonation is rapid and nearly complete if a Ca/Mg ratio below about 1.1 is used.

Asboth (5) recommended an "artificial dolomite", prepared by precipitating CaCO_3 and MgCO_3 in the molar ratio 40:60 upon freshly made silica gel.

Curran et al (19) subjected a number of dolomites to tests of their suitability for the CO_2 Acceptor Process, which inherently requires use of a high calcination temperature (of the order of 1950°F). Stone from the Greenfield formation of Western Ohio was selected as the best available. This stone has the unusually low Ca/Mg ratio of 0.987. The stone was cycled many times between a calcination at high temperature and a recarbonation at 1650°F . There was no significant loss of reactivity. Calcination temperatures of 1900° , 1950° and 2000°F were used in these tests. Practically no degradation in particle size occurred, although the tests were conducted in fluidized beds. In a similar series of tests, the Greenfield stone was converted to $[\text{CaS}+\text{MgO}]$, from which $[\text{CaO}+\text{MgO}]$ was regenerated at 1950°F by a fuel-rich calcination expelling SO_2 . The latter solid displayed good reactivity after a number of the sulfur cycles.

Curran et al's experience with the Greenfield stone provides important evidence bearing upon the probable feasibility of the proposed new desulfurization processes. With use of the Greenfield stone, the new processes should be operable in gas-production and gas-purification steps at pressures ranging upward from 100 atmospheres.

Glud et al (24) reported that CO_2 was taken up by $[\text{CaO}+\text{MgO}]$ at 570°F . Dry CaO absorbs only an insignificant amount of CO_2 at this temperature; it reacts markedly at 660° , and rapidly at 790°F (46); but the reaction proceeds readily only to an extent such that about one-half of the CaO is recarbonated (9, 14, 24, 40, 49, 67). The solid $[\text{CaCO}_3+\text{CaO}]$ decomposes at a rate some 4 to 6 times faster than calcite (14). Shushunov and Fedyakova (58) studied the kinetics of $\text{CaO} + \text{CO}_2$.

As Glud et al recognized, calcination of a Mg-poor dolomite probably puts some CaO in a state such that only about one-half of it can absorb CO_2 , in accordance with the behavior of lime. This accounts for the poor performance of dolomites having high Ca/Mg ratios. Glud et al warned against selecting a dolomite having calcite strata.

Although MgO takes up CO_2 readily at atmospheric temperature in presence of water vapor (47), its reaction with CO_2 at high temperature is extremely slow (9, 14, 33). Little recarbonation of MgO will occur even if CO_2 exceeds the equilibrium decomposition pressure of MgCO_3 when reaction (1) is carried out.

3.03 Use of [CaO+MgO] to Promote CO-Shift and the H₂O-C Reaction

DuMotay (21) first proposed use of lime to promote CO-shift in 1880, and this idea received persistent attention without its ever coming into commercial use (1). Greenwood (31) and Taylor (68) reviewed the state of the art in 1920 and 1921 respectively, and Schmidt (55) reviewed the subject in 1935. The most highly developed ideas were advanced by Gesellschaft für Kohlentechnik (24) and Bössner and Marischka (12).

The Gesellschaft für Kohlentechnik recognized that MgO crystallites in [CaO+MgO] are catalytic for CO-shift. Magnesia can be prepared in far more active forms than can any of the other alkaline earth oxides; active magnesias are produced for use as industrial adsorbents having surface areas of the order of 200 m²/gram (48). Gluud et al demonstrated that [CaO+MgO] is catalytic for CO-shift at temperatures above about 750° F, while CaO showed no catalytic activity at any temperature. The catalytic worth of MgO was not altered as the solid was converted to [CaCO₃+MgO]. From this fact, as well as from the ease with which CaO in [CaO+MgO] may be recarbonated, it may be inferred that [CaCO₃+MgO] has an open, porous structure.

The Gesellschaft für Kohlentechnik's CO-shift process was conducted at atmospheric pressure in a fixed bed of [CaO+MgO]. The operation was cyclic, a period of H₂ manufacture being followed by a period in which [CaCO₃+MgO] was calcined, the bed of solid remaining in place in a reactor. Low final CO concentrations, generally below 0.1%, were achieved in operations at 930° F. Break-through of CO occurred at a space velocity of about 130 V/hr-V based upon CO content of gas and upon the [CaO+MgO] remaining in the bed. In operations of a pilot plant on the scale of 200,000 SCF per day, no decrepitation or loss of absorptive capacity was found after many cycles of operation, and it was reported that the life of a dolomite charge should be three months at the very least.

A serious defect in the Gesellschaft für Kohlentechnik's process thinking was exposed when operations were conducted on a large scale. So much heat was generated during the shift step that the temperature became too high for good CO₂ removal unless untreated gases were introduced cold, but this proved infeasible since Ca(OH)₂ formed and the solid quickly decrepitated. The difficulty was got around, after a fashion, by introducing a cooling phase in the cycle, in which the reaction bed was cooled by circulating air at 750° F after the bed had been partly used up. Another defect was that several hundred per cent excess air had to be used in order to keep the calcination temperature below a level at which solid reactivity would suffer. One consequence of the large amount of excess air was that thermal efficiency of the overall process was extremely poor. Another consequence was that both fuel gas and the CO-containing gas to be treated had to be low in sulfur to avoid conversion of large amounts of CaO to CaSO₄, which not only would destroy its usefulness but would probably also lead to losses of H₂ through reduction of CaSO₄ to CaS in the shift step.

DuMotay and Marechal (22) first proposed use of lime to aid the gasification of carbon by steam in 1867, and a large patent literature has ensued (2). Taylor (68) and Schmidt (55) reviewed the art. Dent (20) reported that "trouble occurred due to the caking of the charge" during a test of the idea at 28 atmospheres. The nature of this trouble was identified by Consolidation Coal Company, and was circumvented in the CO₂ Acceptor Process by keeping the

partial pressure of steam below 13 atmospheres.

A patent literature has developed around the idea of using heat from $\text{CaO} + \text{CO}_2$ to supply endothermic heat needed for the reforming of hydrocarbons by steam (3). Marisic (44) visualized using heat from this reaction to sustain catalytic cracking.

3.04 Use of Lime and $[\text{CaO}+\text{MgO}]$ for Desulfurization

An historical method of desulfurizing town gas was treatment with $\text{Ca}(\text{OH})_2$ at atmospheric temperature. The process was used until 1870 in Europe and until 1905 in England. General information may be found in Seil (57).

Mellor (46) reported that dry H_2S does not react with dry CaO in the cold, but when heated, water is evolved, and the mass becomes yellow owing to separation of some elemental sulfur. Wickert (70) showed that the speed of reaction of H_2S with CaO rises sharply between 750° and 1100°F , and stated that CaS is much harder and tougher than CaO . Taylor (68) stated that CaO at around 930° to 1020°F catalytically converts CS_2 in presence of steam to CO_2 and H_2S , both of which are fixed by the lime. A patent literature has grown up about the idea of using lime for fuel desulfurization (4).

Schenck and Hammerschmidt (54) reported that CaS prepared by contacting CaCO_3 with H_2S and CO_2 at 1450° to 1830°F was unsintered and showed no loss of chemical reactivity. It had a pinkish cast, as did the $[\text{CaS}+\text{MgO}]$ prepared by McCrone Associates.

A British patent (8) reported that CS_2 , thiophene, and other organic sulfur compounds are dissociated, with formation of H_2S , if contacted with hot MgO . Carbon is deposited, and may be burned off.

Glud and Klempt (25) stated that organic sulfur compounds are split, with formation of H_2S , when town gas is contacted with calcined dolomite above about 1100°F . Kirillov and Budanov (41) showed that the decomposition of CS_2 over dolomite was a maximum at 1200°F , independent of steam concentration. Kakabadze (37) patented the use of hot calcined dolomite to purify gases of organic sulfur compounds. Zahn (73) reported the calcined ankerite in the Bössner-Marischka process (12) was highly effective in removing organic sulfur, and he claimed that its catalytic worth for CO -shift was not impaired after prolonged use to remove such sulfur.

Dolomite is used in a moving bed to remove sulfur from hot "carburettor gas" of the Wiberg process used in Sweden for production of sponge iron (65). The quantity of dolomite charged is the temperature control on reducing gases to the Wiberg furnace, and dolomite is discharged typically containing only about 5% to 10% sulfur. No decrepitation of the dolomite lumps is experienced. (11)

3.05 Converting $[\text{CaS}+\text{MgO}]$ to $[\text{CaCO}_3+\text{MgO}]$ and H_2S

Riesenfeld (50) studied the reaction of steam and CO_2 with CaS at atmospheric pressure, conducting four exploratory experiments between 896° and 1526°F . He did not intend to measure equilibria for the reaction, and he did not estimate equilibria from his data. The measurement at 1526°F was more

carefully made than the other three, and one can derive a reasonably good estimate of the equilibrium from Riesenfeld's results at this temperature: the estimate falls only about 10% above the curve of Figure 2. Crude estimates of equilibria from Riesenfeld's other three points lie 20% below, 50% below, and 120% above the curve of Figure 2. Riesenfeld did not report H₂S concentrations in product gas, but one can deduce (very roughly) that about 2% H₂S was present in a run at 941°F, and lesser amounts at other temperatures. Riesenfeld concluded that the conversion of CaS to CaCO₃ by its reaction with steam and CO₂ is not a practicable proposition, although his results may now be regarded as confirmatory evidence in support of the conclusions which have been drawn from the tests conducted by McCrone Associates at higher pressure.

The reaction of liquid water and CO₂ with CaS has been recognized since 1817, when the towns gas industry adopted dry purification with slaked lime. Used-up lime was decomposed by action of water and CO₂ when left in the open air, a process which contributed to the poisoning of air around old-time gas works (46, 60). The reaction was put to commercial use in the Claus-Chance process (53), which recovered H₂S from CaS waste from the Leblanc soda process.

Wickert (70) incorporated the reaction in a proposed process to eliminate sulfur from flue gases derived from heavy residual fuel oil. Wickert would employ partial oxidation of the oil with air; would desulfurize the resulting lean fuel gas with CaCO₃ at around 1460° to 1830°F; and would cool the resulting CaS to atmospheric temperature, slurry this solid with water, and react the slurry with CO₂-bearing flue gases. By comparison with the new desulfurization processes proposed here, Wickert's scheme has disadvantages including: (1) much heat would be discharged at low temperature and could not be put to use; and (2) CaCO₃ would probably be recovered in such finely divided form that its separation from desulfurized fuel gases might be difficult.

4.0 Process Applications

A cataloging and evaluation of potential applications of the new desulfurization processes would fall outside the scope of this paper, which can only indicate briefly some of the possibilities.

Figure 6 illustrates a scheme for making a rich fuel gas from heavy residual oil, suitable for use in a top heat power cycle (63, 64) in which the temperature of steam is raised by direct addition of the products of combustion of the rich fuel gas with oxygen. A solid comprising mainly [CaCO₃+MgO] is fed to a fluidized bed in which oil is gasified by oxygen and steam. The temperature should preferably be a little below the equilibrium decomposition temperature of CaCO₃, so that CaO is not produced in the fluidized bed. Gaseous products are desulfurized by the reverse of reaction (1). Wickert (70) reported that CaS is catalytic for the steam-carbon reaction, and one may be able to operate the gasification step in Figure 6 with only a small excess of steam beyond the amount called for by steam-carbon equilibrium. Solid is conveyed from the gasifier to an elevated cyclone, which delivers solid via a standpipe to the sulfur desorber. Here reaction (1) is conducted in a fluidized bed with use of CO₂ supplied from the heat exchange in which steam is condensed from top heat cycle fluid. Heat from reaction (1) is used to raise or superheat high-pressure steam. In a top heat cycle using Kuwait heavy residue (4.73% sulfur), this heat amounts typically to about 1.5% of the total water-heating, steam-raising, and steam-superheating

duty. Offgas from the sulfur desorber is cooled to condense excess steam, and gas rich in H_2S is sent to a sulfur plant. Rich fuel gas for use in a top heat cycle must be absolutely free of dust. Various arrangements for removing dust from the gas may be considered (63), but schemes which work at high temperature are preferred. An interesting possibility is to use oil to be fed to the gasifier in a scrubber working at about $600^\circ F$, say, which removes at least a major part of the dust.

Figure 7 shows equipment for sulfur recovery when desulfurization is accomplished by means of reaction (3), so that the solid charged to the sulfur desorber contains CaO . The sulfur desorber in Figure 7 houses two fluidized beds: a lower bed for conducting reaction (1), and an upper bed in which reactive values of CaO in the solid are converted to $CaCO_3$ in the absence of steam. Provision of the upper bed allows one to use a higher steam partial pressure in reaction (1) than would otherwise be possible, for one does not have to worry about the formation of $Ca(OH)_2$.

In the context of the top heat power cycle, there is advantage in operating the Claus system under pressure, since equipment exists both to provide high-pressure air and to recover power from Claus-system offgases.

Figure 8 illustrates an application in which CO-shift is conducted by means of reaction (4). Shift is carried out in reactor A, which houses two fluidized beds, the upper bed being held at a lower temperature. Spent solid is calcined in reactor B. Flow of gas and solid in reactor A is countercurrent. By conducting the greater portion of the shift reaction in the lower bed, at higher temperature, the calcining duty in reactor B is reduced. Also, the upper bed of reactor A can be operated at a much lower temperature than that needed in a single-bed reactor in order to avoid $Ca(OH)_2$.

The scheme of Figure 8 is obviously more attractive if one has need for high-level heat, available to the heat-transfer surfaces shown in reactor A, as well as need for H_2 . The scheme of Figure 8 would permit the production of extremely cheap byproduct hydrogen in future power stations which employ some combination incorporating pressurized fuel gasification, fuel-gas cleanup, and an advanced power cycle.

Figure 9 illustrates representative schemes in which oil-cracking is practiced together with desulfurization. In general, reactor A of Figure 9 would operate at a lower temperature than the gasifier of Figure 6. If less steam is used than the amount called for by steam-carbon equilibrium, coke generated by cracking reactions in reactor A could serve as at least part of the fuel used to calcine the solid in reactor B. The splitting of the oil into two fuel fractions, one rich in hydrogen and the other lean, is advantageous in the context of the top heat cycle. H_2 in rich fuel gas is ultimately discharged from the cycle as liquid water. There is an advantage in putting as much of the fuel's H_2 content as possible into the rich-fuel-gas path, in order to keep the water-vapor content of flue gas generated by combustion of the lean fuel gas from reactor B as small as possible.

The air or oxygen requirements for reactor A can be considerably reduced by drawing upon heat of recarbonation of CaO , as well as heat from reaction (4). A fuel gas of high calorific content can be produced even with the use of air. Such a gas is well suited for use in a top heat cycle using air instead of oxygen.

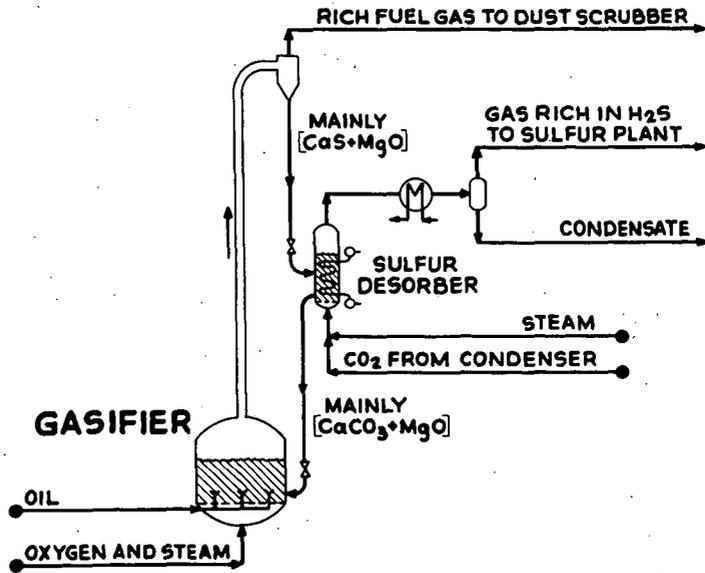


Figure 6. SCHEME FOR MAKING RICH FUEL GAS FOR TOP HEAT POWER CYCLE

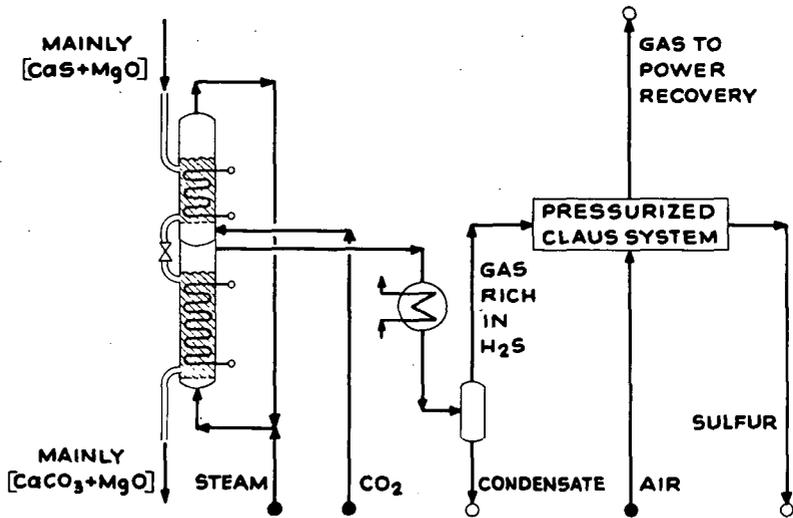


Figure 7. SULFUR DESORBER AND SULFUR RECOVERY

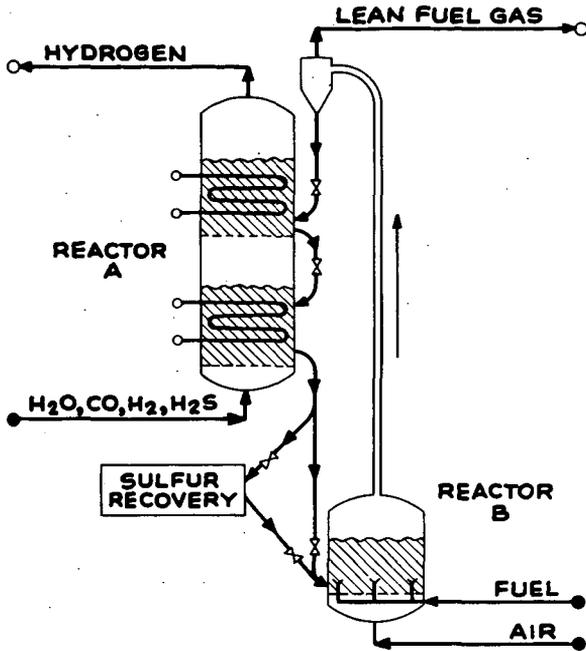


Figure 8. CONDUCTING CO-SHIFT IN A POWER-STATION CONTEXT

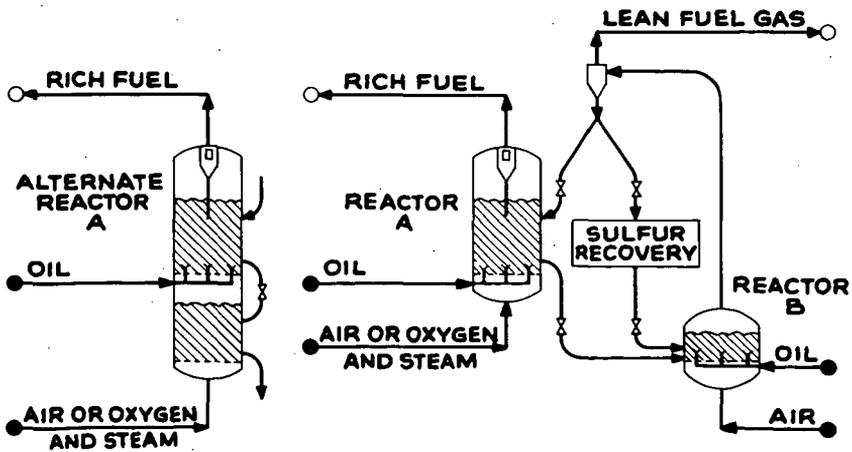


Figure 9. REPRESENTATIVE SCHEMES INVOLVING OIL CRACKING

An interesting possibility is to use air in reactor A to produce clean fuel of high calorific value for existing power-station boilers in communities which place restrictions upon SO_2 in flue gas. A gas-turbine plant would be required to supply air to reactor B and to recover power from the lean fuel gas. Power generated in this gas-turbine plant would represent a small fraction of the capacity of the existing power station to which clean fuel is supplied.

Alternate reactor A in Figure 9 provides for gasification of oil in two steps: oil is cracked in an upper bed in an atmosphere containing H_2 , the H_2 being generated from coke in a lower bed.

The foregoing examples by no means exhaust the possibilities. Modifying Consolidation's CO_2 Acceptor Process to incorporate the recovery of elemental sulfur has been mentioned. Hydrocracking or hydrogasifying oil, by using H_2 as the fluidizing gas to reactor A of Figure 9, is an interesting possibility.

Acknowledgment: Marvin A. Salzenstein directed the experimental studies performed by Walter C. McCrone Associates. He was assisted by Jan Markussen; now of Copenhagen, Denmark.

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| 1, 583, 673 (1926) | 137, 340 (1920) | 428, 580 (1926) | 723, 837 (1932) |
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| 151, 969 | NA = not accepted | 284, 298 (1928) | 156, 699 (1932) |
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PRESENT STATUS OF PROCESSES FOR GASIFICATION OF PETROLEUM

by

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INTRODUCTION

Gasification of petroleum fractions, ranging from liquefied petroleum gases through the highest boiling Bunker "C" fuel oils, is practiced throughout the world for the purpose of producing basically two classes of fuel gases: town gases of approximately 450 to 550 Btu/SCF gross heating value, and high-Btu gases with heating values ranging from 900 to 1100 Btu/SCF. The lower heating value town gases are used in areas in which fuel gas distribution and utilization still follow the practices of the manufactured gas era during which coal was used as the basic raw material. They are characterized by a relatively high hydrogen and carbon monoxide content, and a high burning velocity. In this way, they simulate the properties of the dominant source of gas supply - coal retort, coke oven and water gas. The high Btu gases are produced in areas which have converted to natural gas as the prime source of supply and, therefore, they attempt to simulate, as closely as possible, the properties of methane - the major constituent of natural gas.

The United States is typical of an area in which essentially all of the gas supply is natural gas and the only significant amount of gas manufactured is to meet peak demands. The dominant source of these gases is liquefied petroleum gas mixed with air to reduce its heating value, with much lesser amounts of high heating value gas produced by various petroleum oil gasification processes and only a negligible amount derived from coal. Much of Europe and parts of Japan and Australia are in an intermediate stage. Here, substantial amounts of natural gas are becoming available, but gas is still largely derived from coal-based processes and most of the gas distribution and utilization equipment is for low heating value manufactured gas.

KEY PROPERTIES OF PETROLEUM FEEDSTOCKS

The properties of petroleum feedstocks for the various gasification processes cover a wide range so that feedstock selection to give optimum results is an important consideration. The feedstock characteristic of primary importance is the carbon to hydrogen ratio, normally expressed in terms of the weight ratio. This is a useful parameter for correlating key properties of petroleum hydrocarbons. The C/H weight ratio was first specifically applied to the selection of feedstocks for gas making processes - primarily pyrolysis and hydrogenolysis - in publications from the Institute of Gas Technology, and is now in general use throughout the world for characterization of petroleum feedstocks for all types of gas making processes. As part of the work at the Institute of Gas Technology, simple means were developed for estimating the C/H weight ratio from physical properties such as API gravity and average boiling point, API gravity and viscosity, and API gravity, aniline point and average boiling point. The lower the C/H ratio, the greater its value for gas making. The reason for this is that fuel gases generally contain a relatively low ratio of bound carbon to free and bound hydrogen, compared to the C/H ratios of commercial petroleum products. Thus, to convert petroleum hydrocarbons to gas, it is necessary to use one or a combination of the following processes:

- 1) Elimination of excess carbon in the form of coke, lampblack and high carbon content liquid products (aromatics). This is the principle used in high-temperature thermal cracking (pyrolysis) processes.
- 2) Destructive hydrogenation to convert excess carbon to low molecular weight paraffins and olefins. This is the principle used in hydrogenolysis processes

- 3) Oxidation of excess carbon to carbon monoxide and dioxide, either by decomposition of steam at high temperatures or by partial oxidation with free oxygen. This principle is used in a variety of processes using steam or steam-air mixtures and a catalyst, or oxygen without a catalyst.

The greater the excess of carbon over hydrogen, the more difficult gasification becomes. Thus, methane, the hydrocarbon with the lowest C/H weight ratio (C/H=3), is already a gas and also the hydrocarbon most readily converted (reformed) to other gases, such as mixtures of carbon monoxide and hydrogen. Propane and butane (C/H=4.5 and 4.8, respectively) are also gases at normal temperature and pressure and are excellent feedstocks for reforming to fuel gases of lower heating value. Near the end of the scale are low-grade residual fuel oils which have C/H weight ratios as high as 10 and which are, therefore, not desirable feedstocks. The effect of C/H ratio on gasification yields is greatest in pyrolysis, less in hydrolysis and gasification with steam or steam-air mixtures, and of least effect in partial oxidation, but it is still important in all these gasification processes.

Another feedstock property of great importance in gasification is the coke forming tendency. This is, of course, indirectly related to C/H weight ratio but more directly dependent on the boiling range or the equivalent molecular weight range of the feedstock, coupled with the distribution of C/H ratio throughout the boiling range. As the boiling point or molecular weight of any class of hydrocarbon - paraffin, olefin, naphthene, aromatic, etc. - increases, its coke forming tendency increases. A simple empirical measure of this coke forming tendency is the Conradson carbon residue value. This is in essence, a destructive distillation test under standardized conditions which can, therefore, be directly related to coke forming tendency in pyrolysis processes. However, in all petroleum gasification processes, the feedstock is exposed to temperatures above its limit of thermal stability, so that pyrolysis occurs to various degrees.

The occurrence of coke formation would make any continuous process eventually inoperable through blockage of the reactor. It would also reduce the activity of any catalysts used in the gasification step. As a result, continuous processes employing empty or catalyst-filled reactors are generally limited to distillate feedstocks, and frequently distillate feedstocks with very low distillation endpoints and C/H ratios to reduce coke forming tendencies to an absolute minimum. Exceptions are processes using oxygen for partial combustion of the feedstock at very high temperatures. In these, coke accumulation is prevented by continuous burn-off.

An indication of the dominance of the coke deposition problem in gas manufacture from petroleum feedstocks is the development of two types of reactor systems particularly designed to overcome this limitation. One is the cyclic system in which deposited coke can be burned off at suitable intervals. The others are continuous systems in which solids pass through the reaction zone to allow deposition and removal of the coke.

Also of great importance is the sulfur content of petroleum feedstocks. In gas manufacture, the sulfur in the feedstock is converted into gaseous sulfur compounds such as hydrogen sulfide, carbon disulfide, carbon oxysulfide, and the variety of mercaptans and other organic sulfur compounds. These contaminants must be reduced to acceptable levels before the gas is distributed. In many gasification processes, there is an additional disadvantage to high sulfur content of the feedstock in that sulfur-sensitive catalysts are employed. In fact, in some processes, sulfur has to be removed from the feedstock before gasification, to levels as low as one part per million or less to avoid poisoning and deactivation of the catalyst.

In Table 1, typical properties of gasification feedstocks are summarized. In addition to the properties discussed above, certain properties affecting the ease and safety of storing and pumping are given such as pour point, the water and sediment content and the flash point.

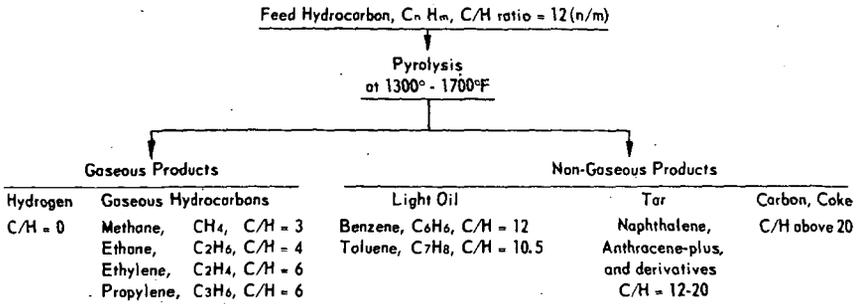


Figure 1.—SCHEMATIC PRODUCT DISTRIBUTION IN HIGH-TEMPERATURE VAPOR-PHASE CRACKING

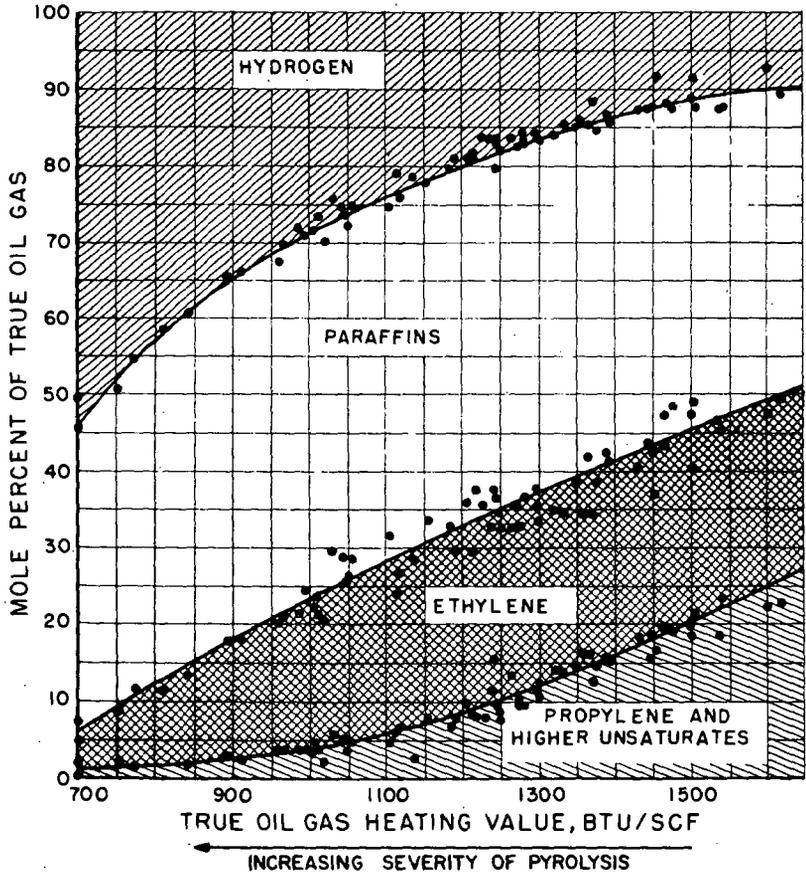


Figure 2.—RELATIONSHIP OF COMPOSITION AND TRUE OIL GAS HEATING VALUE

PYROLYSIS PROCESSES

Thermal cracking or pyrolysis reduces the average molecular weight of hydrocarbon mixtures by subjecting them to temperatures at which they are not stable; that is, at which the energy holding together some of the carbon and hydrogen atoms in the molecule is overcome. In its extreme form, pyrolysis can, therefore, result in the formation of carbon and hydrogen as the principal products. This occurs, for example, in the manufacture of carbon black. More generally, however, the desired products are hydrocarbons of lower molecular weight than the hydrocarbon making up the feedstock.

Pyrolysis is not a very selective operation and normally results in a broad spectrum of products, ranging from those of lowest molecular weight - hydrogen and methane - to the highest - pitch and coke. However, by proper control of operating conditions - pressure, temperature and residence time - the relative abundance and composition of the gaseous, liquid and solid products can be controlled to a considerable extent.

In the petroleum industry, mild pyrolysis is used in refinery operations to increase the ratio of low-boiling (distillate) products to high-boiling (residual) products. Thus, what is desired is breakage of carbon-carbon bonds without too radical a rearrangement of the hydrocarbon molecules. To achieve this, the temperature range is usually limited to 800°-1200°F, and superatmospheric pressures are generally employed to minimize gas formation.

The petroleum industry also uses pyrolysis of low-boiling feedstocks, such as propane, butane and naphthas, to produce ethylene and propylene and some higher molecular weight olefins and diolefins. This is done in externally heated alloy tubes at the lowest practical total pressures and with substantial steam dilution to lower the partial pressure and the residence time of the reaction products. This promotes gaseous olefin formation and minimizes any tendency to pitch and coke formation which could cause tube blockage. Pyrolysis severities are greater than in the type of thermal cracking practiced in oil refining processes but still below those necessary to obtain acceptable fuel gas yields and compositions. A substantial amount of pilot plant and full scale plant test work has been done to develop continuous pyrolysis processes for production of high heating value (high-Btu) gas employing tube furnaces, but this has not yet proved commercially feasible.

In the gas industry, pyrolysis of petroleum oils is primarily used to produce high heating value gases for enriching lower heating value gases, or for supplementing natural gas. The operating conditions used are relatively severe compared to the refinery and petrochemical pyrolysis processes: 1300° to 1700°F, residence times of one to five seconds, near-atmospheric pressure and the use of small amounts of steam as a carrier gas. Within this range of conditions, inert-free product gas heating values range from 900 to 1600 Btu/SCF and the weight percent conversion to gas is relatively constant and near the optimum obtainable at approximately one atmosphere partial pressure of gaseous reaction products.

Pyrolysis Fundamentals

The yields of gaseous and nongaseous products over this relatively narrow range of operating conditions are determined largely by the feedstock C/H weight ratio. The reason for this is given in Fig. 1 which shows schematically that the gaseous products consist essentially of high hydrogen content, low C/H ratio materials, whereas the nongaseous products consist of low hydrogen content, high C/H ratio materials. Thus, the gas yield can be related directly to feedstock C/H weight ratio. The weight percent gas yield, in turn, is directly related to the recovery of the heat of combustion of the feedstock in the form of stable gas (Btu heat of combustion or thermal recovery). This is shown in Table 2 with data derived from correlations based on laboratory pyrolysis tests. Typical test results of this type

Table 2. --PROCESS DATA FOR HIGH-BTU OIL GAS PRODUCTION

C/H Weight Ratio	Gas Yield, weight percent of make oil	Btu Recovery		Liquid Products Plus Coke, weight percent of make oil
		MBtu Per Pound of Make Oil	Percent of Make Oil Heat of Combustion	
5.0	74	16.7	80	26
5.5	68	15.3	75	32
6.0	63	13.9	70	37
6.5	58	12.5	64	42
7.0	53	11.1	58	47
7.5	48	9.8	52	52
8.0	42	8.7	47	58
8.5	37	7.7	42	63
9.0	32	6.8	37	68
9.5	27	6.1	34	73

Note: Make oil is the process oil feed and does not include any oil used to meet the heat requirements of the process (heat oil).

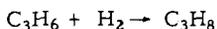
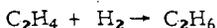
are given in Table 3 for No. 2 Diesel Oil. It can be seen that as the pyrolysis severity — that is, the temperature and/or residence time — is increased, increased volume of gas containing substantially more hydrogen and less higher molecular weight hydrocarbons are produced. This is accompanied by increased coke formation, and formation of lesser amounts of liquid products having a higher specific gravity and free carbon content. However, Btu recoveries remain relatively constant except that at very severe pyrolysis conditions they tend to decrease somewhat. Incomplete pyrolysis at low severities is indicated by the high paraffin content (high unsulfonatable residue) of the liquid products.

An excellent empirical method for correlating gaseous pyrolysis product composition with operating conditions is by means of the true (inert or diluent-free) oil gas heating value — the heating value of the hydrogen-gaseous hydrocarbon fraction of the pyrolysis products. As shown in Fig. 2, this applies to a wide range of feedstocks and pyrolysis severities at relatively constant oil gas partial pressures. The true oil gas heating value may also be used to correlate the nongaseous product yields and compositions for any given feedstock and true oil gas partial pressure. As would be expected, the true oil gas heating value is an empirical measure of pyrolysis severity.

The essential independence of gaseous products composition on feedstock properties exists only when the primary decomposition reactions of the feedstock have been completed; otherwise, the product distribution may be distorted. For natural gasoline, naphtha and higher boiling petroleum oils, gaseous product distribution will be independent of feedstock properties at reaction temperatures above 1300°F and residence times above 1 second. Propane and butane, as a result of their higher thermal stability, will require somewhat more severe conditions, and, if used as feedstocks at low pyrolysis severities, will appear in abnormal concentrations in the gaseous products.

It has been found in extensive laboratory tube furnace studies at the Institute of Gas Technology that the gaseous product distribution in high-severity pyrolysis operations can be interpreted by assuming that it is determined primarily by these overall reactions:

- a) Hydrogenation of olefins to paraffins with an equal number of carbon atoms, such as:

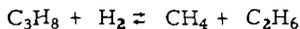
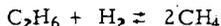


or in more general terms:



where n , the number of carbon atoms, can be 2, 3, or more.

- b) Destructive hydrogenation of paraffins to methane, and a paraffin with one less carbon atom, such as:



or in more general terms:



Table 3.—LABORATORY PYROLYSIS TEST RESULTS FOR THE PRODUCTION OF HIGH-BTU OIL GASES FROM NO. 2 DIESEL OIL AT ATMOSPHERIC PRESSURE WITH APPROXIMATELY 10-30 VOLUME PERCENT STEAM OR INERT CARRIER GAS DILUTION (From Reference 5)

Oil	37.3		
°API	6.39		
Carbon/Hydrogen Weight Ratio	0.004		
Conradson Carbon Residue, wt %			
Residence Time, sec	1.20	5.15	1.58
Reaction Temp, °F	1400	1400	1550
Btu Recovery, MBtu/gal	87.6	90.8	86.8
True Oil Gas Yield, SCF/gal	61.5	72.8	73.5
Liquid Products Yield, wt % *	39.5	37.7	38.6
Carbon Deposition, wt %	0.4	1.3	2.9
True Oil Gas Properties			
Composition, mole %			
Hydrogen	13.8	17.8	20.4
Methane	33.4	42.5	43.6
Ethane	4.9	4.7	3.1
Propane	0.4	0.9	0.1
Iso-Butane	0.1	--	--
n-Butane	--	--	--
Pentane	--	--	--
Ethylene	29.5	25.6	26.2
Propylene	11.1	3.8	2.9
Butylenes	2.1	0.6	0.3
Butadienes	2.5	1.2	1.0
Pentenes	0.4	--	--
Cyclopentadiene	0.6	0.3	0.2
Acetylene	0.3	0.4	0.5
Benzene	0.8	1.9	1.4
Toluene	0.1	0.3	0.3
Total	100.0	100.0	100.0
Heating Value, Btu/SCF **	1425	1247	1182
Specific Gravity, Air = 1 **	0.843	0.706	0.695
Liquid Products Properties			
Specific Gravity, 60°F/60°F	0.970	1.070	1.075
Free Carbon, wt %	0.3	3.6	6.7
Sulfonation Index: ml unsulfonated residue/100 g tar			
For Distillate 0°-300°C	10.9	1.9	6.4
For Distillate 300°-355°C	0.9	0.6	2.4

* Corrected to 100% material balance based on volume and specific gravity of total raw product gas, including small amounts of N₂, CO, CO₂ and sulfur compounds produced from oil; true oil gas yields and properties based on hydrogen-hydrocarbon fraction of stabilized gas

** Experimental value corrected to inert-free basis

When $n = 2$, the forward and reverse reactions of System 1 must be extremely rapid, since ethylene, hydrogen and ethane are always recovered in the approximate chemical equilibrium concentrations corresponding to the effective reaction temperature and pressure. The same appears to be true with propylene-hydrogen-propane ($n = 3$) and, probably, higher molecular weight gaseous olefin-hydrogen-paraffin subsystems (except when the olefin or paraffin is also the feedstock, and the severity of cracking is too low to allow completion of the primary decomposition reactions).

In comparison to the rapid hydrogenation-dehydrogenation of System 1, methane formation by System 2 is very slow. Consequently, the components in System 2 are recovered in concentrations far removed from those corresponding to chemical equilibrium at the effective reaction conditions. However, the approach to equilibrium of the ethane-hydrogen-methane and propane-hydrogen-methane-ethane subsystems is determined by only the reaction temperature and residence time. Thus, the composition of the major gaseous products of high-temperature pyrolysis can be predicted from the effective temperature, pressure and residence time, and from equilibrium constants for the subsystems covered by Systems 1 and 2. These equilibrium constants, when expressed in terms of the partial pressures of the products and reactants, are dependent on the reaction temperature only.

The abundance of the minor constituents, butadiene and acetylene, is indicated by:



Similar to System 1, Systems 3 and 4 also appear to closely approach chemical equilibrium in the pyrolysis zone. However, in gas production processes, butadiene, and particularly acetylene, are recovered in less than the equilibrium concentrations corresponding to the effective pyrolysis temperature. This is probably due to continued reaction of these highly reactive constituents at the lower temperatures prevailing in the product offtakes and separators. (Butadiene and acetylene are directly related to the hydrocarbon fragments responsible for the formation of a substantial portion of the liquid products.)

The relationships determining gaseous products distribution which have been described above are of great importance in the selection of the conditions for a process designed to produce methane as the major product. For example, the presently used pyrolysis processes operate at near-atmospheric pressure and relatively short residence times. This favors the production of olefins. To produce a higher percentage of paraffins, higher pressures would have to be used to force to the right the hydrogenation reactions of System 1, and Systems 3 and 4 in conjunction with System 1. This will happen because these reactions are in approximate equilibrium and cause a large overall volume decrease.

An increase in pressure will also produce a higher percentage of methane because of the increased rate of destructive hydrogenation of the higher molecular weight paraffins by the overall reactions of System 2. Further, since methane formation by secondary vapor-phase reaction is so slow, an increase in residence time will result in increased methane concentrations. However, this is the case only within the range of pyrolysis severities used in high heating value gas production.

Unfortunately, an increase in gasification pressure will result in a decrease in feedstock conversion to gaseous products unless hydrogen is added. The same conclusion can be reached from chemical considerations: without an external supply of hydrogen, increases in pressure or in partial pressure of hydrogen-gaseous hydrocarbon constituents will favor the condensation and polymerization reactions of intermediate reaction products which form the high molecular weight nongaseous products; competing reactions which form the low molecular weight gaseous prod-

ucts will consequently be suppressed.

Extensive laboratory pyrolysis studies have shown that nongaseous products formation from the entire range of liquid hydrocarbon fuels can be substantially decreased by the use of a hydrogen-rich carrier gas as a reaction atmosphere. This is accompanied by an increase in the formation of gaseous paraffins by the hydrogenation reactions which maintain equilibrium. As will be shown in the section on hydrogenolysis processes, there exists a combination of hydrogen/hydrocarbon feed ratio, pressure, temperature, and residence time, at which most hydrocarbon fuels can be converted to gaseous products, with only a minor quantity of liquid products formation. Under these conditions, the net Btu recovery (gross Btu recovery less heat of combustion feed hydrogen) approaches the heat of combustion of the hydrocarbon feedstock. However, to achieve this with high C/H ratio and high molecular weight feedstocks requires high pressures.

Conversion of liquid feeds at normal storage temperature into pyrolysis products at 1400°-1500°F requires approximately 1500-2000 Btu per pound, which includes sensible heat, heat of vaporization, and endothermic heat of reaction. The methods of supplying this heat, and the maintenance of continuity of operation under conditions leading to the formation of coke and pitch, are the basic processing problems which have led to the development of the various pyrolysis processes summarized in Table 4 and discussed below in greater detail.

Cyclic Pyrolysis Processes

Cyclic pyrolysis of distillate and residual oils in an atmosphere of steam at near-atmospheric pressures until recently was the only process used commercially to produce high-Btu gas from these feedstocks. This situation existed because manufactured gas companies already had available carbureted water gas sets which could be converted at moderate cost to sets capable of producing 1000 Btu/SCF gas from petroleum feedstocks. This conversion resulted in a substantial increase in the thermal capacity of the set, and in considerable simplification in operation through ultimate elimination of solid-fuel handling. In some of the early development solid fuel was used. Subsequently the use of solid fuel was discontinued for economic reasons and grates were either removed or covered with a refractory screen.

Cyclic pyrolysis processes for converting distillate and residual petroleum oils into high-Btu gas, light aromatics, tar and deposited coke are conducted in refractory-lined or -filled vessels. Deposited coke is burned off by periodic air blasting, supplying part of the process heat requirements. The remainder of the heat to maintain the desired cracking temperature (1300°-1700°F) is supplied by the combustion of heat oil during the blast period. This period is followed by a steam purge, a make period during which process oil is introduced into the heated pyrolysis zone, and finally a second steam purge and a blast purge. The length of a cycle (or half-cycle in a symmetrical array of vessels allowing operation in either direction) is usually 3 to 8 minutes, with about one-fourth to one-half of the time devoted to the make period.

If regenerative heating of the blast air and steam is used, the thermal efficiency of the process may be as high as 85 percent (including the heat of combustion of liquid byproducts). Liquid byproducts constitute up to 50 weight percent of the feed oil. Recovery of these products requires considerable investment in plant and labor. Consequently, in peak load operation net byproduct credits are reduced not only because of this, but also because the irregular production adversely affects marketability.

High-Btu oil gases produced in cyclic processes contain substantial quantities of nitrogen and carbon dioxide formed during the blast purge part of the cycle. Furthermore, depending on condensing conditions, the aromatic content of raw oil gas can be as high as 5 volume percent. As a result, combustion characteristics of such

Table 4.—PYROLYSIS PROCESSES

Reactor Type	Continuous		Cyclic		Moving or Fluid Bed
	Externally heated alloy tubes		Internally heated refractory		
Heat Source					Circulating heated solids — coke, sand, etc.
Feedstocks					
C/H Weight Ratio	4.5-5.7		5.0-10		
Conversion	0		0-18		
Carbon Residue, wt %	Below 300°F		No limit		
Distillation Range	No limit		No limit		
Sulfur, wt %	Propane, butane, natural gasoline, light naphtha		All petroleum feeds from light naphtha to Bunker "C" fuel oil		
Types					
Process Conditions					
Temperature, °F	1300-1600		1300-1700		Same as Cyclic Reactor
Pressure, psig	Below 50		Atmospheric		
Residence Time, sec	0.5-10		1-5		
Reactant Feeds	Up to 1 (diluent only)		Up to 0.5 (diluent only)		
Steam, lb/lb					
Heat of Combustion of Product Gas Due to Process Oil, %	75-90		35-85		
Products					
Gas	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , C ₄ H ₁₀ , H ₂		CH ₄ , C ₂ H ₆ , C ₃ H ₈ , C ₄ H ₁₀ , H ₂ , N ₂ , CO ₂		CH ₄ , C ₂ H ₆ , C ₃ H ₈ , C ₄ H ₁₀ , H ₂
Composition	Light and midboiling aromatics		Light aromatics, aromatic, tar, coke		Light aromatics, aromatic tar, coke
Other					
Commercial Processes (including related petrochemical processes)	Various processes for ethylenic and propylene production		High-Btu Oil Gas Process (wide variety of equipment designs)		Lurgi-Ruhrgas Sanderker (for ethylene and propylene)
Pilot Plant Processes	Several tube furnace pilot plants and industrial tests		Clean Regenerator Process (ICT)		Thermoform Pyrolytic Cracking Process (Surface Combustion Corp., Socoony Mobil Oil Co.) Fluid Gasification Process (IGT)

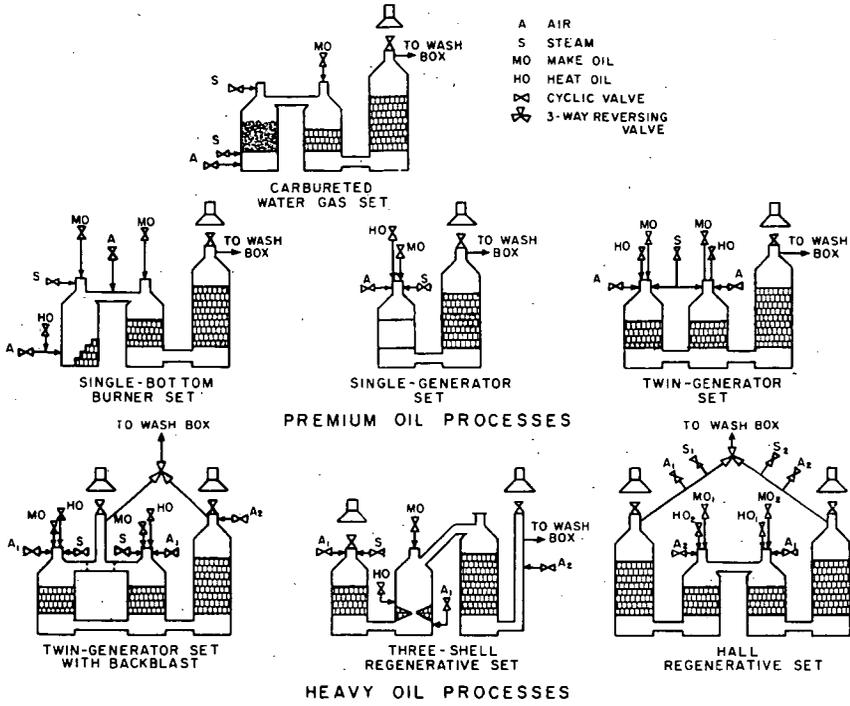


Figure 3.—BASIC CARBURETED WATER GAS SET (TOP), AND TYPICAL CONVERSIONS TO HIGH-BTU OIL GAS OPERATION

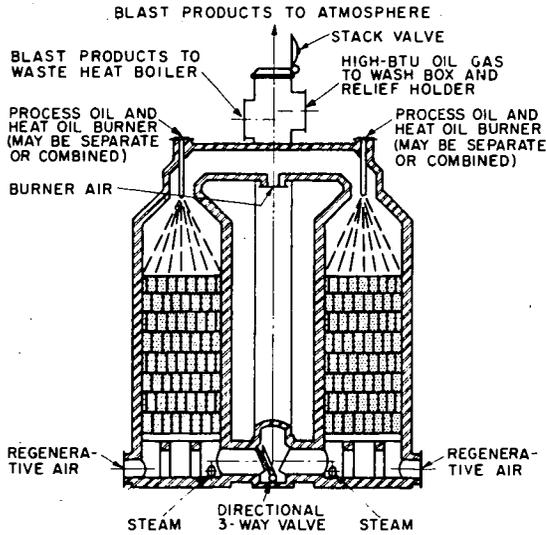


Figure 4.—HALL HIGH-BTU OIL GAS PROCESS TWO-SHELL SET (Gas Machinery Company)

high-Btu oil gases differ radically from those of natural gas, which normally has much lower specific gravity and consists primarily of the slow burning paraffins, methane and ethane. Oil gases tend to flash back because of their higher burning velocities, and to produce luminous flames because of their high content of unsaturated hydrocarbons. Scrubbing with absorption oil to remove low molecular weight aromatics (light oil) reduces yellow-tipping. In general, high-Btu oil gases produced in conventional cyclic pyrolysis processes are not substituted for natural gas in concentrations above 50 volume percent.

The major types of converted high-Btu oil gas sets which have been used are

- 1) The single-generator set consisting of two shells — the oil gas generator and the superheater;
- 2) The single, bottom burner-fired set consisting of three shells — the combustion chamber, the oil gas generator, and the superheater;
- 3) The twin-generator set consisting of three shells — the two oil gas generators and a superheater,
 - a) without backblast, and
 - b) with backblast;
- 4) The three-shell regenerative set consisting of a regenerator, a generator, and a superheater; and
- 5) The Hall regenerative set, consisting of four shells — two generators and two superheaters.

Schematic diagrams of representative examples of these various types of conversion are shown in Fig. 3.

Single- and twin-generator units are primarily suited for operation with distillate oils. Twin-generator units, although requiring a more costly conversion, have substantially greater gas-making capacity and can be adapted to residual oil operation by addition of generator stacks and a backblast (Fig. 3) to remove carbon deposited in the generators. However, operation on Bunker "C" oil is not entirely satisfactory, and thermal efficiencies are relatively low because sensible heat is lost through the generator stacks, thereby increasing the heat oil requirements. The three-shell regenerative set design also appears to have limited flexibility in regard to feedstock quality.

In contrast, the Hall high-Btu oil gas process, which is completely regenerative, has operated well at high thermal efficiencies on residual oils with 13 percent Conradson carbon residue, and has gained widest acceptance for winter base load operation with low-cost oils. Both new and converted units of the original four-shell design, as well as newly constructed units of two-shell design (Fig. 4), were put into service in many locations and have been used to provide significant quantities of base load, winter base load, or peak shaving gas. Typical operating data are given in Table 5. Many Hall high-Btu oil gas process designs in addition to that depicted in Fig. 4 are available such as those developed by the Koppers Company, the Semet-Solvay Division of Allied Chemical Corporation, Ibing/Ibeg, etc. A new set design with clean regenerators and capable of handling even the heaviest feedstock without smoke formation has been developed to a large pilot plant scale by the Institute of Gas Technology but has not yet found commercial use.

Successful high-Btu oil gas operation with low-grade residual oils was also achieved in partially and fully regenerative, upright "U", twin-shell Pacific Coast oil gas sets originally designed for low-Btu oil gas (town gas) production and byproduct lampblack recovery. The Pacific Coast oil gas process operates at much higher

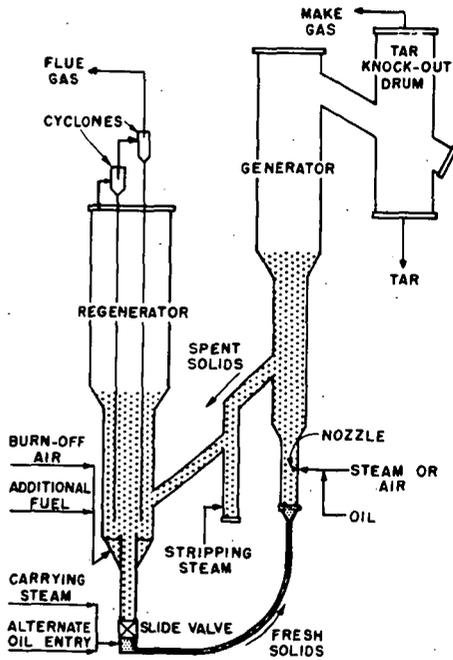


Figure 5.—SIMPLIFIED FLOW DIAGRAM OF FLUID-BED PILOT UNIT (From Reference 55)

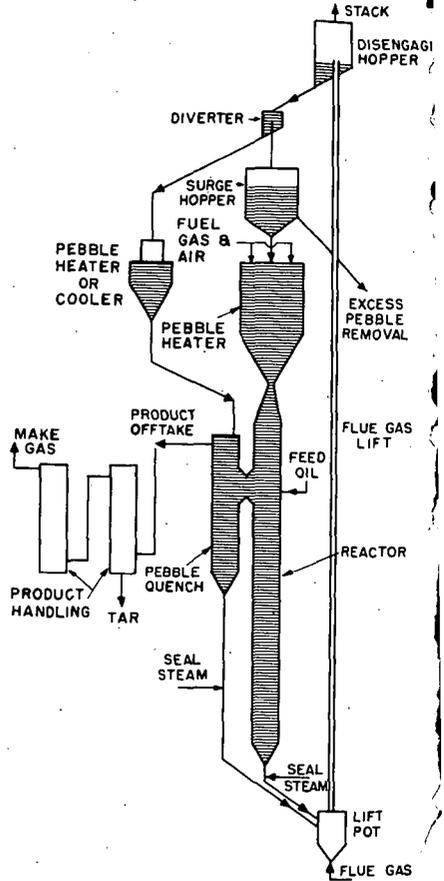


Figure 6.—FLOW DIAGRAM OF THERMOFORM PYROLYTIC CRACKING PILOT UNIT (Surface Combustion Corporation)

pyrolysis severities than the high-Btu oil gas process, which is responsible for the lampblack formation and the low product gas heating value. It is now obsolete in the U.S. However, three new Pacific Coast (Jones) type oil gas sets were built for town gas, tar and lampblack production in the U. K. after World War II and are operating satisfactorily on medium grade fuel oil.

Btu recoveries on a weight basis from Table 2 can be used directly to estimate relative set capacities as a function of oil properties where heat storage capacity is the limiting factor, on the assumption that the heat requirements for cracking a unit weight of oil do not vary significantly with C/H weight ratio.

A good approximation for coke or carbon deposition is given by the expression:

$$\text{Wt \% deposited coke} = \text{wt \% Conradson carbon residue plus a constant}$$

The value of the constant is usually taken as 3 weight percent, but must be increased when the true oil gas heating value falls below 1200 Btu/SCF, to account for greater coke formation and retention of pitch in the set. With the computed value for deposited coke, the yield of liquid products can be estimated from the total nongaseous product yields given in Table 2.

Heat oil requirements depend on the quantity of coke deposited, the efficiency of utilization of deposited carbon, and the efficiency of heat recovery from effluent process streams. Fully regenerative sets require substantially less heat oil than partially or nonregenerative sets. Heat oil requirements also decrease with increase in the size of the set. The heat oil required may be estimated by assuming an average heat requirement of 1800 Btu per pound of make oil, a thermal efficiency of utilizing heat oil and deposited coke of 60 percent, and a heat of combustion of deposited coke of 16,000 Btu per pound:

$$\text{Heat oil requirement, MBtu/MMBtu of make gas} =$$

$$\frac{3000 - (160)(\text{weight percent deposited coke})}{\text{Btu recovery, MBtu per pound of make oil}}$$

On the basis of this expression, at a total coke deposition of approximately 19 weight percent (a Conradson carbon residue of approximately 16 weight percent), no heat oil would be required in typical high-Btu operation.

Continuous Pyrolysis Processes

A. Fluid-Bed Cracking

Oil gas can be produced in fluid-bed pyrolysis units similar to the fluid catalytic cracking equipment used in the oil industry. As shown in the flow diagram, Fig. 5, oil is contacted with hot, finely divided solid particles (heat transfer medium) in a bed maintained in the fluidized state by an upward flow of steam and oil vapors. Pyrolysis on the surface of the hot solids yields the normal distribution of gaseous and nongaseous products, with coke being deposited on the solids. The vapor-phase pyrolysis products are withdrawn from the generator vessel overhead and passed through condensation and separation equipment. Coke-covered solids are continuously transferred from the reaction zone to a regenerator vessel located adjacent to the generator, where deposited coke and supplemental fuel are burned to reheat the solids for feed oil vaporization and pyrolysis. To complete the cycle, regenerated solids are returned to the generator to be contacted with fresh oil feed. Solids conveyance between the two vessels is accomplished pneumatically or by gravity, or by a combination of these methods.

The heat transfer medium used in one pilot plant process was 30-mesh silica gel, at circulation rates generally ranging from 5 to 20 pounds per pound of feed oil. Other materials which resist attrition, such as granular refractories, silica-alumina, and high-temperature coke breeze, are satisfactory, since unlike in the fluid processes used in refinery operations, the heat transfer solids are not depended upon for any catalytic effect at the elevated temperatures necessary for oil gasification.

Distillate and premium residual feedstocks can be utilized in the fluid-bed gasification process. The use of low-grade residual oils would require further development of the oil feed system to prevent agglomeration of heat transfer solids from excessive pitch and coke formation at the point of oil introduction.

Fluid-bed gasification has the advantages of continuous coke removal, and continuous production of high-Btu gas with no flue gas dilution. High pyrolysis severities can be achieved at relatively low temperature levels, since heat transfer is more rapid in a bed of hot fluidized solids than on cyclically heated stationary refractories. This permits the production of low specific gravity oil gases of greater substitutability for natural gas. The absence of cyclic temperature variations and large temperature gradients improves process control, and eliminates partial over-cracking and undercracking typical of cyclic operation.

Operating results are equivalent to those presented in Table 3. Estimates of equipment costs indicate that only very large fluid bed units would offer any savings over conventional cyclic equipment. A full-scale plant based on an extensive pilot plant development by Farbenfabrik Bayer, AG, has been operated on naphtha at relatively mild pyrolysis severities for the production of ethylene, propylene and C₄ olefins and butadiene. The full-scale process is known as the Lurgi-Ruhrgas Sand-cracker.

B. Thermofor Pyrolytic Cracking

High-temperature thermal cracking of residual oils in a moving bed of 1/4- to 3/4-inch diameter coke pebbles has been investigated by the Surface Combustion Corporation in a pilot plant (Fig. 6) of about one barrel per hour capacity. In this process, originally developed by the Socony Vacuum (now Mobil) Oil Company for a moving bed of refractory pebbles, oil is introduced into the bottom of a moving bed of hot coke pebbles, where pyrolysis takes place to produce oil gas and the usual by-products. The pebbles flow downward through the reactor by gravity, while the oil vapors flow counter-currently upward at velocities too low to establish fluidization. Coke laid down during the pyrolysis step increases the weight of pebbles in the system. Coke is, therefore, continuously withdrawn from the system in the form of fines and oversize pebbles.

Pyrolysis products are withdrawn through a pebble quench which cools them to a temperature at which coke and pitch deposition problems are minimized. To provide for this pebble quench, a side stream of solids is diverted from the circulation system at the top of the pneumatic lift, which is the coolest point in the system. After passing through a heat exchanger where the temperature level is adjusted to 750°-800°F, the coke is contacted with the cracked products coming off the top of the reactor through a crossover section. After quenching the effluent product stream, the coke is combined with the stream of coke pebbles flowing from the bottom of the reactor.

Coke pebbles from the bottom of the reactor are transferred by means of a pneumatic lift to the pebble heater on top of the reactor. Gas is burned there to reheat the coke pebbles to 1400°-1650°F. Oil firing and coke burnoff may also be a practical means for reheating the pebbles. The hot coke flows back to the reactor by gravity to complete the cycle of this continuous gasification process. Oil gas and vaporized liquid products are prevented from circulating with the solids by steam seals.

The TPC process has the advantage of producing gases of good substitutability because of the severe pyrolysis conditions which can be maintained without by-product handling difficulties, and because dilution with high specific gravity combustion gases can be minimized. The compositions of the product gases at equivalent true oil gas heating values correspond closely to those shown in Table 3. However, difficulties in designing a full-scale plant exist because feed oil is not readily distributed over the heat transfer medium, due to lack of turbulence. Heat transfer between the moving bed and the hydrocarbon vapor phase is better than in fixed refractory cyclic operation, but not as rapid as in fluid-bed operation.

The economics of the TPC process are highly dependent on byproduct credits. As a result of pitch removal during the pebble quench, the highly aromatic liquid products have a low viscosity and a very low free carbon content. The coke produced from low ash-content oils will meet the specifications for electrode-grade petroleum coke.

HYDROGENOLYSIS PROCESSES

The concept of producing high heating value fuel gases from hydrocarbon fuels by pressure hydrogenolysis was first proposed by the Institute of Gas Technology and the process designated as hydrogasification. Later, the British Gas Council also reported extensive work on the same concept, although employing a somewhat different approach. Hydrogasification involves pyrolysis in an environment rich in hydrogen and preferably at superatmospheric pressure to achieve the following advantages:

- 1) Total gas formation is increased by suppression of net hydrogen production from the hydrocarbon feed, even at atmospheric pressure, with attendant reduction of formation of nongaseous products, including coke and carbon.
- 2) The ratio of gaseous paraffins to olefins is increased, thereby increasing the substitutability of the product gas for natural gas.
- 3) Nearly complete conversion of low-boiling, low C/H ratio feedstocks to a high-methane content gas can be achieved by proper adjustment of hydrogen/oil feed ratio and reaction time in the usual reaction temperature range for pyrolysis and at relatively moderate pressures.
- 4) Processes can be designed for continuous operation with minimum by-product formation for a wide range of hydrocarbon fuels.

In Table 6, the various hydrogenolysis processes are summarized. Except for the Gas Recycle Hydrogenation (GRH) process, none of the continuous processes have been commercialized, although interest is great in areas with a large supply of low-cost naphtha and a need for supplementing natural gas supplies. The oldest hydrogenolysis process is carburation of water gas to increase its heating value to town gas specifications. In this cyclic process the make oil is introduced into the hot hydrogen-rich gas leaving the solid fuel bed (a mixture of hydrogen, carbon monoxide, and some carbon dioxide and undecomposed steam) at essentially atmospheric pressure. Even under these conditions, there is a substantially higher yield of gaseous hydrocarbons than in the equivalent cyclic high-Btu oil gas process in which there is no hydrogen-rich carrier gas present. A modification of the carbureted water gas process eliminating the need for solid fuel as a source of hydrogen-rich carrier gas developed to a large pilot plant scale by the Institute of Gas Technology but, again, this process has not been commercialized.

The nature of the various processes for continuous hydrogenolysis is best illustrated by Tables 7, 8, and 9 based on pilot plant operation with tubular empty reactors or with a circulating fluidized coke bed. In Table 7, operation with natural

Table 6.—HYDROGENOLYSIS PROCESSES

Reactor Type	Continuous (Empty)	Continuous (with fixed bed or medium to high catalyst activity)	Cyclic (Fixed reactor and solid fuel beds)	Fluid Bed (Circulating Powdered Coke)
Heat Source	Exothermic heat of reaction plus reactant preheat	(with fixed bed or medium to high catalyst activity)	Externally heated refractory and coke plus hot carrier gas	Exothermic heat of reaction plus reactant preheat
Feedstocks	1, 5, 6, 7	1, 5, 6, 7	5, 6, 8, 9	5, 6, 8, 9
C/H Weight Ratio	Below 500 F	6, 1-2, 0	5, 6, 8, 9	5, 6, 8, 9
Distillation Column Reaction	Below 700 F	Below 1,000 F	0-18	0-18
Substrate, wt %	Propane, butane, natural gasoline, light and heavy diesel oil, premium gas fuel oil	Kerosene, No. 1 and No. 2 diesel oil, premium gas fuel oil	No limit	No limit
Type	Kerosene, No. 1	Kerosene, No. 1 and No. 2 diesel oil, premium gas fuel oil	All petroleum feeds from light naphtha to bunker "C" fuel oil	All petroleum feeds from light naphtha to bunker "C" fuel oil
Process Conditions	1, 5, 6, 7	1, 5, 6, 7	5, 6, 8, 9	5, 6, 8, 9
Temperature, F	1,000-1,500	1,500-1,700	1,000-1,500	1,000-1,700
Pressure, psia	50-750	100-1,000	Atmospheric-50	30-100
Reactant Flow	5-15	10	Less than 50 sec	10-100
Hydrogen, SCF/lb	10-25	30-50	5-20	20-70
Steam, lb/lb	(for higher or cleared for product gas dilution)	(as part of raw steam plus catalyst or as an external stream in catalytic reformer effluent)	Up to (diluent only)	-
Heat of Combustion of Product Gas Due to Process Oil, %	80-100	100	40-90	60-95
Process Gas	80-100	100	40-90	60-95
Heating Value, Btu/SCF	800-900 (for lower with increased hydrogen dilution)	800-900	500-1000	500-1000
Composition	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , H ₂	CH ₄ , H ₂ , CO ₂	CH ₄ , C ₂ H ₆ , C ₃ H ₈ , C ₄ H ₁₀ , H ₂	CH ₄ , C ₂ H ₆ , H ₂
Other	Light aromatics	None	Light aromatics, aromatic tar, coke	Light aromatics, aromatic tar, coke
Commercial Processes (including related petrochemical processes)	None	None	Process (Low Pressure Hydrogenation Council)	None
Plant Processes	Gas Recovery Hydrogenation Process (British Gas Council)	High Pressure Hydrogenation Process (IGT)	Cycle Pressure Hydrogenation Process (IGT)	Fluidized Bed Hydrogenation Process (British Gas Council)

Table 7.—SELECTED PROCESS DATA FROM PRESSURE GASIFICATION AND HYDROGASIFICATION OF DISTILLATE FEEDSTOCKS

Hydrocarbon Type	Pressure Gasification (From Ref. 22)		Pressure Hydrogasification (From Ref. 22)		Gas Recycle Hydrogenator (From Ref. 77)	
	—26 RVP Natural Gasoline—		Heavy Naphtha	Kerosine	Light Naphtha	
*API	88.7		61.1	43.1	69.5	
C/H Weight Ratio	5.0		5.75	6.21	5.62	
Distillation-End Point, °F ¹	334		389	527	324	
OPERATING CONDITIONS						
Average Temp., °F						
Reaction Mass	1393	1404	1322	1316	1316	1337
Reactor Tube Wall	1535	1591	1437	1438	1439	--
Reactor Pressure, psia	50.8	66.5	70.3	71.5	71.4	465
Residence Time, sec	5.20	3.64	4.64	4.29	3.95	--
Hydrocarbon Feed, gal/hr	47.55	91.81	49.36	47.83	45.10	88.9
Hydrogen Feed, SCF/gal ^a	--	--	60.31	87.33	104.26	113.0
OPERATING RESULTS						
Hydrogen Reacted						
SCF/gal	--	--	26.1	34.1	38.9	75.8
%	--	--	43.2	39.0	37.3	70.1
Product Gas Yield, SCF/gal	75.54	72.52	116.96	133.20	153.37	142.3
Btu Recovery, Net, MBtu/gal	89.44	92.68	107.76	103.79	111.17	100.8
Liquid Products, wt % ^b	24.2	21.3	--	18.2	20.0	12.2
Material Balance, %	102.0	101.5	101.1	100.6	100.5	--
Net Thermal Recovery, % ^c	79.8	82.6	96.7	87.0	86.4	88.1
PRODUCT GAS PROPERTIES						
Composition, mole %						
Hydrogen	13.8	11.9	29.3	40.0	42.6	22.6
Methane	56.3	56.5	43.0	34.3	30.3	49.5
Ethane	8.1	8.1	10.7	11.5	12.5	21.2
Propane	0.2	0.1	0.3	0.4	0.8	
Butanes	0.1	0.2	0.3	0.1	0.1	
Pentanes-plus	--	--	0.2	--	--	
Ethylene	17.0	15.8	10.6	8.7	7.8	
Propylene	1.6	3.5	2.5	1.6	2.5	
Butenes	0.4	0.2	0.3	0.5	0.6	
Pentenes	--	0.1	0.1	--	0.1	
1,3-Butadiene	0.4	0.8	0.1	0.2	0.2	
Cyclopentadiene	0.1	0.2	0.1	0.1	0.1	
Acetylene	--	0.5	0.2	0.2	0.2	
Benzene	1.8	0.5	1.2	1.5	1.0	
Toluene	0.2	0.2	0.3	0.3	0.2	
Carbon Dioxide	Trace	0.1	0.2	Trace	Trace	1.8
Nitrogen	--	1.3	0.6	0.6	1.0	0.9
Carbon Monoxide	--	--	--	--	--	2.7
Total	100.0	100.0	100.0	100.0	100.0	100.0
Heating Value, Btu/SCF						
As Made	1184	1278	1089	992	951	
Calculated	1187	1196	1060	973	961	962
Specific Gravity, Air = 1						
As Made	0.72	0.77	0.64	0.54	0.51	
Calculated	0.67	0.68	0.59	0.53	0.52	0.58

^a Essentially 100% pure

^b Weight percent of Hydrocarbon Feed

^c $100 \left[\frac{\text{Ht of combust of prod. gas} - \text{Ht of combust of feed H}_2}{\text{Heat of combustion of feed oil}} \right]$

Table 8.—TYPICAL HYDROGASIFICATION TESTS OF DISTILLATE
AND UPGRADED CRUDE OILS
(From Reference 85)

Feed Oil	Kerosine ^d	Diesel ^e Oil	0°-360°C Fraction ^f Prehydrogenated Tapparito Crude
Oil Rate			
lb C/hr	3.06	1.50	1.50
lb oil/cu ft reactor-hr	24.7	12.1	12.1
Hydrogen Feed Ratio, ^a % of stoichiometric	98.0	99.9	100.3
Pressure, psig	500	1500	1500
Temperature, °F			
Average ^b	1325	1335	1305
Maximum	1400	1395	1395
Residence Time, sec ^c	51.0	301	319
Hydrogen Consumption, SCF/gal oil	109	156	158
Product Recovery, wt % of oil+H ₂ fed	103.5	101.7	97.2
Product Distribution, wt %			
Gas	88.9	93.2	91.0
Liquid	11.1	6.8	9.0
Solid Residue	nil	nil	nil
Product Gas Yield, SCF/gal oil	198	211	205
SCF/cu ft reactor-hr	726.9	362.8	354.2
Net Thermal Recovery, %	90.4	88.9	80.1
Product Gas Properties			
Composition, mole %			
N ₂ + CO + CO ₂	0.8	0.4	0.4
H ₂	38.8	23.8	27.2
CH ₄	40.5	69.7	66.2
C ₂ H ₆	17.1	5.3	5.4
Higher Paraffins	0.5	--	0.1
Olefins	1.0	0.1	--
Benzene + Toluene	1.3	0.7	0.7
Total	100.0	100.0	100.0
Heating Value, Btu/SCF	909	893	868
Specific Gravity (air = 1)	0.495	0.482	0.466

^a Stoichiometric for complete conversion of C/H in feed oil to CH₄

^b Based on average of temperatures measured at centers of three equal zones

^c Based on dry product gas volume at reactor pressure and average temperature

^d 44.2°API, C/H = 6.11, 0.0% CCR

^e 37.3°API, C/H = 6.39, 0.0% CCR

^f 36.5°API, C/H = 6.63, 0.0% CCR

Table 9.—HYDROGASIFICATION OF PETROLEUM OILS
OVER FLUIDIZED COKE
(From References 70 and 77)

<u>Feed Oil</u>	<u>Gas Oil^c</u>	<u>Crude Oil^d</u>	<u>Crude Oil^e</u>	<u>Heavy Fuel Oil^f</u>
Oil Rate				
lb C/hr	122	132	1110	101
lb oil/cu ft reactor-hr	18.7	25.2	25.6	19.3
Hydrogen Feed Ratio, ^a % of stoichiometric	207	163	83	210
Pressure, psig	470	470	725	470
Temperature, °F	1436	1409- 1454	1382	1391- 1445
Hydrogen Consumption, SCF/U. S. gal oil ^b	119	116	111	127
Conversion, wt % C in feed				
Gas	80.7	75.5	80.5	65.8
Liquid	19.3	22.1	25.7	29.2
Benzene	12.9	10.0	11.5	9.5
Naphthalene	4.3	2.8	3.9	6.4
Higher Aromatics	2.4	9.3	10.3	13.3
Solid Residue	0.0	2.4	2.4	5.0
Product Gas Yield, ^b				
SCF/U. S. gal oil	435	357	205	543
SCF/cu ft reactor-hr ^b	1175	1256	731	1314
Net Thermal Recovery, %	78.4	72.0	71.5	63.5
Product Gas Properties				
Composition, mole %				
N ₂ + CO + CO ₂ + H ₂ S	3.20	3.15	7.5	2.15
H ₂	68.0	64.2	35.6	75.15
Paraffins (C _n H _{2n+2})	28.8	32.4	56.9	22.6
Unsaturation	0.0	0.25	--	0.1
Heating Value, ^b Btu/SCF	559	597	792	499
"n" in C _n H _{2n+2}	1.25	1.25	1.24	1.17

^a Stoichiometric for complete conversion of C + H in feed oil to CH₄

^b SCF undefined

^c 38.6°API, C/H = 6.46, 0.0% CCR

^d 33.2°API, C/H = 6.85, 5% CCR

^e 32.7°API, C/H = 6.84, 3.5% CCR

^f 16.4°API, C/H = 7.59, 11.0% CCR

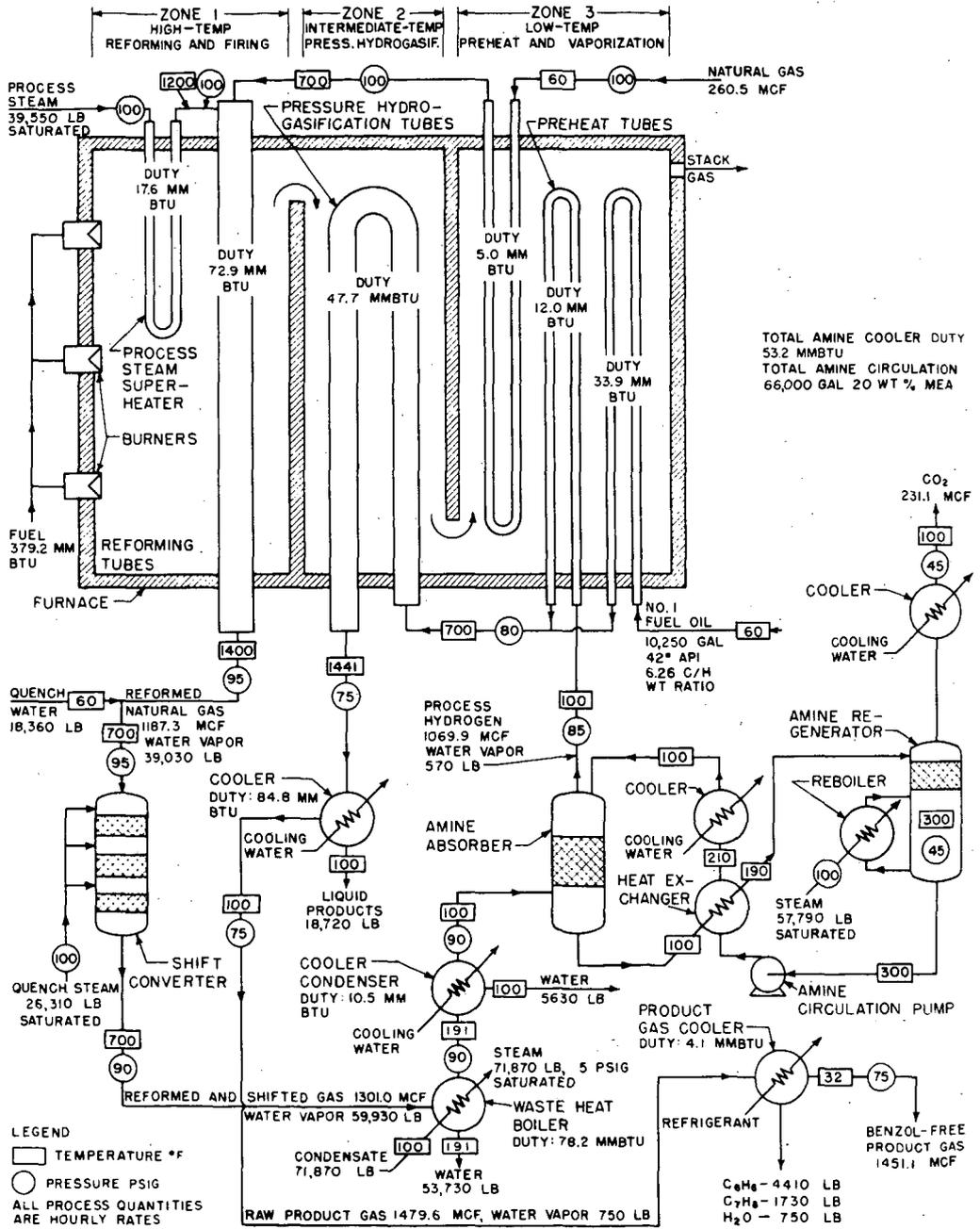


Figure 7.—PRODUCTION OF 1000 MMBTU/HR OF NATURAL GAS SUPPLEMENTS FROM NO. 1 FUEL OIL BY IGT INTEGRAL PRESSURE HYDROGASIFICATION PROCESS

gasoline, with and without hydrogen, is first compared to illustrate the tremendous effect of hydrogen addition at pressures of only 50 to 60 psig on this low C/H ratio and low-boiling feedstock. Liquid products of over 20 weight percent of the feedstock are completely eliminated by addition of 60 SCF/gal of hydrogen at 4 to 5 seconds residence time, and gaseous olefins greatly reduced. With heavy naphtha and kerosene at 50 to 60 psig pressure and a residence time of about 4 seconds, about 20 weight percent of liquid products are formed at 90-100 SCF/gal hydrogen addition, but they are valuable low-boiling aromatics. At 450 psig and with 113 SCF/gal of hydrogen, gas quality is further improved and liquid products are reduced by about half. IGT and Gas Council pilot plant data for the light and heavy naphtha-type feedstocks are essentially the same at the same pressure.

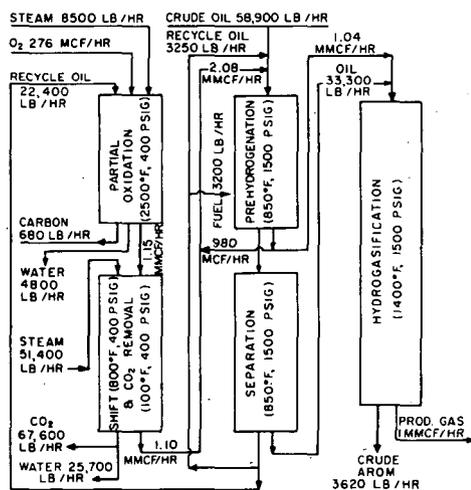
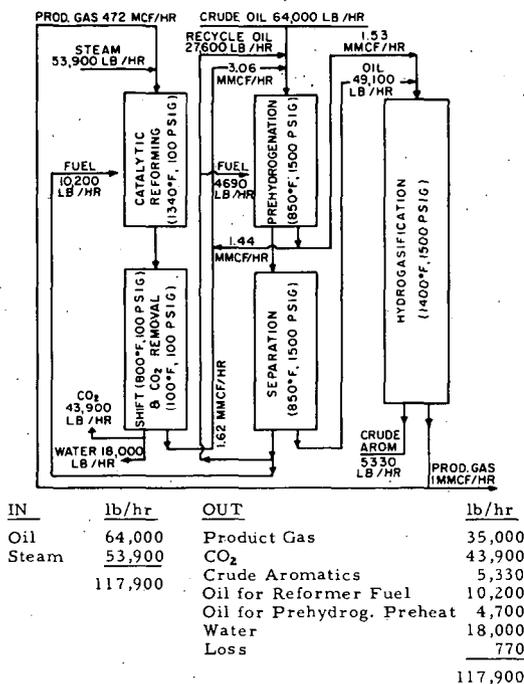
In IGT hydrogasification pilot plant operation at pressures of 500 to 1500 psig, with feedstocks of up to 6.6 C/H weight ratio and negligible Conradson carbon residue (Table 8), liquid products were on the order of 10 weight percent, again mostly low-boiling aromatics. This was accomplished at residence times of 50 to 300 seconds and sufficiently high hydrogen to oil feed ratios to meet the stoichiometric requirements for complete conversion of the feedstock to methane, while still maintaining product gas heating values of nearly 900 Btu/SCF. In the Gas Council fluidized coke bed hydrogenation pilot plant, operation with feedstocks up to 7.6 C/H weight ratio and 11 percent Conradson carbon residue was feasible (Table 9).

The basic problem in commercialization of all of these hydrogasification processes is an economic source of hydrogen supply. When the IGT integral pressure hydrogasification process was developed, the catalyst improvements necessary to efficiently convert the lower boiling liquid feedstocks to hydrogen by catalytic steam reforming at superatmospheric pressure had not yet been achieved, so that the only practical source of high-pressure hydrogen in a self-sufficient plant was by catalytic steam reforming of a portion of purified product (recycle) gas. Such a scheme is shown in Fig. 7.

After Imperial Chemical Industries (I.C.I.) developed its steam-naphtha reforming process, this became a preferred source of hydrogen supply for any continuous hydrogasification process for light distillates, and this is the hydrogen source used for the British Gas Council's GRH process, as shown in Fig. 8. A variant of this process has recently been announced by I.C.I. in which the hydrogasification step is not carried out in an empty reactor but in presence of a nickel catalyst; the hydrogen supply is, of course, the I.C.I. steam-naphtha reforming process. The flow sheet for this approach is given in Fig. 9.

Finally, the IGT high-pressure hydrogasification process, which is designed to utilize high-boiling materials such as crude oils, approaches the problem of hydrogen supply either by reforming of recycled product gas, or by partial oxidation of a portion of the feed oil. These schemes are shown in Fig. 10. It should be noted that, in this process, the feedstock cannot be fed directly to the reactor but must be prehydrogenated (hydrocracked) over cobalt molybdate catalyst, the remaining high-boiling materials must be separated, and the distillate fraction, which is equivalent to No. 2 diesel oil, fed into the hydrogasification reactor. In the British Gas Council version of the hydrogasification process for high-boiling, high C/H weight ratio feedstocks this is, of course, not necessary since the fluidized coke bed serves to remove the pitch and coke from the reactor.

In view of the advanced state of commercialization of the GRH process combined with the I.C.I. steam-naphtha reforming process (Fig. 8), it should be described in more detail. Light or heavy naphtha is first vaporized, mixed with some recycled hydrogen and desulfurized to less than 1 ppm of residual sulfur at a temperature of about 750°F using a hydrodesulfurization catalyst (nickel molybdate), followed by Luxmasse (alkaline iron oxide) and/or zinc oxide. The latter materials absorb the hydrogen sulfide formed in the hydrodesulfurizer and must be discharged and replaced when they are spent. About 58 percent of the naphtha vapor is diverted



IN	lb/hr	OUT	lb/hr
Oil	58,900	Product Gas	35,000
O ₂	22,900	CO ₂	67,600
Steam to Partial Oxidation	8,500	Crude Aromatics	3,620
Steam to Shift	51,400	Carbon from Partial Oxidation	680
	141,700	Water from Partial Oxidation	4,800
		Water from Shift	25,700
		Oil for Prehydrog. Preheat	3,200
		Loss	1,100
			141,700

Figure 10.—TWO FORMS OF IGT HIGH-PRESSURE HYDROGASIFICATION PROCESS

to the hydrogenator plant while the remainder is mixed with superheated steam in the ratio of about 4 lb steam per lb naphtha. This mixture passes to the tubular I.C.I. process reforming furnace where it is converted to hydrogen, carbon monoxide, methane and carbon dioxide. The gases leaving the tubes are normally at a temperature of about 1380°F, at pressures of up to 400 psig. They are first cooled in a waste heat boiler to about 660°F which is a convenient temperature for catalytic carbon monoxide conversion. This is carried out in a single stage with a conventional chromia-promoted iron oxide catalyst since sufficient undecomposed steam remains to give a reduction of carbon monoxide from 10 percent to 3 percent. More heat is recovered in a secondary waste heat boiler and this is followed by feedstock and water preheating and reduction of carbon dioxide content to 1.5 percent in an activated hot potassium carbonate absorption system. At this point, the lean gas has a heating value of about 435 Btu/SCF and contains some 78 percent hydrogen.

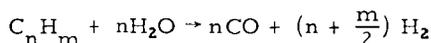
The reforming furnace is fired with liquid naphtha and heat is recovered from the flue gases in a steam superheater, boiler, naphtha vaporizer and combustion air preheater.

The lean gas from carbon dioxide removal is blended with naphtha vapor and enrichment takes place in the GRH unit. The product rich gas, after serving to pre-heat the reactants in an exchanger, passes through a waste heat boiler to a quench tower where it is cooled and heavier hydrocarbons condense. The gas remains saturated with benzene and this is then removed in a standard oil scrubbing process.

This process combination has already formed the basis for the considerable number of commercial plants which are in operation or under construction. They are all designed to produce town gas with a heating value of about 500 Btu/SCF. This has no significant effect on the design of the hydrogenator since in these plants a portion of the lean reformed gas bypasses the hydrogenator and is mixed again with the enriched stream after benzol has been removed. A higher proportion of carbon dioxide is also returned in the bypassed gas since this is required as a diluent for specific gravity control in the final gas mixture. The maximum heating value obtained in commercial operation so far has been 800 Btu/SCF at 92 percent overall thermal efficiency. However, as noted in the discussion of various pilot plant data, higher heating values can be achieved by the proper combination of pressure, residence time and hydrogen to oil feed ratio.

CATALYTIC STEAM REFORMING OR CRACKING PROCESSES

These processes involve the reactions of hydrocarbons with steam in the presence of a catalyst — normally nickel containing — at temperatures of 800° to 1900°F. Carbon monoxide and hydrogen are formed as the dominant products at temperatures of 1200° to 1900°F:



These reactions are highly endothermic (heat consuming) so that the question of heat supply is an important consideration in process design. It is accomplished in three ways: 1) heat is supplied continuously from an external source through alloy steel tubes containing the catalyst; 2) heat is supplied cyclical by storage in the catalyst bed and refractory shapes; 3) heat is supplied by partial combustion through addition of air to the steam-hydrocarbon feed. Air addition is used both to supply all of the heat requirements not met by reactant preheat, or as a partial source of heat in both externally heated tube furnaces or cyclic operation.

At temperatures of 800° to 1000°F, methane, carbon dioxide and hydrogen are the major products. For example, with butane:

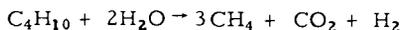


Table 10.—CATALYTIC STEAM REFORMING OR CRACKING PROCESSES

Reactor Type	Continuous (with fixed bed of high activity nickel catalyst)	Continuous (with fixed bed of medium to high activity nickel catalyst)	Continuous (with fixed bed of low activity nickel catalyst)
Heat Source	Reactant preheat	Externally heated alloy tubes	Partial combustion and reactant preheat
Feedstocks			
C/H Weight Ratio	4.5-6.0	4.5-6.0	4.5-5.7
Conradson Carbon Residue, wt %	0	0	0
Distillation Range	Below 420°F	Below 420°F	Below 300°F
Sulfur, wt %	Below 0.0001	Without air at high pressure Below 0.0001 With air at low pressure, Below 0.1	Below 0.1
Types	Desulfurized propane, butane, natural gasoline, light and heavy naphtha	Propane, butane, natural gasoline, light and heavy naphtha	Propane, butane, natural gasoline, light naphtha
Process Conditions			
Temperature, °F	800-1000	1200-1900	1400-1600
Pressure, psig	250-400	Atmospheric-450	Atmospheric
Residence Time, sec	0.5-15	0.2-10	Below 1
Reactant Feeds			
Steam, lb/lb	1-3	2-6	0.7-2
Air, SCF/lb	-	0-20	50-75
Heat of Combustion in Product Gas Due to Process Oil, %	100-110	110-120	90
Products			
Gas			
Heating Value, Btu/SCF	600-800	250-350	150-200
Composition	CH ₄ , H ₂ , CO ₂	H ₂ , CO, CO ₂ , CH ₄ , N ₂	H ₂ , CO, CO ₂ , N ₂ , CH ₄
Other	None	None	None
Commercial Processes (including related petrochemical processes)	Catalytic Rich Gas Process (British Gas Council)	Girdler Co. Process, I. C. I. Process, Surface Combustion Co. Process, Hercules Powder Co. Process, Otto Process, Klöfne Process, M. W. Kellogg Co. Process, plus many others	Continuous O. N. I. A., G. E. G. I. Process, Compagnie Générale de Construction de Fours- Distrigaz Process, Grande Paroisse Air Cracking Process, Gaz de France P-2 Process
Pilot Plant Processes	Low Temperature Steam Re- forming (LCT)		

Table 10, Cont.—CATALYTIC STEAM REFORMING OR CRACKING PROCESSES

Reactor Type	Cyclic (with fixed bed of low activity nickel catalyst)	Cyclic (with fixed bed of low activity nickel catalyst)	Cyclic (with fixed bed of low activity nickel catalyst)
Heat Source	Internally heated catalyst and refractory	Internally heated catalyst and refractory	Internally heated catalyst, partial combustion and reactant preheat
Feedstocks			
C/H Weight Ratio	4.5-8.0	4.5-8.0	4.5-6.0
Conradson Carbon Residue, wt %	0-12	0-12	0
Distillation Range	No limit	No limit	Below 420°F
Sulfur, wt %	No limit	No limit	No limit
Types	All petroleum feeds from propane to better grades of Bunker "C" fuel oil	All petroleum feeds from propane to better grades of Bunker "C" fuel oil	Propane, butane, natural gasoline, light and heavy naphtha
Process Conditions			
Temperature, °F	1300-1800	1300-1800	1300-1800
Pressure, psig	Atmospheric	Atmospheric	Atmospheric
Residence Time, sec	0.2-1	0.2-1	Below 1
Reactant Feeds			
Steam, lb/lb	1-3	1-3	1-3
Air, SCF/lb	-	-	5-15
Heat of Combustion in Product Gas Due to Process Oil, %	60-110	60-110	90-100
Products			
Gas			
Heating Value, Btu/SCF	300-1000	300-1000	300-500
Composition	CH ₄ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₆ , H ₂ , CO, CO ₂ , N ₂ Light aromatics, aro- matic tar, coke	CH ₄ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₆ , H ₂ , CO, CO ₂ , N ₂ Light aromatics, aro- matic tar, coke	CH ₄ , C ₂ H ₄ , H ₂ , CO, CO ₂ , N ₂
Other			None
Commercial Processes (including related petrochemical processes)	Cyclic O. N. I. A.-G. E. G. I. Process, Sugas Process, U. G. I.-CCR Process, plus others	Cyclic O. N. I. A.-G. E. G. I. Process, Sugas Process, U. G. I.-CCR Process, plus others	Micro-Simplex (MS) or Stein et Roubaix Process, S. S. C./O. G. I. and O. G. 2 Processes, Otto-CC3P Process, Gaz de France P-9 Process, Silmit Indugas P-3 Process, Cyclic Catalytic Koppers Process

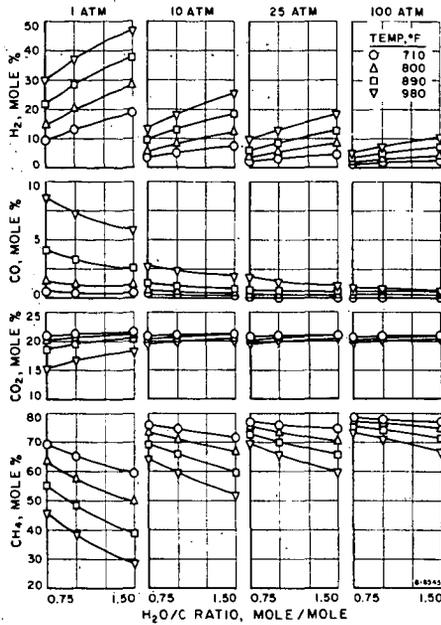


Figure 11.—IDEAL GAS EQUILIBRIUM COMPOSITIONS (WATER-FREE) FOR LOW-TEMPERATURE STEAM REFORMING OF n-HEXANE

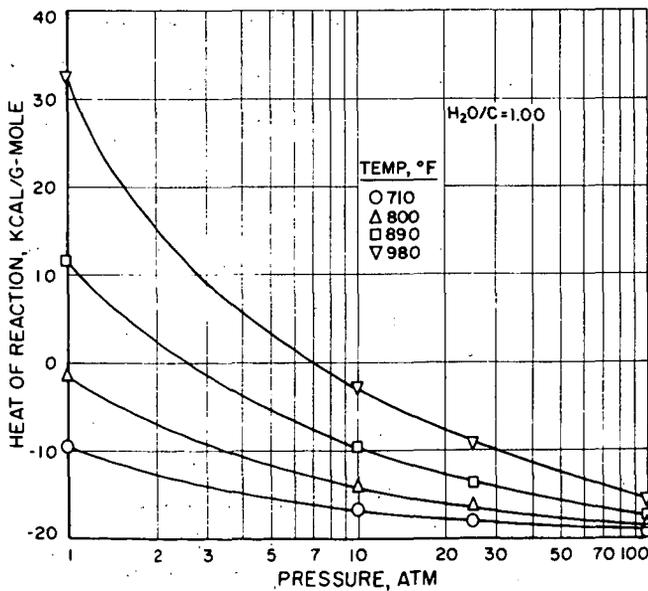


Figure 12.—EFFECT OF PRESSURE ON EQUILIBRIUM HEATS OF REACTION FOR LOW-TEMPERATURE STEAM REFORMING OF n-HEXANE

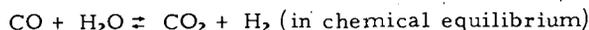
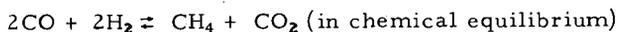
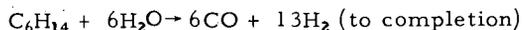
This overall reaction is essentially thermally neutral after preheat of the reactants to near the reaction temperature and, therefore, not limited by heat transfer rates.

A basic problem in catalytic steam reforming and cracking is that the pyrolysis reactions discussed in the preceding section compete with the steam-hydrocarbon reactions. Thus, the higher the C/H ratio, the higher the boiling range and the higher the Conradson carbon residue value, the more difficult it becomes to convert the feedstock by reaction with steam because of its increased tendency to undergo pyrolysis side reactions leading to olefinic gaseous products, aromatic liquid products and coke. This can be counteracted only to a limited extent by use of excess steam and the addition of air. High molecular weight liquid products (tar and pitch), and coke, in addition to reducing gas yield and choking the reactor, also deactivate the catalyst above and beyond deactivation by sulfur poisoning. Another problem is mineral contaminants in the feedstock which generally act as catalyst poisons.

In Table 10 are summarized the various processes developed to handle the problems of heat supply and feedstock properties in catalytic steam reforming or cracking. The term reforming is normally applied to conversion of one gas to another, whereas cracking refers to conversion of a liquid feedstock to gas. All of the processes are in extensive commercial use, many on a worldwide basis. In fact, the vast majority of new manufactured gas plant construction falls within the general category of catalytic steam reforming or cracking. Inasmuch as this presentation is concerned with gasification of petroleum, catalytic steam reforming of natural gas and refinery gas is not included. However, processes for these feeds are essentially the same as those for propane and butane.

Continuous Low-Temperature Steam Reforming or Cracking

This process involves the reaction of vaporized, desulfurized low-boiling feedstocks, ranging from propane through heavy naphtha, with 1 to 3 lb of steam per lb of hydrocarbon at superatmospheric pressure, preferably 250 to 400 psig, and at temperatures of 800° to 1000°F. A very active nickel catalyst is required. An alkali promoted, coprecipitated nickel-alumina catalyst is used in the British Gas Council process (the Catalytic Rich Gas, or CRG process) and a skeletal nickel-alumina-aluminum catalyst is used in the IGT process. The 600 to 800 Btu/SCF product gases, consisting of more than 50 percent methane and lesser amounts of hydrogen and carbon dioxide, can be upgraded to 800 to 900 Btu/SCF by carbon dioxide removal. No byproducts are formed. Some of the process fundamentals are shown in Figs. 11 and 12 for an idealized feedstock — normal hexane. The assumed reaction scheme, closely approached in practice, is:



From Fig. 11, it can be seen that increases in pressure, decreases in steam-to-carbon feed ratio, and decreases in temperature all increase methane concentrations and decrease hydrogen and carbon monoxide concentrations, with relatively little effect on carbon dioxide concentrations. Fig. 12 shows that within the range of preferred operating conditions, the heat of reaction changes from moderately endothermic to moderately exothermic. Generally, the same conditions that increase methane formation also increase the tendency toward exothermicity, including decreases in feedstock C/H ratio.

In practice, minimum reaction temperatures are set by feedstock reactivity and catalyst activity; for example, operation with propane at temperatures as low as 750°F has been found feasible. Minimum steam-to-hydrocarbon feed ratios are de-

terminated by the requirement to prevent the formation of coke or other high molecular weight byproducts on the catalyst.

Conversion rates are extremely fast and, as noted before, not significantly limited by heat transfer considerations with the proper adjustment of reactant ratios, preheat, and operating temperatures and pressures. As shown in Table 11, with the IGT catalyst, space-time yields of 10,000 to 20,000 SCF/CF catalyst-hr are readily attainable, about ten times those typical in high-temperature steam reforming and cracking.

Continuous High-Temperature Steam or Steam-Air Reforming or Cracking

Two basic process types exist here, neither capable of producing utility gas directly because the heating values are too low: 1) reforming or cracking in externally heated alloy tubes with steam, or steam and relatively little air, at pressure levels up to the limits of tube design (normally 450 psig), and 2) reforming or cracking at atmospheric pressure with steam and sufficient air to make the operation autothermic. Both types are limited to naphtha or lower boiling feedstocks and are widely commercialized (Table 10).

Nickel catalysts of substantially lower activity than required in low-temperature steam reforming are used, although with the advent of high-pressure alloy tube furnace operation, catalysts of increasing activity are being developed to allow lowering of reaction temperatures. The I.C.I. steam-naphtha cracking process described in the section on hydrogenolysis processes (Fig. 9), also depends on an improved, more active catalyst to successfully handle the difficult problem of high-pressure operation with a nongaseous feedstock.

The tube furnace process, utilizing either natural gas, where available, or naphtha, if of sufficiently low cost, is a major source of ammonia synthesis gas (3/4 hydrogen and 1/4 nitrogen). In this application, in addition to the steam reaction section, a secondary air reformer is generally used to convert most of the already low methane content to hydrogen and carbon oxides, and to enrich the gas with nitrogen. Carbon monoxide is then catalytically converted to additional carbon dioxide and hydrogen and the carbon dioxide removed by one of the regenerative scrubbing processes.

Many modern town (450 to 550 Btu/SCF) gas plants in areas with economical supplies of propane, butane, and natural or refinery gas, or of naphtha and one of the above high heating value gases, utilize pressure tube furnace plants to produce about 300 Btu/SCF carrier gas and then add high heating value gas (cold enrich) to the desired level. To optimize this type of operation requires close matching of the combustion characteristics of the product gas with those of the base gas (normally derived from one of the coal gasification processes) while maintaining the lowest possible operating cost. In case of complete replacement of gases produced by obsolete coal gasification processes, the problem is still essentially the same, if costly appliance burner adjustment or conversion is to be kept at a minimum.

This is the broad area of gas interchangeability (also exchangeability or substitutability) already referred to in the section on pyrolysis as related to substitution of high-Btu oil gas for natural gas. In the context of gas manufacture, the rules for interchangeability control are generally:

- 1) If technically and economically feasible, attempt to duplicate the composition of the base or burner adjustment gas.
- 2) If complete composition matching is not feasible, attempt to roughly match heating value, specific gravity and flame speed.

Table 11. -LOW-TEMPERATURE STEAM REFORMING OF
HYDROCARBONS WITH SKELETAL NICKEL
CATALYST
(Institute of Gas Technology)

	<u>Propane</u>	<u>Hexane</u>	<u>Light Naphtha</u>	<u>Light Kerosine</u>
FEED PROPERTIES				
°API	--	--	70.3	48.8
Distillation Range, °F	--	--	167-203	361-445
C/H Weight Ratio	4.47	5.11	5.42	5.85
OPERATING CONDITIONS				
Pressure, psig	355	375	355	375
Reaction Temperature, °F	710	839	935	846
Steam/Hydrocarbon Weight Ratio	2.59	1.84	2.16	2.34
Hydrocarbon Space Velocity, lb/CF catalyst-hr	684	512	328	231
OPERATING RESULTS				
Product Gas Composition, mole %				
N ₂	--	0.4	--	0.1
CO	--	trace	0.2	0.5
CO ₂	18.8	20.8	21.5	24.5
H ₂	10.6	10.5	12.1	21.3
CH ₄	70.6	68.3	66.2	53.6
C ₆₊	--	--	--	trace
Total	100.0	100.0	100.0	100.0
Product Gas Specific Gravity, (air = 1.00)	0.685	0.706	0.705	0.690
Product Gas Heating Value, Btu/SCF	737	714	699	604
Product Gas Yield, SCF/lb	27.9	30.2	31.2	35.3
Product Gas Space-Time Yield, SCF/CF catalyst-hr	19,100	15,470	10,230	8,140
Material Balance, wt %	106	102	101	102
Heat of Combustion Recovery, %, *	95	104	101	99
SCRUBBED GAS PROPERTIES**				
Composition, mole %				
N ₂	--	0.5	--	0.1
CO	--	trace	0.2	0.6
CO ₂	2.0	2.0	2.0	2.0
H ₂	12.9	13.0	15.1	27.7
CH ₄	85.1	84.5	82.7	69.6
C ₆	--	--	--	trace
Total	100.0	100.0	100.0	100.0
Specific Gravity (air=1.00)	0.511	0.514	0.508	0.442
Heating Value, Btu/SCF	889	883	883	783

$$* \quad 100 \left[\frac{\text{Heat of combustion of product gas}}{\text{Heat of combustion of feed hydrocarbon}} \right]$$

** Calculated composition assumes 2 mole percent CO₂ present in scrubbed product gas

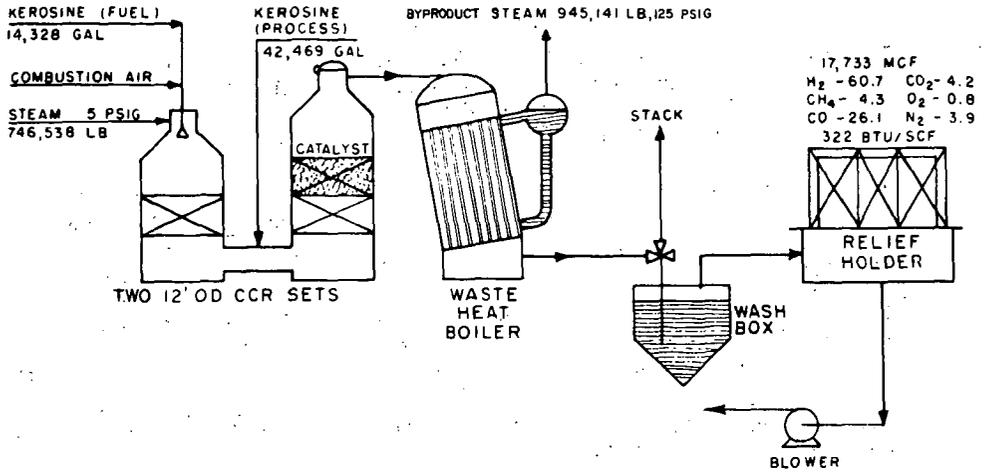


Figure 13.—TYPICAL U.G.I. CCR PLANT OPERATING ON KEROSENE FEEDSTOCK

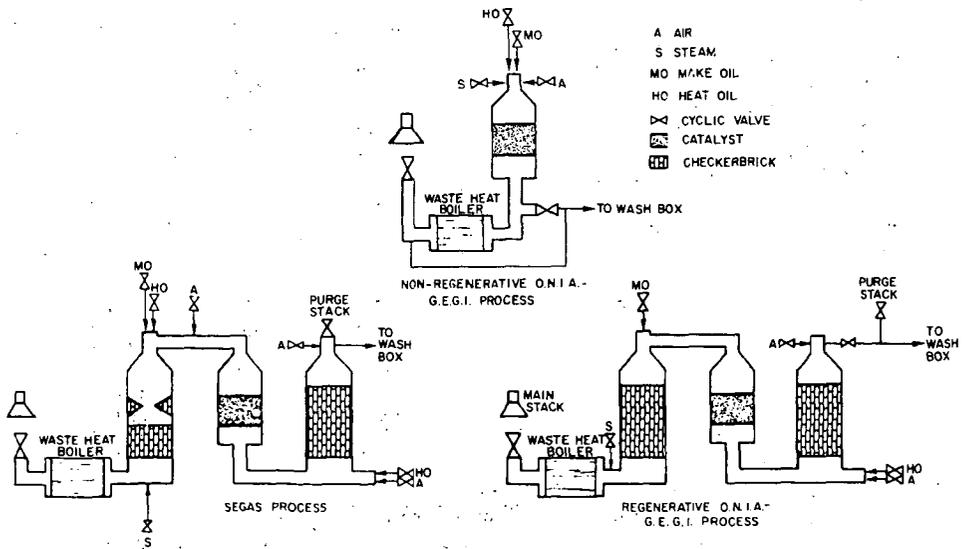


Figure 14.—TYPICAL CONFIGURATIONS OF O.N.I.A.-G.E.G.I. AND SEGAS CYCLIC CATALYTIC STEAM CRACKING OR REFORMING PLANTS

- 3) If this still is not feasible, maintain the closest possible match of Wobbe index (heating value in Btu/SCF divided by the square root of the specific gravity relative to air) and flame speed.

The Wobbe index is designed for application to atmospheric gas burners, the most commonly used type, in which the primary combustion air is inspirated by the kinetic energy of a fuel gas jet emanating from a small orifice. In such burners, the total heat input or burner port loading is roughly proportional to the Wobbe index of the fuel gas, and the primary aeration is inversely proportional. Together with the gas composition, the Wobbe index thus largely determines the flame stability: flashback due to high flame speed and/or low port loading and high primary aeration; blow-off due to low flame speed and/or high port loading; luminous and soot-producing flames due to a high content of hydrocarbons, particularly of higher molecular weight and of nonparaffinic character, combined with high port loading and low primary aeration.

As applied to town gas manufacture by continuous reforming or cracking with steam and air, the most critical variable is the ratio of hydrogen, with its low specific gravity and high flame speed, to inerts (nitrogen and carbon dioxide), with their high specific gravity and diluent effect. The relative amounts of "steam gas" and "air gas" largely control the Wobbe index and permit close matching of burning characteristics with any base or adjustment gas in the town gas category. The autothermic processes which depend on air addition to achieve the necessary reaction temperatures will, of course, produce gases with lower hydrogen and high inert contents. They will, therefore, have higher specific gravities and lower heating values, and will require more high heating value gas addition. The lower intrinsic flame speed resulting from lower hydrogen content is, however, counteracted by the higher primary aeration which increases burning velocity up to about 100 percent primary aeration.

Cyclic Catalytic Reforming or Cracking

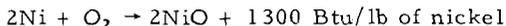
These processes differ from the continuous processes in that the endothermic heat requirements are met in part by heat storage in the catalyst bed and the nickel catalyst is alternately exposed to reducing and oxidizing conditions. In the continuous processes, the catalyst is always in reduced condition. Further, all of the cyclic processes operate essentially at atmospheric pressure. They are widely commercialized (Table 10) and, as of 1965, comprise the largest number of manufactured gas installations utilizing petroleum feedstocks.

There are two types, distinguished by the use of steam only during the make period, and by the use of both steam and air (Table 10). The most widely used types of the cyclic catalytic steam reforming or cracking processes are the U.G.I. CCR process, the Segas process and the O.N.I.A.-G.E.G.I. process. Typical set configurations for these processes are shown in Figs. 13 and 14. These processes are often regenerative - that is, a portion of the sensible heat in the hot flue gas leaving the catalyst bed during the air blast period, as well as of the hot product gas and unreacted steam leaving the catalyst bed during the make period, is stored in refractory shapes to be given up later to reactant steam and combustion air. This is entirely analogous to cyclic-regenerative high-Btu oil gas operation discussed in the section on pyrolysis processes, except that much more steam is used during the make period and steam is a reactant instead of just a diluent and sweep gas. The nonregenerative apparatus uses a waste heater boiler for heat recovery, and often a waste heat boiler is also used with regenerative apparatus (Figs. 13 and 14).

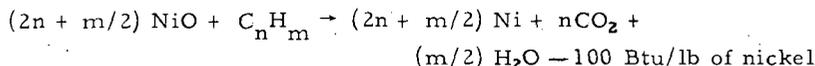
The cyclic processes which use steam and air during the make period are usually similar in design to the nonregenerative O.N.I.A.-G.E.G.I. process (Fig. 14) and are limited to the use of feedstocks in the propane through naphtha range. They are normally used to produce only gases in the 300 to 500 Btu/SCF range. This contrasts with the cyclic reforming and cracking processes using only steam, which are

being used with the entire range of petroleum feedstocks to produce gases from 300 to 1000 Btu/SCF.

It is important to note the function of the catalyst beyond that of simple accelerating steam-hydrocarbon reactions. During the heating period of the cycle, the oxidation of the nickel releases a substantial amount of heat:



During the make period, the feed hydrocarbon reduces the nickel oxide in a slightly endothermic reaction:



Thus, the catalyst becomes a very effective heat transfer and oxygen transfer medium. Because of the very high heat release during nickel oxidation, some of the processes control the free oxygen contacting the reduced catalyst.

Cyclic operation allows the use of sulfur-containing feedstocks as well as feedstocks depositing coke and pitch. Although the activity of the catalyst declines during each make period, in essence changing the process from steam reforming or cracking to simple pyrolysis in every cycle, these contaminants are burned off during the subsequent heat period.

It is apparent that the catalyst must be extremely stable to withstand such radical treatment. The major cause of permanent activity loss for nickel catalysts supported by alumina is spinel formation. This is readily determined by the loss of acid-soluble nickel.

The co-impregnation of a small amount of magnesium oxide with the nickel oxide has been found to improve the activity and stability of alumina-supported catalysts. Magnesia-supported nickel catalyst does not lose activity due to spinel formation, but rather due to solid solution of nickel oxide in magnesia. Both types of activity loss are accelerated by exposure to excessive temperatures (say, 1900°F or more) in an oxidizing atmosphere.

The United Gas Improvement Company cyclic catalytic reforming (CCR) process (Fig. 13) was originally developed to convert carbureted water gas sets to the production of carrier gas by placing in the former superheater a bed of nickel catalyst on a refractory support, and by using the carbureter as a combustion chamber and process steam superheater. Natural gas or other hydrocarbon fuels are burned in the combustion chamber to heat the refractories and the catalyst bed, and to remove deposited carbon and sulfur compounds from the catalyst. Heat from the blast gas is recovered in a waste-heat boiler. In the subsequent make period, steam is superheated by checkerbrick at the bottom of the combustion chamber, and the process hydrocarbon is introduced into the bottom connection between the combustion chamber and the catalyst chamber.

Although this process was originally developed for use with natural gas and LPG to produce low heating value, low specific gravity, carrier gases suitable for re-enrichment with natural gas or propane, in the past several years it has been used with hydrocarbon feeds of increasing molecular weight, and is also suitable for high-Btu gas production at reduced operating temperatures. Typical operation for low-Btu gas production with kerosene is shown in Fig. 13.

The Segas process was developed by the South Eastern Gas Board in Great Britain, and is similar to the CCR process and the French O.N.I.A.-G.E.G.I. process. Originally, lime-bauxite or lime-magnesite catalysts were used instead of

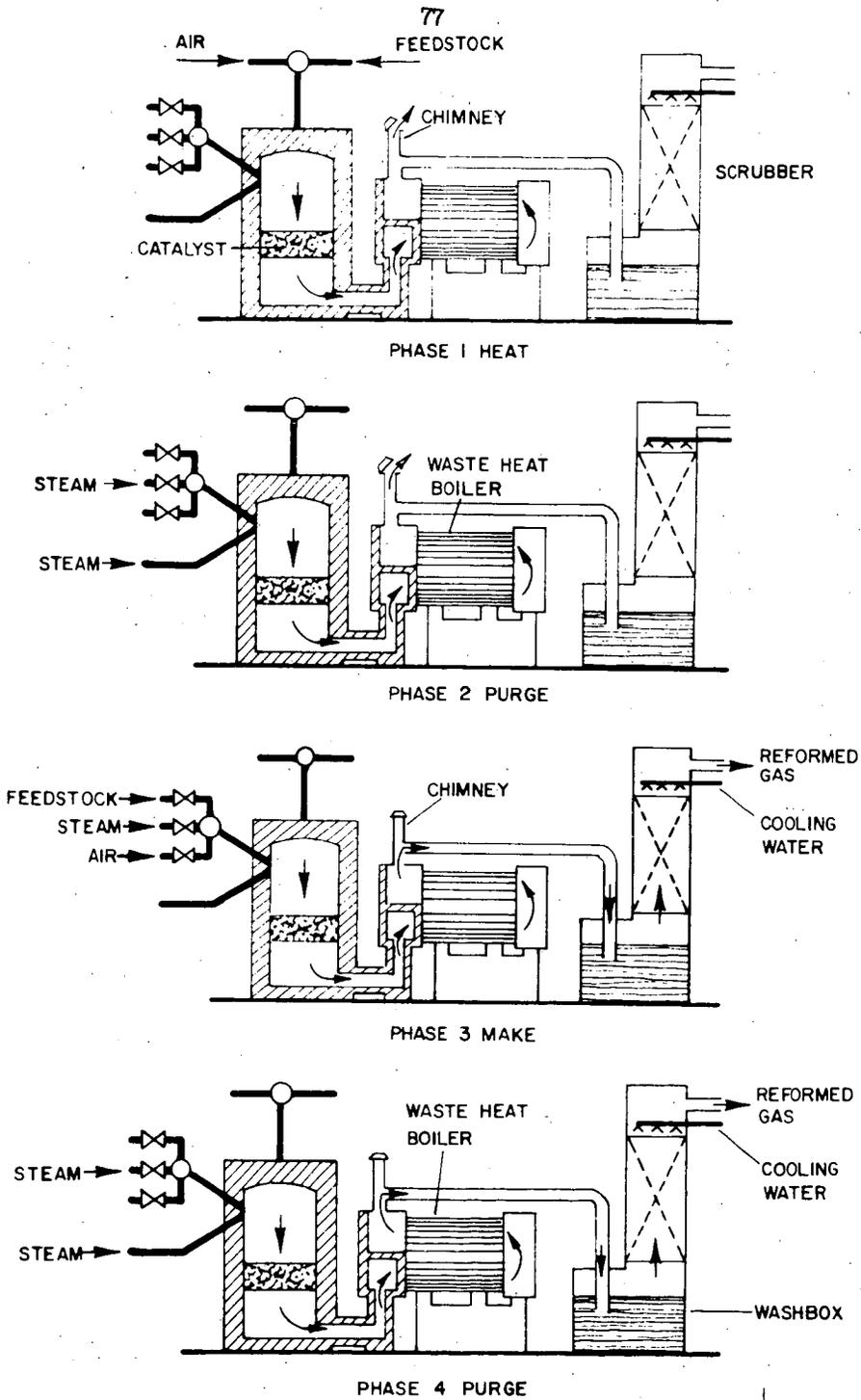


Figure 15.—MICRO-SIMPLEX PROCESS CYCLE

supported metal catalysts. The Segas process also uses only regenerative heat recovery in the commercial designs described in the literature. Further, in the Segas and O.N.I.A.-G.E.G.I. processes, the reactants flow downward through the catalyst bed, whereas in the CCR process the flow is upward. The most recent designs of all of the three cyclic catalytic cracking processes employ the principle of process hydrocarbon introduction into superheated steam at a point where no direct contact of feed hydrocarbon and catalyst bed is possible.

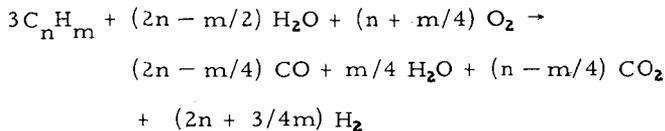
When a carbureted water gas set is converted to the Segas process, the blue-gas generator becomes the steam preheater, the carburetor becomes the catalyst chamber, and the superheater becomes the air preheater. During the make period, steam is superheated in the first vessel, oil is introduced at the top of the first and second vessels, and the cracked products are regenerated in the air preheater and then pass through the washbox. The blast is in the reverse direction. Deposited carbon is burned off, and additional fuel is introduced in the bottom of the air preheater. The Segas and O.N.I.A.-G.E.G.I. processes are also capable of producing gases over the entire range of utility gas requirements. Operating results for self-steaming and regenerative O.N.I.A.-G.E.G.I. plants typical of all of the cyclic catalytic steam cracking processes are given in Table 12.

A typical cyclic catalytic reforming or cracking process for light distillates, employing both steam and air during the make period, is the Micro-Simplex process. Many commercial installations of this process have been made in France and England. The cycle is shown in Fig. 15. A typical product gas analysis for light naphtha operation is (in volume percent): $\text{CO}_2 = 3$; $\text{H}_2 = 43$; $\text{N}_2 = 17$; $\text{CO} = 20$; $\text{CH}_4 = 9$; $\text{C}_2\text{H}_6 = 1$; Olefins = 7; heating value = 450 Btu/SCF; specific gravity (air = 1) = 0.57.

PARTIAL COMBUSTION PROCESSES

Two types of partial combustion processes are in commercial use (Table 13). In one, air is used at temperatures below 2000°F. These are essentially pyrolysis processes in which the heat requirements are met by burning a portion of the feed, so that the same feedstock properties are critical as in pyrolysis and the same basic considerations apply. For example, liquid aromatic byproducts are formed from feedstocks boiling above butane and only premium (low C/H ratio, negligible Conradson carbon residue) distillate feedstocks can be used because of coke and pitch deposition problems.

In the second type of partial combustion processes, petroleum feed is reacted with oxygen in the presence of steam at temperatures of 2000° to 3000°F to form hydrogen and carbon oxides. A generalized reaction characterizing this process is:



In this version of the process, feedstock properties are the least critical. Gas yields still decrease as C/H ratio increases, steam requirements increase and there is a tendency for increased carbon (lampblack) formation. However, no basic changes in partial combustion processes employing oxygen need to be made over the entire range of possible petroleum feedstocks, which is in sharp contrast with pyrolysis, hydrogenolysis and catalytic steam reforming or cracking processes.

Three oxygen processes are in wide commercial use for the production of ammonia and other synthesis gases from feedstocks ranging from methane to Bunker "C" fuel oil (Table 13). The Koppers-Totzek process operates at atmospheric pres-

Table 12.—TYPICAL DATA FOR VARIOUS O.N.I.A.—G.E.G.I. PLANTS
(From Reference 128)

Oil Properties	Fuel-Oil "A"	Fuel-Oil "B"	Fuel-Oil "C"	Gas-Oil "D"	Fuel-Oil "A"
°API	18.2	15.7	13.0	35.6	18.2 18.2
Conradson Carbon Residue, wt %	7.2	9.7	13.0	0.0	7.2 7.2
Sulfur, wt %	3.5	5.1	4.0	1.04	3.5 3.5
C/H Weight Ratio	7.35	7.48	8.00	6.45	7.35 7.35
Product Gas Properties					
Composition, vol %					
CO ₂	5.4	9.0	6.6	5.0	7.5 7.4
O ₂	0.7	0.2	0.6	0.2	0.0 0.0
CO	23.2	19.8	22.8	23.5	25.8 6.2
H ₂	51.8	52.2	53.0	54.5	50.4 24.4
N ₂	2.3	2.6	1.7	2.8	5.1 2.0
C _n H _m	4.1	3.5	3.3	4.5	1.5 29.1
C _n H _n (zn + z)	12.5	12.7	12.0	9.5	9.7 30.9
Total	100.0	100.0	100.0	100.0	100.0 100.0
Heating Value, Btu/SCF*	468	466	438	504	363 996
Specific Gravity (air = 1)	0.50	0.54	0.50	0.51	0.52 0.78
Thermal Efficiency, %**	64	63	59	69	70 59

* Standard cubic foot at 60°F, 30 in. of mercury, saturated with water vapor

** Excluding tar averaging about 8 percent of total oil used

Table 13.—PARTIAL COMBUSTION PROCESSES

Reactor Type	Continuous (empty)	Continuous (empty)	Cyclic (fixed beds of refractory)
Heat Source	Partial combustion with air and reactant preheat	Partial combustion with oxygen	Internally heated refractory plus partial combustion with air
Feedstocks	4, 5, 6, 5 0-trace Up to 650°F No limit	4, 5, 10 0-18 No limit	4, 5, 5, 7 0 Up to 300°F No limit
C/H Weight Ratio			
Conradson Carbon Residue, wt %			
Distillation Range			
Sulfur, wt %			
Types	Propane, butane, natural gasoline, light and heavy naphtha, No. 1 and No. 2 diesel oil, No. 1 fuel oil, premium gas oil	All petroleum feedstocks from propane to Bunker C fuel oil	Propane, butane, natural gasoline, light naphtha
Process Conditions			
Temperature, °F	1300-1900	2000-3000	1200-1700
Pressure, psig	Atmospheric-30	Atmospheric-600	Atmospheric
Residence Time, sec	Below 2	Below 10	Below 1
Reactant Feeds			
Steam, lb/lb	—	0-1	—
Air, SCF/lb	14-40	—	10-20
Oxygen, SCF/lb	—	—	—
Heat of Combustion of Product Gas Due to Process Oil, %	70-95	80-85	90-95
Products			
Gas			
Heating Value, Btu/SCF	300-700 (not including gases containing substantial unreacted propane)	Approx. 300	500-1200 (including unreacted feedstock components)
Composition	CH ₄ , C ₂ H ₄ , H ₂ , CO, CO ₂ , N ₂	H ₂ , CO, CO ₂	CH ₄ , C ₂ H ₄ , C ₃ H ₆ , C ₄ olefins and diolefins, unreacted C ₃ -C ₅ paraffins, H ₂ , CO, CO ₂ , N ₂
Other	Light aromatics and aromatic tar with liquid feeds only	Carbon	Light aromatics with liquid feeds only
Commercial Processes (including related petrochemical processes)	Improved Dayton Process, G. E. I. M. Process, Gas Light and Coke Co. Process	Shell Process, Texaco Process, Koppers-Totzek Process	Koppers-Hasche Process
Pilot Plant Processes	Autothermic Cracking Process (Universal Oil Products Co.), Dayton-Faber Process (oxygen-enriched air gas heating values up to 900 Btu/SCF)		

Table 14.—PARTIAL COMBUSTION OF PROPANE IN
A KOPPERS-HASCHE REFORMER
(From Reference 145)

Make Gas Heating Value, Btu/SCF	590	680	785	890	991	1091
Make Gas Composition, vol %						
CO ₂	2.1	2.0	1.4	1.0	0.7	0.7
C ₂ H ₂	0.7	0.3	0.2	0.2	0.2	0.2
C ₃ +	2.2	4.0	6.1	7.4	7.6	7.5
C ₂ H ₄	12.8	12.9	12.6	12.1	11.5	10.7
O ₂	1.8	1.7	1.7	1.7	1.7	1.7
CO	6.0	5.0	4.4	3.9	3.6	3.3
H ₂	8.7	7.1	6.4	5.9	5.5	5.2
CH ₄	12.3	12.5	12.2	11.7	11.0	10.2
C ₃ H ₈	5.9	8.2	11.0	14.5	19.2	24.2
N ₂	47.5	46.3	44.0	41.6	39.0	36.3
Make Gas Specific Gravity, air = 1	0.89	0.93	0.97	1.01	1.04	1.07
Air/Propane Feed Ratio	2.3	1.9	1.6	1.4	1.2	1.1
Average Combustion Zone Temperature, °F	1550	1490	1430	1370	1310	1250
Thermal Recovery, %	92	93	94	95	96	96.7

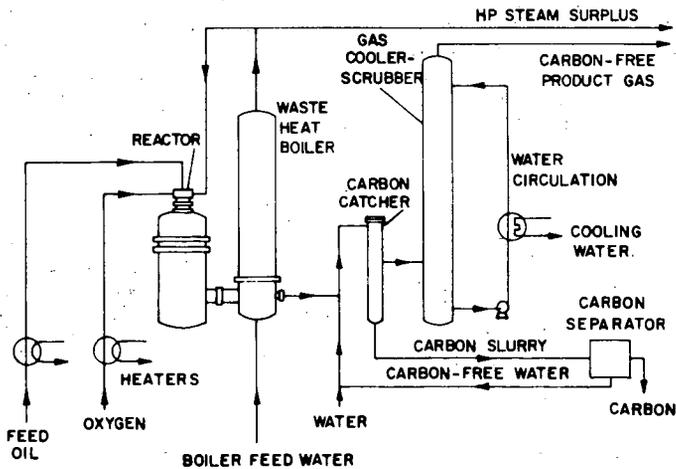


Figure 16.—BASIC SHELL GASIFICATION PROCESS FLOW DIAGRAM

sure; the Texaco and Shell partial oxidation processes can operate at up to 600 psig. Only a single unit of this type (Shell) is known to be used for utility gas manufacture. This plant is located in the U.K. and refinery gas is used to cold enrich the low Btu product gas to town gas specifications. High investment and operating cost have made these processes non-competitive for utility gas manufacture with the processes discussed in the preceding sections. Typical operating data for a feedstock equivalent to a high-grade residual fuel oil and based on Texaco results have already been given in Fig. 10 as part of an overall high-pressure hydrogasification scheme. A flow sheet for the very similar Shell process is given in Fig. 16.

Several continuous partial air combustion processes are still in commercial use (Table 13), but they are now considered obsolete because of the inferior gas quality and higher liquid byproduct formation than with the various catalytic air-steam-hydrocarbon gas manufacturing processes. There is little prospect for further development.

There is, however, a cyclic partial air combustion process that has found wide commercial use and holds continuing interest. This is the Koppers-Hasche process (Table 13) which is characterized by very low investment cost and simplicity of operation.

It is a regenerative partial combustion process of high thermal efficiency, in which a mixture of hydrocarbon gas over vapor and air is fed in sequence through a regenerator, a combustion chamber, and a second regenerator. The regenerator tiles are of a special design allowing high sensible heat recoveries. The flow is reversed after suitable intervals to maintain minimum discharge temperatures. At present, the Koppers-Hasche process is primarily used for partial-combustion reforming of feedstocks ranging from propane to light naphtha, to 500-700 Btu/SCF gases of high specific gravity which are used to supplement or replace gases produced by less economical manufacturing processes (Table 14).

When the partial combustion cycle is used to produce 1000 Btu/SCF gases, the high nitrogen content and the large percentage of unconverted C_3 -plus hydrocarbons results in specific gravities of over one and, consequently, low burner heat inputs. However, after cold enrichment with propane to about 1200 Btu/SCF, the substitutability for natural gas has been found to be higher than that of propane-air gases of equal heating value. Low specific gravity, high-Btu gases have been produced in experimental operation by pyrolysis in the presence of various amounts of steam, with a conventional heat-make cycle similar to that used in the cyclic high-Btu oil gas process.

GAS PROCESSING

In all of the catalytic steam or steam-air gasification processes, and in the partial combustion processes, substantial amounts of highly toxic carbon monoxide are formed. The carbon monoxide concentration can be lowered to acceptable levels, normally below 3 to 5 volume percent in the send-out gas, by the well-known catalytic carbon monoxide shift reaction:



With the standard sulfur-resistant chromia-promoted iron oxide catalyst, this reaction proceeds at space velocities of 300-1000 SCF/CF catalyst-hr at temperatures of 700° to 850°F. An excess of steam is required to maintain catalyst activity. Conversion is favored by excess steam, and by the lowest practical temperature that allows reasonable approach to equilibrium. Pressure has no effect.

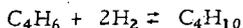
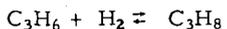
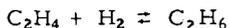
Many petroleum gasification processes now incorporate this reaction as an integral process step, particularly when the exit gas from the gasification step is at

the proper temperature and contains sufficient unreacted steam, or can be adjusted to this condition by water or steam injection. No prior sulfur removal is normally required.

The carbon dioxide formed in carbon monoxide conversion, or excessive concentrations of carbon dioxide present as the result of the gasification reaction, may be removed by a number of regenerative scrubbing processes — monoethanolamine, hot carbonate, Rectisol and others. These processes also remove hydrogen sulfide, a major and highly undesirable contaminant of all fuel gases manufactured from sulfur-bearing petroleum feedstocks. A more common method for hydrogen sulfide removal is with fixed beds of alkaliized iron oxide on a suitable support. A fluid-bed process and various selective scrubbing processes are also available.

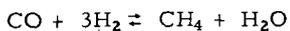
Organic sulfur — mercaptans, disulfides, carbonyl sulfide, carbon disulfide, thiophene, etc. — is normally not removed except when special catalytic processing with nickel or other Group VIII metal catalyst is required. The acid gas (carbon dioxide and hydrogen sulfide) scrubbing processes noted above remove various proportions of the organic sulfur compounds, and the iron oxide processes may also be used to oxidize mercaptans to the more easily removed corresponding disulfides. Partial removal of many of the organic sulfur compounds is also accomplished by oil scrubbing, practiced to recover the aromatic light oil content (primarily benzene, toluene and the xylenes) from gases produced in many of the petroleum gasification processes. However, essentially complete removal of organic sulfur usually requires passage through activated carbon, periodically regenerated with superheated steam or hot gases.

In addition to carbon monoxide conversion, two types of catalytic processing of manufactured gases are becoming of increased interest. One is autohydrogenation of gases containing large proportions of olefins and diolefins as well as hydrogen. This process was first proposed by the Institute of Gas Technology to improve the substitutability of such gases for natural gas by increasing their proportion of paraffins by such reactions as:



These proceed readily over active Group VIII metal catalysts, such as nickel on kieselguhr support, at 300° to 500°F and at pressures from atmospheric on up. Work is underway in France and Italy to put this process into commercial operation.

A similar catalytic process is methanation of carbon monoxide and hydrogen, common constituents of steam reforming or cracking and partial combustion processes. This reaction,



proceeds rapidly over highly active nickel catalyst at 650° to 900°F and is favored by pressure. Feed gas sulfur content must be reduced to 0.1 ppm or less to avoid rapid catalyst deactivation. Methanation has been considered actively as a means for manufacturing town gases and natural substitutes from low heating value gases for many years, although largely with coal as the basic raw material. However, as early as 1951, the Surface Combustion Company reported pilot plant results on a naphtha steam cracking-methanation process, similar to the ones now being actively considered in Europe.

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PYROLYTIC GASIFICATION OF Na, Ca AND Mg BASE SPENT PULPING LIQUORS

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ABSTRACT

One high temperature process presently being developed for pollution control and pulping chemical recovery is the Atomized Suspension Technique (AST). When this technique is applied to the treatment of spent pulping liquors under purely pyrolytic conditions, it offers the possibility of obtaining commercially significant quantities of by-product ammonia and methanol synthesis gases and certain unsaturated hydrocarbons from the lignin and other organics present in the spent liquors. Results of pilot scale pyrolytic experiments carried out in a 1' x 15' AST reactor with Na, Ca and Mg base spent liquors at 600 to 900 C reactor wall temperatures and 5 - 45 psig reactor pressures are described. The data is examined primarily from the gasification point of view, with particular attention to the influence of inorganic matter (the pulping base) on the product gas yields and compositions. At identical operating conditions, the Na base liquor gave the highest yields of synthesis gas, and the lowest yields of unsaturated hydrocarbons, while the Mg base liquor showed an opposite behaviour. The Ca base liquor produced intermediate yields of both products. Addition of Na_2CO_3 to the Mg base liquor produced gas yields similar to the Na base material. The experimental results are compared to equilibrium data, and the effect of the various inorganic bases on the kinetics of the gasification reactions is discussed.

GASIFICATION OF COAL UNDER CONDITIONS SIMULATING STAGE 2
OF THE BCR TWO-STAGE SUPER-PRESSURE PROCESS

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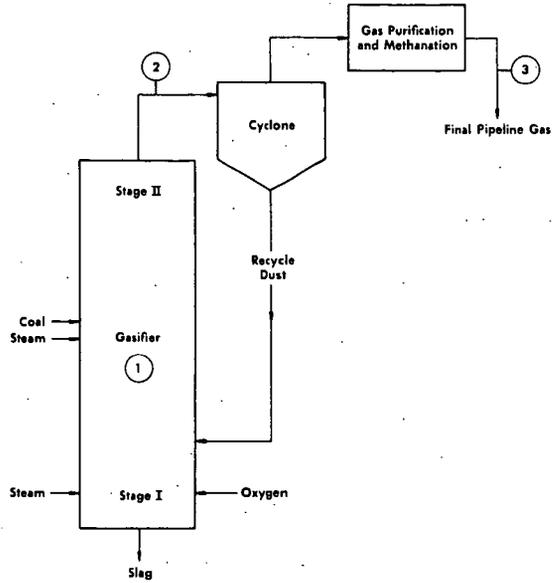
INTRODUCTION

For the production of pipeline gas, coal gasification processes operating at elevated pressure and a low gas exit temperature produce a raw gas with a high methane content; this in turn leads to lower investment and operating costs than for processes that produce CO and H₂ as the principal products and do not form significant amounts of methane.(1, 2)* An entrained coal gasification process using two reaction stages operating at 70 atm pressure offers promise for high yields of methane and the ability to process all types of coal regardless of caking properties or size consist.

To achieve the required rapid reaction in an entrained system, both a reactive fuel and a means for rapid heating are necessary. The volatile portion of bituminous coal or lignite is such a fuel and to utilize it properly for generation of gas of a high methane content, a two-stage super-pressure process has been devised. (See Figure 1.) In this process, heat and "Stage 1" or synthesis gas are generated in Stage 1 by gasifying recycle char under slagging conditions with oxygen and steam. In Stage 2 fresh coal and steam are introduced into the hot synthesis gas issuing from Stage 1. The fresh coal is thereby rapidly heated to reaction temperature of about 1750 F and partially converted into gas with a high methane content, mainly by pyrolysis of the volatile portion of the coal by reaction with steam and Stage 1 gas. For ultimate conversion into high Btu pipeline gas, the combined gases laden with unreacted char leave Stage 2 and pass successively through dust removal, shift reaction, acid gas removal and methanation steps.

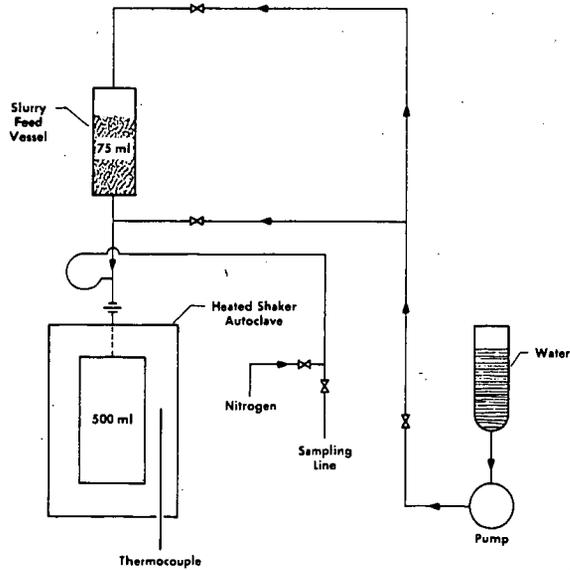
As the process contains two stages, it has two types of problems that required further study: The first pertains to the slagging zone or Stage 1 of the process. The production of gas by slagging gasification of coal at atmospheric pressure has been done successfully on a commercial scale.(3) For slagging gasification at elevated pressure, processes have been developed on an experimental scale by various groups including the Bureau of Mines in the United States, and the Gas Council in England.(4) These investigations have shown that slagging coal gasification at elevated pressure is feasible and that development of a commercial process will, except for the control of metallic iron formation, be primarily a design problem. This previous work has also

* Numbers in parenthesis refer to Literature References listed at end of paper.



Bituminous Coal Research, Inc. 8008G10

Figure 1. Simplified Flow Diagram for BCR Two-stage Super-pressure Gasifier



Bituminous Coal Research, Inc. 8008G78

Figure 2. Flow Diagram of Batch Autoclave Reactor

shown that meaningful results can only be obtained by experimentation on a scale that provides a minimum slag flow of 200 lb/hr, corresponding to a 1 ton/hr pilot plant using coal with 10 percent ash.

The second pertains to the "direct methanation" zone, or Stage 2 of the process. Although various processes have been devised for utilization of the volatile portion of coal for gas production, little information is available on the primary formation of methane directly from it.

This paper reports the results of laboratory-scale research which has been conducted to fill the gap in our knowledge concerning the rate of formation of methane under conditions prevailing in Stage 2 of this proposed two-stage super-pressure process.

EXPERIMENTAL

In the experimental studies, tests have been made on the direct steam methanation of coal in two types of equipment. Batch tests have been conducted in small rocking-type high-pressure autoclaves. Continuous flow experiments have been made in a 1-inch reactor, 5 ft long, under Stage 2 conditions using simulated Stage 1 gas.

Tests in Batch Autoclaves

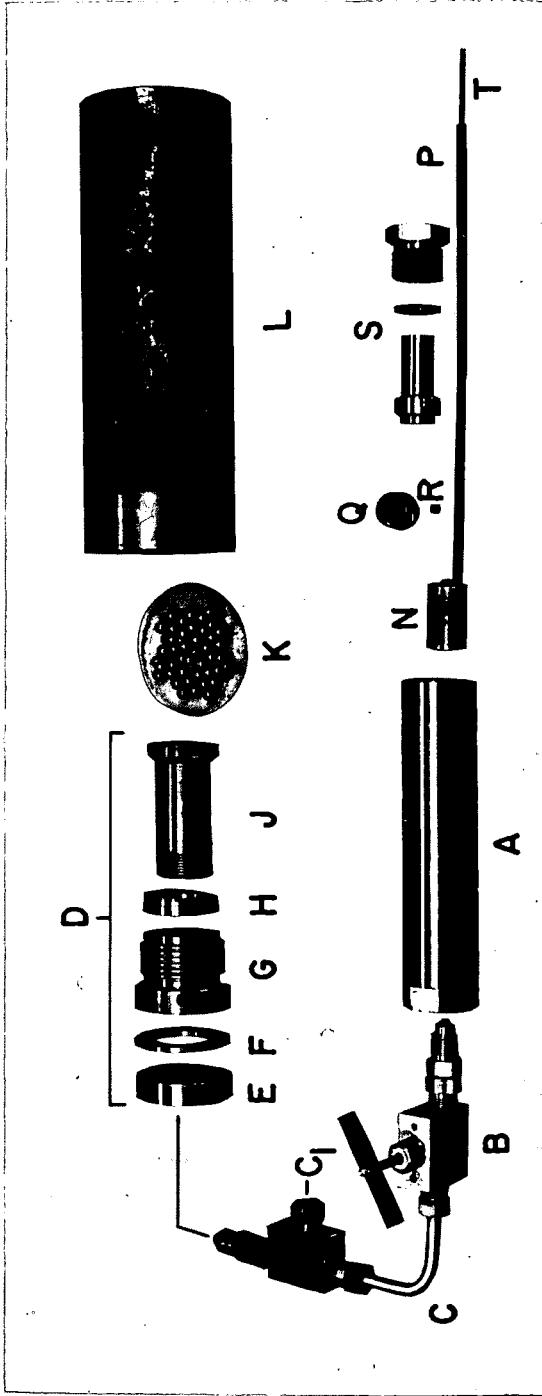
In the batch studies of the direct steam methanation of coal, duplicate autoclave systems were employed to obtain data as rapidly as possible without delay for cooling and reheating. One of the systems is shown diagrammatically in Figure 2. Both the feeder and reactor vessels are fabricated of super-strength alloys, 19-9 stainless steel DL alloy, to permit operation at temperatures up to 1500 F and pressures up to 10,000 psi. The specially designed 75 ml auxiliary feed vessel provides means for charging up to 30 g coal as a 40 weight percent slurry. A view of the overall reactor assembly is shown in Figure 3 together with an exploded view of the feed vessel fittings.

In a typical operation, a weighed charge of coal slurry, consisting of a mixture of 40 weight percent of minus 325 mesh coal and 60 weight percent water with or without added sodium carbonate catalyst, was injected rapidly by means of hydraulic pressure into the preheated, rocking autoclave containing a measured volume of nitrogen tracer gas. The water in the slurry flashed into steam and reacted with the coal forming methane and other gases.

The gaseous reaction products were sampled on a specified time schedule and analyzed by chromatography. After the system had cooled following the test, the residual gases were collected and the residues, consisting mainly of carbon and ash, were removed, weighed, and analyzed.

Tests were made under controlled, but widely varied, conditions. The time of reaction was varied from 2 to 120 minutes; the temperature from 730 C to 770 C; the pressure from 60 to 350 atmospheres. The experimental data and results are summarized in Tables 1 and 2.

In Table 1, the data and results are given for those tests in which gas samples were taken only at the end of the tests. In Table 2, the data and results are given for those tests in which gas samples were taken at stated



(8008P147)

Slurry Feeder

- A** — Slurry Feeding Cylinder Without Fittings
B — Valve
C — Connections, Feeder to Reactor T
C₁ — Gas Outlet Connection

Reactor

- D** — Cover
E — Locknut
F — Thrust Washer
G — Main Nut
H — Seal Ring
J — Main Body
K — 50 3/8" Diameter Stainless Steel Balls
L — Reactor Body

- N** — Piston Attached to Placement Rod (P)
Q — Front View of Piston Showing Center Threaded Bleed Hole and Off-Center Threaded Hole for Rod
R — Allen Set Screw to Plug Center Bleed Hole
S — Cylinder Closure Fittings
T — Allen Wrench to Fit Allen Set Screw

Figure 3. Exploded View of Components of Slurry Feeder and

TABLE 1. RESULTS OF BATCH AUTOCLAVE EXPERIMENTS
WITHOUT INTERMITTENT SAMPLING

	Test 12	Test 13	Test 14	Test 16	Test 18	Test 19	Test 20	Test 22
Temperature, C	730	730	730	730	730	770	770	770
Time, min	120	120	120	120	12	120	120	12
Coal Used, g daf	8.71	9.26	10.50	10.40	10.42	10.84	8.45	10.14
Catalyst, Wt % of Coal	42.1	33.0	0	0	0	15.2	0	0
Residue, g daf	4.43	4.47	6.37	6.71	7.23	4.63	4.97	6.75
Total Pressure Developed, atm	354	326	308	181	263	243	168	188
Product Partial Pressures, atm								
H ₂ O	306	283	273	145	247	165	130	161
CO ₂	14.3	13.0	10.0	9.1	3.2	24.5	9.9	5.9
CO	0	0.1	0.4	0.6	0.4	0.6	0.6	0.5
H ₂	15.3	13.6	9.3	9.3	2.9	26.4	11.4	6.3
CH ₄	18.1	16.8	16.2	17.4	7.8	24.6	14.3	12.9
Gas Volume, scf/lb daf Coal	12.45	10.90	7.80	7.94	3.47	15.55	9.76	5.82
Coal Converted, % daf	49.1	51.8	39.4	35.6	30.6	57.3	41.2	33.4
Btu in Gas, % Btu in Coal*	45.6	43.2	31.5	31.8	15.8	52.7	35.6	24.8
Carbon in Gas, % C in Coal	31.1	27.8	21.4	21.7	9.6	37.6	20.4	16.0
Carbon in CH ₄ , % C in Coal	17.4	15.7	13.2	14.3	6.5	18.5	11.7	10.6
Preformed Methane, %	83.0	83.2	87.0	87.7	90.9	78.5	82.8	88.5

* Based on total carbon in products.

TABLE 2. RESULTS OF BATCH AUTOCLAVE EXPERIMENTS WITH INTERMITTENT SAMPLING

	Test 35		Test 37		Test 39		Test 40		Test 42		Test 43		
	35-2	35-60	37-4	37-60	39-8	39-60	40-2	40-60	42-8	42-13	42-60	43-4	43-60
Temperature, C	753	753	753	753	748	748	749	749	746	746	746	751	751
Time, min	2	60	4	60	8	60	2	60	8	13	60	4	60
Coal Used, g daf	-	10.88	-	10.37	-	11.85	-	9.29	-	-	12.21	-	13.23
Catalyst, wt % of Coal	0	0	0	0	0	0	28	28	18.9	18.9	18.9	20.3	20.3
Residue, g	-	7.20	-	6.84	-	7.61	-	5.21	-	-	7.70	-	7.13
Total Pressure Developed, atm	191.4	188.7	211.8	183.2	271.4	241.0	203.3	184.8	242.4	209	135.5	227.1	222.5
Product Partial Pressures, atm													
H ₂ O	177.9	152.6	190.3	141.0	242.6	188.7	183.0	135.3	214.1	182.0	95.8	206.0	166.1
CO ₂	0.42	6.23	1.60	9.65	2.98	11.23	2.50	10.77	4.48	4.76	9.06	3.04	13.9
CO	0.56	0.45	1.04	0.73	0.89	0.82	0.06	1.03	0.20	0.14	0.47	0.04	0.74
H ₂	0.97	7.65	2.73	10.52	4.30	11.95	2.60	14.43	5.43	4.64	9.46	3.30	12.85
CH ₄	2.88	15.34	8.78	15.50	11.96	21.40	6.10	16.40	9.09	9.90	14.62	6.30	21.35
C ₂ H ₄	0.15	-	-	0.11	0.15	-	0.20	-	-	-	-	0.11	-
C ₂ H ₆	0.42	0.12	0.68	-	0.84	0.09	0.90	0.09	1.00	0.64	0.17	0.90	0.25
N ₂	8.10	6.3	6.7	5.7	7.7	6.8	7.9	6.8	8.1	7.0	5.9	7.4	7.3
Gas Volume, scf/lb daf Coal	1.05	6.33	3.38	8.77	4.23	9.47	3.01	10.74	3.95	3.92	7.69	2.44	8.92
Coal Converted, % daf	-	33.8	-	34.0	-	35.8	-	43.9	-	-	36.9	-	46.1
Btu in Gas, % Btu in Coal*	10.3	28.5	17.1	33.4	21.8	38.5	16.1	41.2	18.3	20.6	31.4	13.0	38.1
Carbon in Gas, % C in Coal	3.7	18.1	11.0	23.4	13.5	23.5	10.1	27.5	11.6	13.5	21.5	7.7	25.0
Carbon in CH ₄ , % C in Coal	2.1	12.4	7.6	14.3	9.0	15.1	5.6	16.3	6.7	8.2	13.3	4.2	15.3
Preformed Methane, %	91.0	88.7	91.3	85.2	91.4	87.5	92.3	81.5	88.5	90.1	86.5	90.6	86.7

* Based on total carbon in products, assuming same correction applied for intermittent samples as for final sample.

intervals during the test as well as at the end. By this latter procedure, additional information was obtained on the effects of time on the reactions.

Tests in Continuous Flow Reactor

In the flow experiments under Stage 2 conditions using simulated Stage 1 gas, a continuous flow reactor with a design capacity of 5 lb/hr, a maximum operating temperature of 1800 F (1000 C) and a maximum working pressure of 1500 psi (100 atm) was used. A schematic illustration of the total system using slurry feeding of coal is shown in Figure 4 and general view of the safety stall and control area is shown in Figure 5.

The 5-foot long reactor is fabricated from Haynes 25 alloy, and has a 3-inch outside diameter and a 1-inch inside diameter (Figure 6). Under operating conditions, the reactor volume of about 800 ml provides for a residence time of several seconds. The preheater furnace and each of the three sections of the reactor furnace are independently controlled by temperature-recorder controllers that regulate saturable core transformers. A metering piston-type pump is used to feed the slurry of coal in water. Pressurized Stage 1 gas, i.e., simulated product gas from Stage 1, is fed into the slurry stream at the discharge port of the pump to facilitate trouble-free flow of the slurry up the vertical lines into the preheater.

The Stage 1 gas-coal-superheated steam mixture is discharged from the preheater into the reactor at a temperature of about 600 F. Upon entering the reactor, the mixture is raised to operating temperature in the upper section, or Zone 1, is reacted in the middle section, or Zone 2, and is cooled back down to about 1000 F in the lower section, or Zone 3, before leaving the reactor.

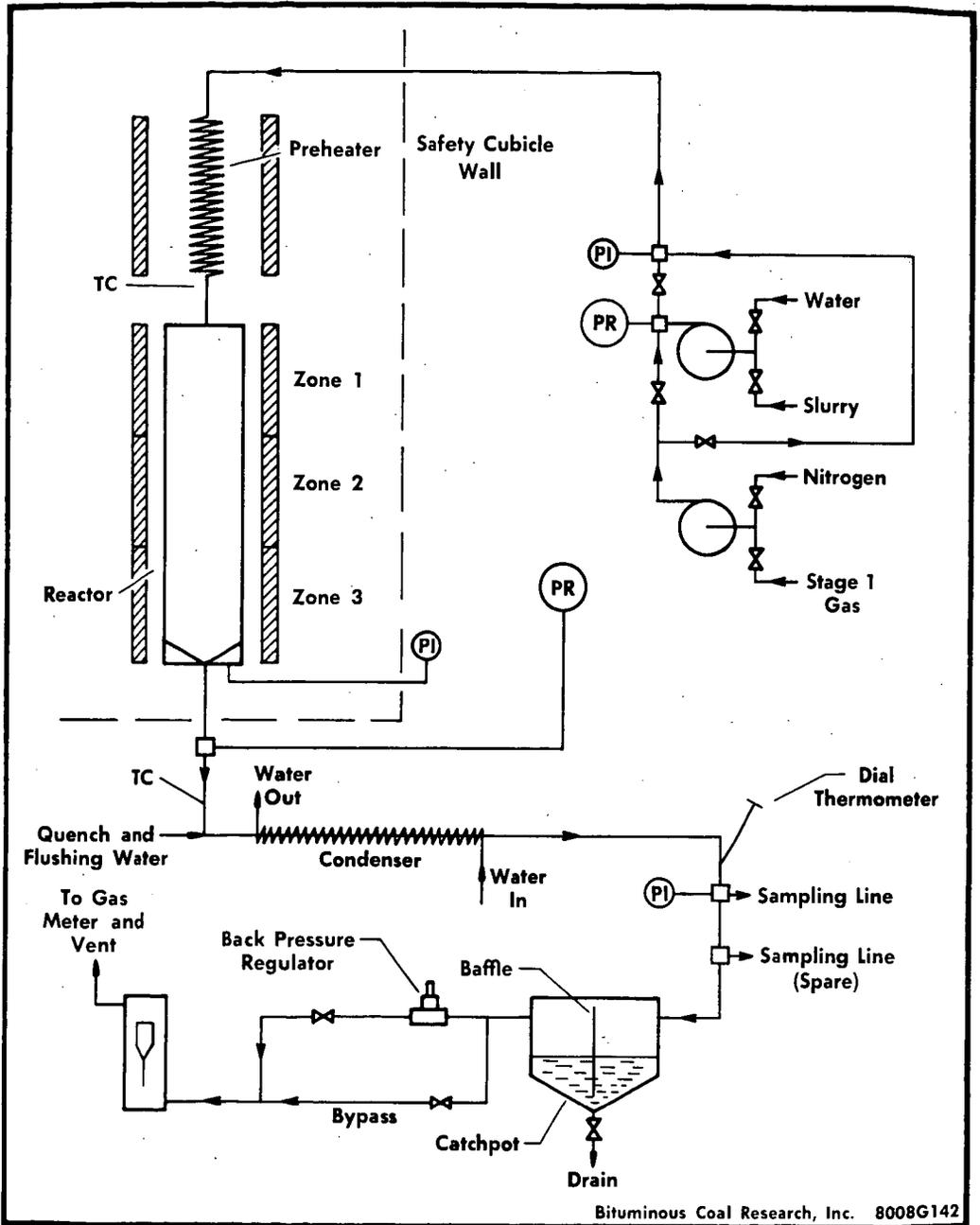
The product gases, containing the finely divided unreacted solids, are discharged from the reactor through a water-cooled condenser into a catchpot where the water condensate and solids are removed. From the catchpot the gases are fed through a pressure reducing valve to a wet test meter for measurement and then on to storage in a gas holder or venting to the atmosphere.

In the condenser, cooling of the gas and flushing of the solids is facilitated by injection of water at the inlet to the condenser at a controlled rate from an auxiliary high pressure metering pump.

Sampling valves are located at the downstream exit of the condenser ahead of the catchpot. Gas leaves in a small stream that is withdrawn continuously from the system and monitored for changes in composition by means of a thermal conductivity meter; during predetermined intervals samples are taken from this stream for chromatographic analysis.

Argon, added to the Stage 1 gas as a tracer, is used to determine any changes in gas quantity that occur during the test. The approximate composition of the Stage 1 gas was as follows: hydrogen, 18 percent; argon, 10 percent; carbon monoxide, 55 percent; and carbon dioxide, 17 percent.

Material balances are established using the usual data obtained from weight, flow, temperature, and pressure measurements; these are verified by comparison with the argon tracer data.



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Figure 4. Flow Diagram for Continuous Flow Reactor Assembly Using Slurry Feeding

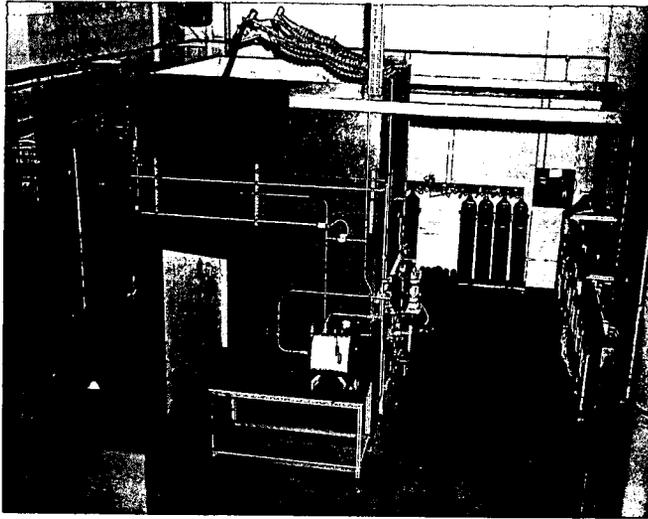


Figure 5. View of Continuous Flow Reactor Safety Cubicle and Control Area (8008P59)

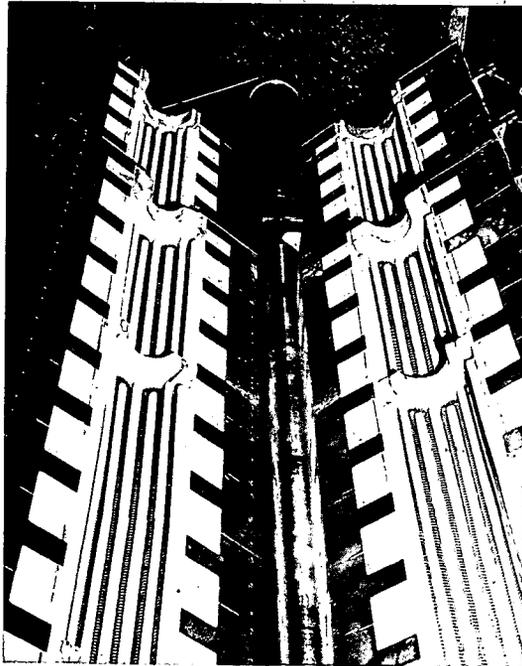


Figure 6. View of Top Zones of Continuous Flow Reactor with Electric Furnace Open for Inspection (8008P54)

To date, tests have been made in the flow reactor using both bituminous coal and lignite over a range of conditions approximating those which, at the moment, are considered optimum for Stage 2 operations.

Experiments with the Pittsburgh seam coal used in the autoclave test showed that it accumulated in the reactor. Even the results of very short operations were falsified by the char present in the reactor and resulted in too high apparent coal conversion. Mixing of the coal with silica of very small particle size (3 microns) remedied this problem and the reactor remained free of deposits in tests of 12-18 duration. However, the addition of silica lead to irregularly occurring and disappearing pressure buildups in the preheater coil and made a reduction of the coal content in the slurry necessary. This was especially the case when temperatures necessary to assure complete vaporization of the water in the slurry and to superheat the steam were used in the preheater. Nevertheless, satisfactory tests could be made. Concentrations of 20 percent lignite in slurry were used. After heating up the system and stabilizing the temperature, while feeding gas and water, tests approaching one hour of coal injection were made with lignite. This established that in runs of short duration reliable results are obtained. The reactor in all cases was practically free of deposits. There were some occasional irregularities caused by transient pressure buildups in the preheater or the condenser.

In the tests made using slurry feeding, the concentration of coal in relation to steam and Stage 1 gas was not as high as visualized for the commercial process. Thus, development of a dry coal feeder in which the coal feed rate is independent of the amount of water fed into the reactor represented a major improvement over the slurry feeding system. The flow diagram for the continuous flow reactor assembly as modified to use the dry coal feeder is shown in Figure 7.

Source and analytical data on the coals used are given in Table 3. The experimental data and results of tests in the continuous flow reactor over a wide range of conditions using both slurry feeding and dry coal feeding are summarized in Tables 4, 5, and 6. The data and results from tests with high volatile A bituminous coal are shown in Table 4. Table 5 presents data and results from tests with lignite fed as a slurry and Table 6, with lignite fed as a dry powder.

DISCUSSION

In the production of high Btu pipeline gas from coal, the objective is to convert the carbon in the coal into as much methane as possible in the initial gasification step, and if not into methane, then into carbon monoxide which in another step can be converted to methane by catalytic hydrogenation.

Thus, in the present study on the direct steam methanation of coal, either in batch autoclave tests or in continuous flow tests, the product gases of principal concern are methane, hydrogen, and carbon monoxide, and the greater the amount of methane in proportion to the amount of carbon monoxide and hydrogen, the smaller will be the final cost of the pipeline gas. As an index of this ratio of methane to carbon monoxide and hydrogen, the term "preformed methane" has been introduced, and, by definition, is the amount of methane in the initial product of gasification expressed as a percent of the total methane potentially available including that from conversion of the carbon monoxide and

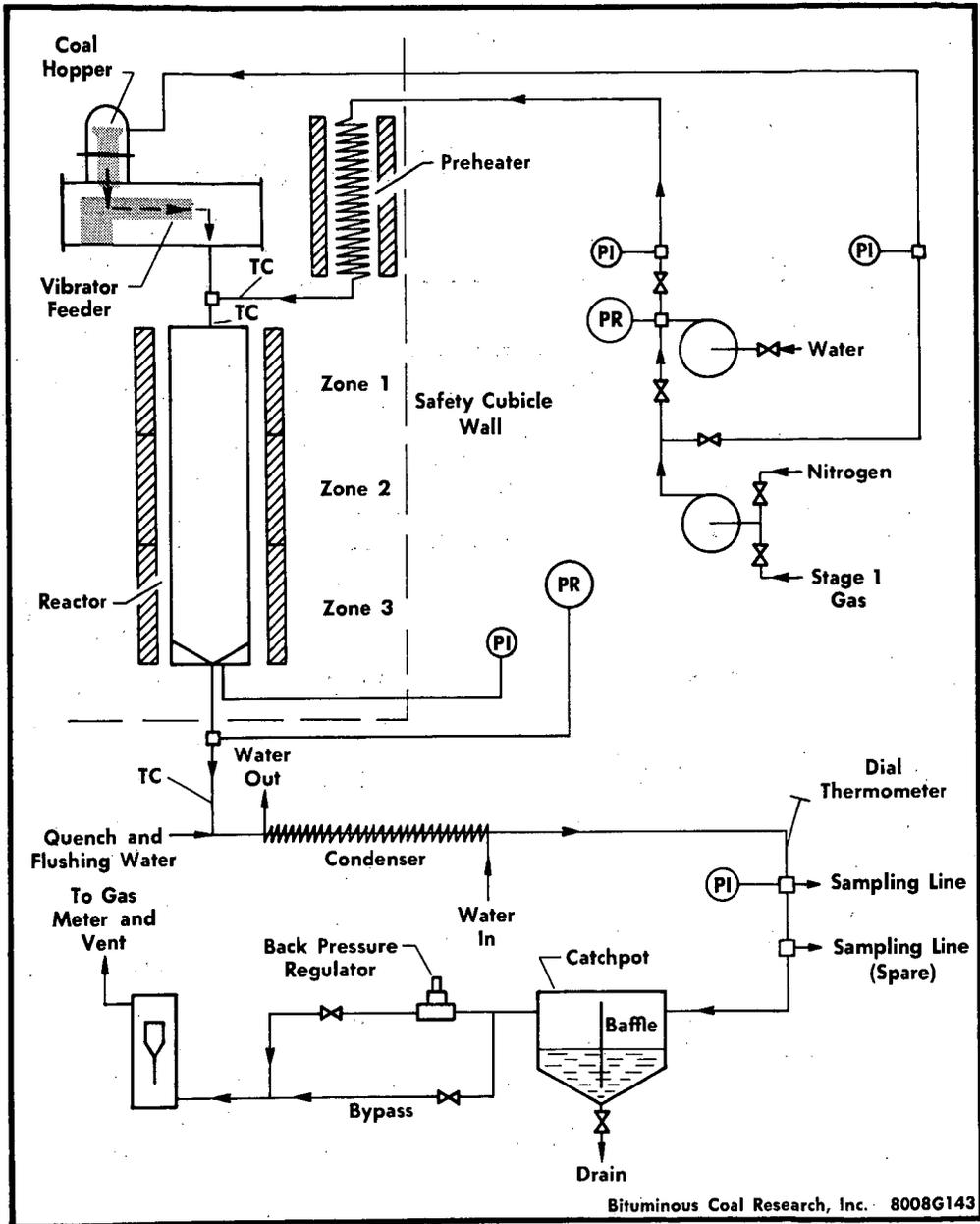


Figure 7: Flow Diagram for Continuous Flow Reactor Assembly Using Dry Feeding

TABLE 3. SOURCE AND ANALYTICAL DATA ON TEST COALS

<u>Source</u>	<u>Coal</u>			
	<u>High Volatile A Bituminous</u>		<u>Lignite</u>	
State	Pennsylvania		North Dakota	
County	Allegheny		Mercer	
Seam	Pittsburgh		--	
<u>Proximate Analysis, %</u>	<u>As Used</u>	<u>Daf</u>	<u>As Used</u>	<u>Daf</u>
Mositure	1.02	-	19.4	-
Ash	4.74	-	10.8	-
Volatile Matter	37.60	39.80	27.8	40.0
Fixed Carbon	56.64	60.20	42.0	60.0
<u>Calorific Value, Btu/lb</u>	14,100	14,970	8,540	12,270
<u>Ultimate Analysis, %</u>				
C	79.19	83.90	51.80	74.27
H	5.48	5.71	5.54	4.85
N	1.52	1.62	0.64	0.91
S	1.35	1.43	1.08	1.55
O (by diff)	7.73	7.34	30.14	18.42
Ash	4.73	-	10.80	-

TABLE 4. OPERATING DATA AND RESULTS FOR TESTS IN CONTINUOUS FLOW REACTOR USING HIGH-VOLATILE BITUMINOUS COAL

	Test Number		
	CFR-4	CFR-7	CFR-8
<u>Operating Conditions</u>			
Temperature, F	1730	1690	1720
Pressure, atm	70	70	70
Reactor Volume, cc*	320	280	180
Residence Time, sec	6.5	5	3.0
<u>Input</u>			
Water, g/min	24	30	32
Partial Pressures of Materials in Feed Stream, atm			
H ₂ O	35.7	38.0	41.5
H ₂	6.2	5.5	5.4
CO	18.8	16.0	15.6
CO ₂	5.6	5.0	4.8
C in Coal, g/min	0.78**	2.68	2.37
Heat in Coal, kcal/min	7.75	26.6	23.5
<u>Output</u>			
Product Gas, N liters/min	33.0	33.0	32.5
Product Water, N liters/min	27.2	35.9	39.8
Partial Pressures of Materials in Product Gas, atm			
H ₂ O	31.6	36.5	38.5
H ₂	11.4	8.6	6.4
CO	15.2	16.0	16.0
CO ₂	8.3	5.0	5.7
CH ₄	0.2	0.7	0.86
Heat in CH ₄ , kcal/min	1.7	6.7	8.5
Heat in (CO + H ₂), kcal/min	5.5	6.5	8.6
Heat in Total Gas, kcal/min	7.2	13.2	17.1
C in Coal Gasified, g/min	0.1	0.71	1.9
Preformed Methane, %	27	60	56
<u>Yields, Percent C in Coal</u>			
C in CH ₄	12	16	20
C in (CO + CO ₂)	3	-	-
C in Total Gas	15	-	-
<u>Yields, Percent Btu in Coal</u>			
Btu in CH ₄	21	29	36
Btu in (CO + H ₂)	71	24	37
Btu in Total Gas	92	53	73

* Within 40 F of maximum temperature.

** Coal without silica in this test.

TABLE 5. OPERATING DATA AND AVERAGE RESULTS FOR TESTS USING
LIGNITE IN CONTINUOUS FLOW REACTOR WITH SLURRY FEEDING

	CFR Test No.				
	29A	29B	30	31	32
<u>Operating Conditions</u>					
Temperature, F	1740	1740	1740	1740	1740
Pressure, atm	70.0	70.0	72.0	84.0	72.0
Reactor Volume, cc*	274	274	283	300	202
Residence Time, sec	3.0	3.9	3.2	3.9	3.4
<u>Input</u>					
Water, g/min	39.1	37.1	39.6	43.5	37.2
Partial Pressures of Materials in Feed Stream, atm					
H ₂ O	39.1	49.3	40.5	51.0	52.6
H ₂	6.1	4.1	6.2	7.2	3.5
CO	16.8	11.2	17.1	17.3	10.7
CO ₂	5.1	3.4	5.2	5.4	3.1
C in Lignite, g/min	4.70	4.60	4.48	5.05	7.60
Heat in Lignite, kcal/min	43.0	42.0	40.8	46.5	70.0
<u>Output</u>					
Product Gas, N liters/min	53.5	31.0	55.1	48.4	24.8
Product Water, N liters/min	40.2	41.1	40.6	44.9	42.5
Partial Pressures of Materials in Product Gas, atm					
H ₂ O	30.0	39.8	30.6	40.4	45.5
H ₂	15.4	11.8	15.3	17.6	12.0
CO	8.3	9.3	8.2	7.3	3.5
CO ₂	12.1	10.0	13.9	13.8	7.6
CH ₄	1.06	1.19	1.13	1.64	1.96
Heat in CH ₄ , kcal/min	13.4	11.4	13.9	17.2	20.1
Heat in (CO + H ₂), kcal/min	10.0	6.9	9.1	2.7	13.3
Heat in Total Gas, kcal/min	23.4	18.3	23.0	19.9	33.4
C in Lignite Gasified, g/min	1.11	1.30	2.40	1.46	1.27
Preformed Methane, %	63.0	68.0	66.0	88.0	66.0
<u>Yields, Percent C in Lignite</u>					
C in CH ₄	16.3	14.4	17.9	19.5	14.5
C in (CO + CO ₂)	7.2	14.1	35.0	9.5	2.2
C in Total Gas	23.5	28.5	52.9	29.0	16.7
<u>Yields, Percent Btu in Lignite</u>					
Btu in CH ₄	31.2	27.2	34.0	37.0	28.9
Btu in (CO + H ₂)	23.1	16.5	22.3	6.0	19.0
Btu in Total Gas	54.3	43.7	56.3	43.0	47.9

* Within 40 F maximum temperature.

TABLE 6. OPERATING DATA AND AVERAGE RESULTS FOR TESTS USING
LIGNITE IN CONTINUOUS FLOW REACTOR WITH DRY FEEDING

	CFR Test No.				
	33	34	35	36	38
<u>Operating Conditions</u>					
Temperature, F	1720	1750	1725	1780	1770
Pressure, atm	72.0	72.0	70.0	70.0	81.5
Reactor Volume, cc*	242	250	210	452	445
Residence Time, sec	3.4	2.4	4.2	10.4	8.5
<u>Input</u>					
Water, g/min	34.0	55.1	6.0	12.4	16.9
Partial Pressures of Materials in Feed Stream, atm					
H ₂ O	43.3	51.1	11.7	24.8	34.0
H ₂	5.2	3.8	10.7	8.3	8.6
CO	15.6	11.6	32.5	25.3	26.4
CO ₂	4.6	3.4	9.5	7.4	8.0
C in Lignite, g/min	9.70	14.80	17.20	5.90	18.80
Heat in Lignite, kcal/min	90.0	137.5	154.0	53.5	174.0
<u>Output</u>					
Product Gas, N liters/min	41.2	60.2	45.3	37.5	49.2
Product Water, N liters/min	36.9	63.4	5.8	7.4	11.6
Partial Pressures of Materials in Product Gas, atm					
H ₂ O	34.1	33.0	6.9	11.5	15.5
H ₂	13.4	14.8	13.1	16.9	18.0
CO	7.5	6.5	24.9	18.5	19.0
CO ₂	12.6	12.2	14.3	16.0	18.0
CH ₄	2.3	2.66	5.6	2.98	7.24
Heat in CH ₄ , kcal/min	28.3	43.9	39.4	18.1	51.1
Heat in (CO + H ₂), kcal/min	6.3	33.7	4.6	5.6	17.6
Heat in Total Gas, kcal/min	34.6	77.6	44.0	23.7	68.7
C in Lignite Gasified, g/min	3.0	5.90	3.94	2.83	6.76
Preformed Methane, %	85.0	60.5	92.0	81.0	79.0
<u>Yields, Percent C in Lignite</u>					
C in CH ₄	15.4	16.8	12.4	17.5	15.5
C in (CO + CO ₂)	13.9	35.8	10.0	30.5	20.9
C in Total Gas	29.3	52.6	22.4	48.0	36.4
<u>Yields, Percent Btu in Lignite</u>					
Btu in CH ₄	29.7	31.9	24.6	33.9	29.4
Btu in (CO + H ₂)	6.6	26.9	2.9	10.5	10.1
Btu in Total Gas	36.3	58.8	27.5	44.4	39.5

* Within 40 F of maximum temperature.

hydrogen to methane by catalysis. The amount of "preformed methane" is calculated according to the following equation:

$$\% \text{CH}_4^* = \frac{\% \text{CH}_4 \times 100}{\% \text{CH}_4 + 1/4 (\% \text{CO} + \% \text{H}_2)}$$

where

$\% \text{CH}_4$, $\% \text{CO}$, $\% \text{H}_2$ = percent CH_4 , CO , H_2 in product gas by analysis

$\% \text{CH}_4^*$ = percent preformed methane

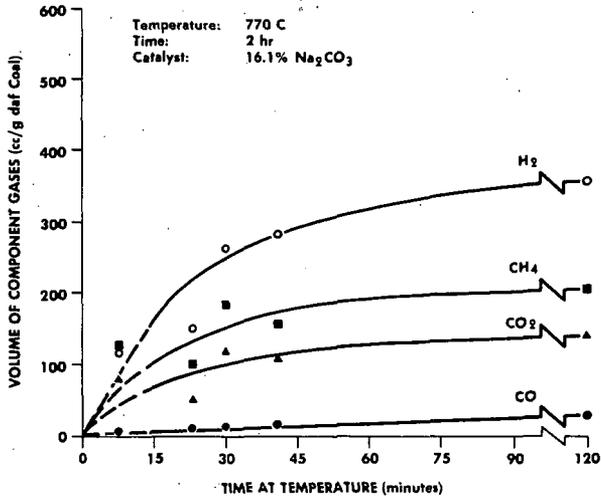
On a volume basis, hydrogen is the main component of the product gas from the direct reaction of steam with coal in the autoclave tests. This is illustrated in Figure 8 which presents data from an experiment at 770 C with a total reaction time of 2 hours.

Over the range of temperature studied, an increase in conversion with an increase in temperature is observed in experiments at both 12 and 120 minutes; and an increase in conversion is observed with an increase in time at the same temperature. This is shown in Figure 9 in which the gas yield, expressed as a function of the Btu content of the coal charged, is plotted versus temperature at the different reaction times. An increase in residence time from 12 to 120 minutes results in an increase in gas yield of about 15 percent of the coal heating value. A similar increase is caused by the addition of sodium carbonate to the coal; however, additional data are needed to establish the full significance of using catalysts.

Over the entire range of experimental conditions covered by these experiments, that is, pressure, 60 to 350 atmospheres; temperature, 730 to 770 C; and, reaction time, 2 to 120 minutes, methane is the main product on a heating value basis. It constitutes more than 90 percent of the total Btu in the gas at the 10 percent conversion level, and it still is more than 70 percent of the total Btu in the gas formed even at 60 percent conversion level. All the data from batch autoclave tests are compared in Figure 10 on the basis of conversion of coal to gas and formation of "preformed methane."

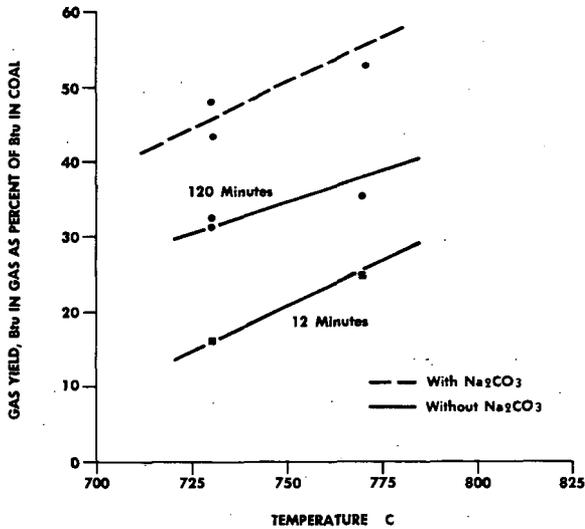
Methane is formed in good yield as well as in high concentration under the conditions of the autoclave tests. However, to attain the same high yields at short residence time as required in a commercial gasifier, the temperatures must be much higher than those explored in the autoclaves. Therefore, the continuous flow reactor was used next to determine the rate of methane formation and to establish the feasibility of using coal entrainment in Stage 2 of the two-stage process.

Data on the quality of the product gas obtained in the continuous flow reactor using both Pittsburgh seam coal and lignite are summarized in Figure 11; in this graph the yield of preformed methane is plotted against conversion expressed on a Btu basis. In addition, the curve for the correlation of the batch autoclave data and the yields used for cost estimating purposes are shown for comparison. On the lower right, a correlation of the results obtained with Pittsburgh seam coal in the presence of silica is given. Lower methane concentrations are indicated than in the autoclave tests.



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Figure 8. Effect of Time at Temperature on Gas Composition in Batch Autoclave Test at 770 C



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Figure 9. Effect of Temperature on Gas Yield without Catalyst in Batch Autoclave Test

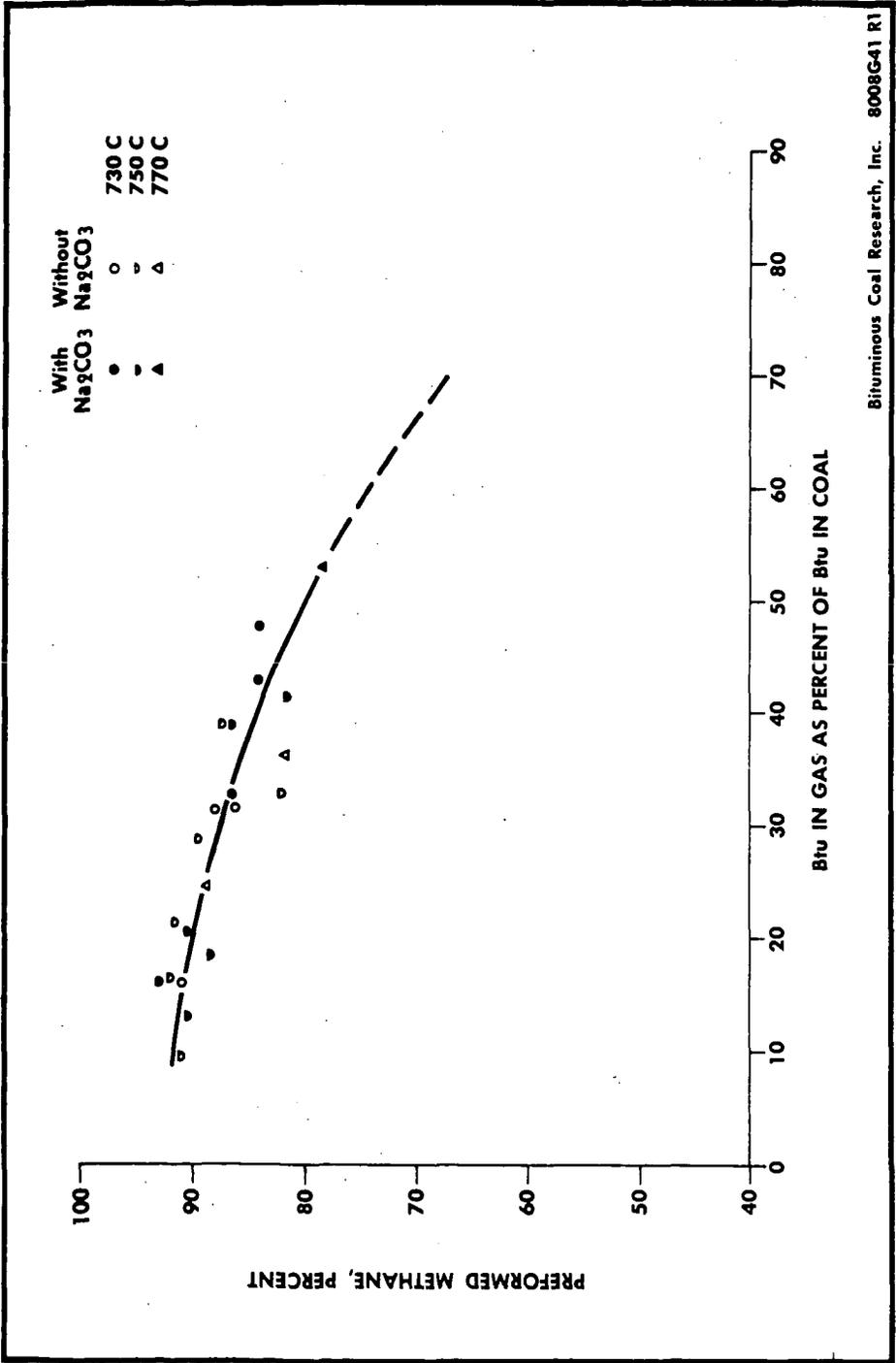


Figure 10. Yields of Gas and Performed Methane in Batch Autoclave Tests

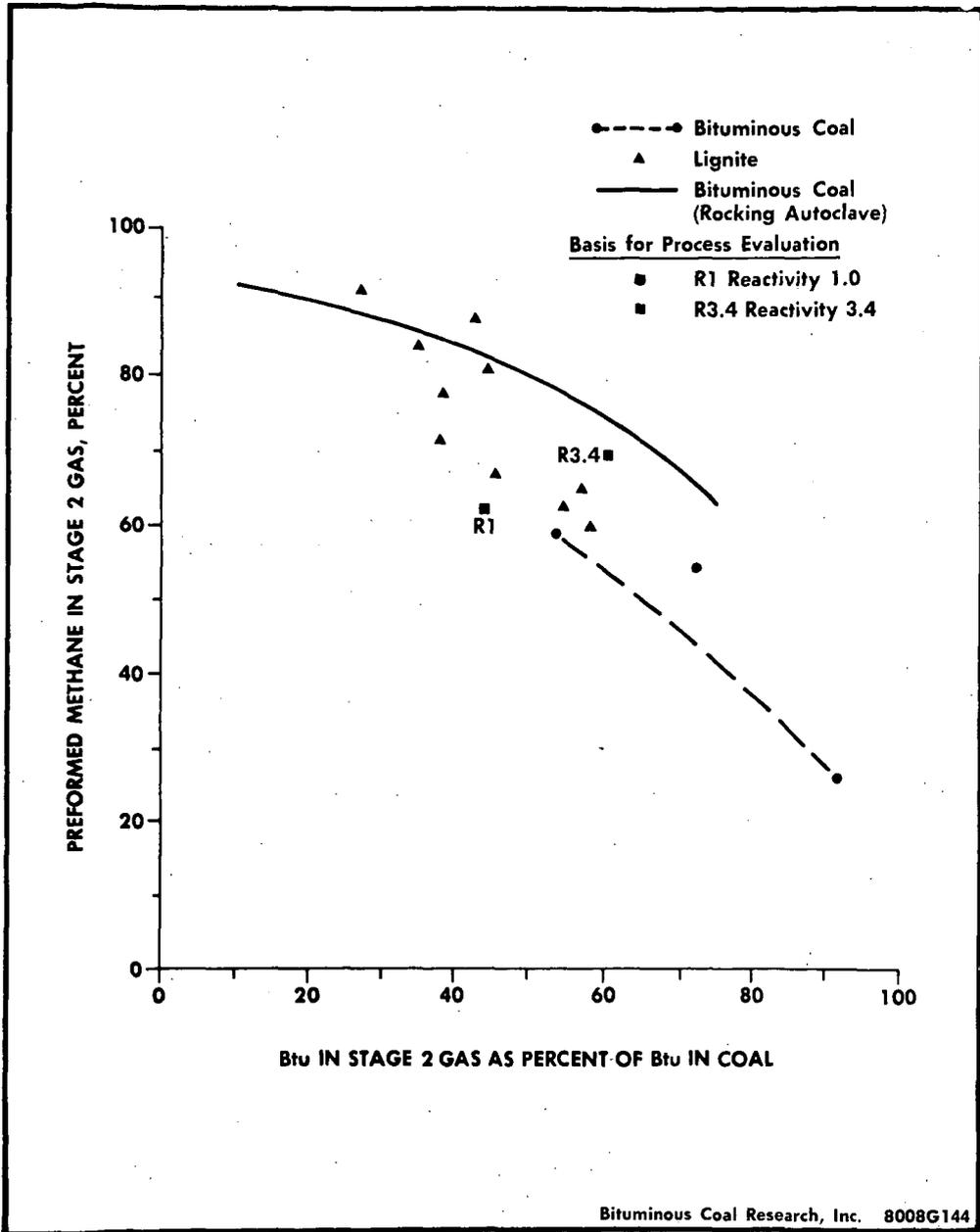


Figure 11. Correlation of Total Gas Yield and Preformed Methane in Continuous Flow Reactor Tests.

Methane concentrations are especially low in those tests in which the preheating of the coal slurry did not lead to complete vaporization of the water. In tests with thermocouples inside the reactor, it was found that the temperature inside the reactor drops considerably below that of the reactor walls under such conditions, and thus would easily cause these low conversions. In later tests with lignite, methane concentrations and conversions were obtained equivalent to those observed in the autoclave tests with bituminous coal.

Experimental results on only the yield of methane in tests in the continuous flow unit are shown in Figure 12; this is a plot of the methane yield, expressed as percent of the calorific value of the coal converted into methane, versus the percent of the Btu in coal converted into gas. The methane concentrations obtained in the flow unit are, as stated above, lower than those in the autoclave tests; consequently, the points in this graph for the continuous flow experiments also lie below the autoclave correlation curve at all levels of conversion. However, the points for the methane yield on a Btu basis are close to those assumed for the cost calculations in the overall engineering evaluation of the process projected to commercial-scale operation.(2)

The wide scatter of points on the Figures 11 and 12 are a reflection of the wide variation in conditions used in the tests, and examination of them reveals certain correlations that merit further consideration and study. For this, the experiments using lignite may be categorized as follows according to the conditions used:

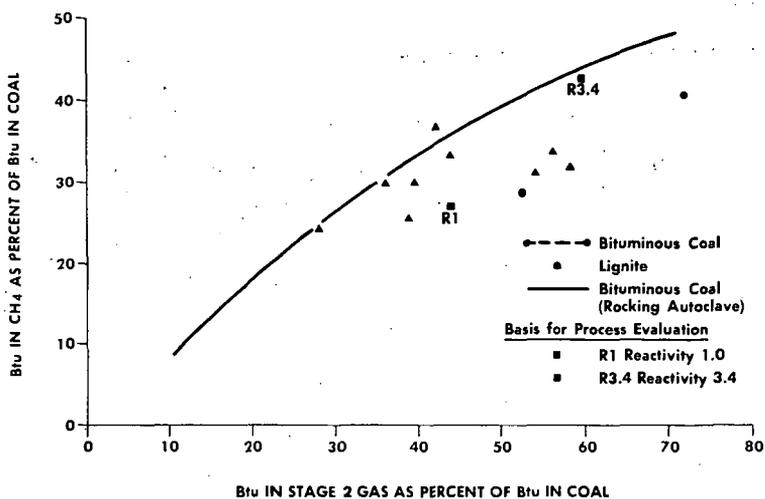
- (a) Less than 3.5 seconds residence at 70 atm and either below or above a peak reaction temperature of 1760 F.
- (b) Same as (a), but more than 3.5 seconds residence time.
- (c) Same as (a), but at 81 atm.
- (d) Same as (a), but more than 3.5 seconds residence time and at 81 atm.

In Figure 13, the rate of formation of methane is shown as a straight line function of the rate of feeding the lignite, and thus as a first approximation independent of other reaction conditions. However, closer examination of the operating conditions for each point on the graph shows that high hydrogen partial pressure (above 15 atm) at the reactor outlet, high total pressure (81 versus 70 atm), and high peak reactor temperature (above 1760 F versus below 1760 F) result in methane formation rates higher than those indicated by the line on the graph. Also data points below the curves are for tests made with hydrogen partial pressures below 13 atm at the reactor outlet.

The effect of hydrogen partial pressure at the reactor outlet (p_{H_2}) on the yield of methane is shown in Figure 14. Except for two points, the correlation is good, showing that increased p_{H_2} results in increased yields of methane.

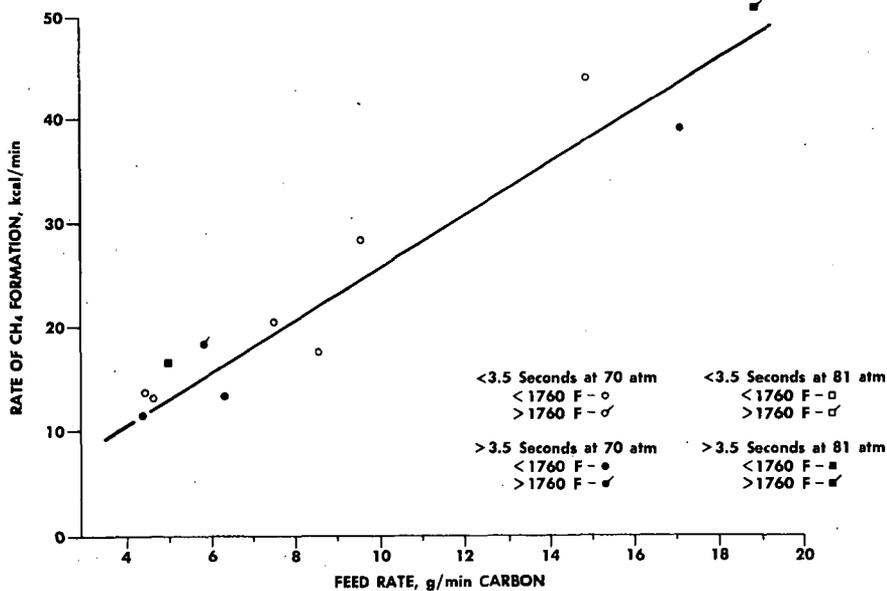
This indicated dependence of methane yield on p_{H_2} leads to a consideration of the factors that affect the hydrogen partial pressure at the reactor outlet. The material balances for the various tests show that the shift reaction is a major source of hydrogen in the product gas. The amount of hydrogen attributable to this source can be calculated from the equation:

$$K = \frac{(H_2 + X)(CO_2 + X)}{(CO - X)(H_2O - X)}$$



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Figure 12. Correlation of Total Gas Yield and Methane Formation in Continuous Flow Reactor Tests



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Figure 13. Effect of Feed Rate on Methane Formation in Continuous Flow Reactor Tests Using Lignite

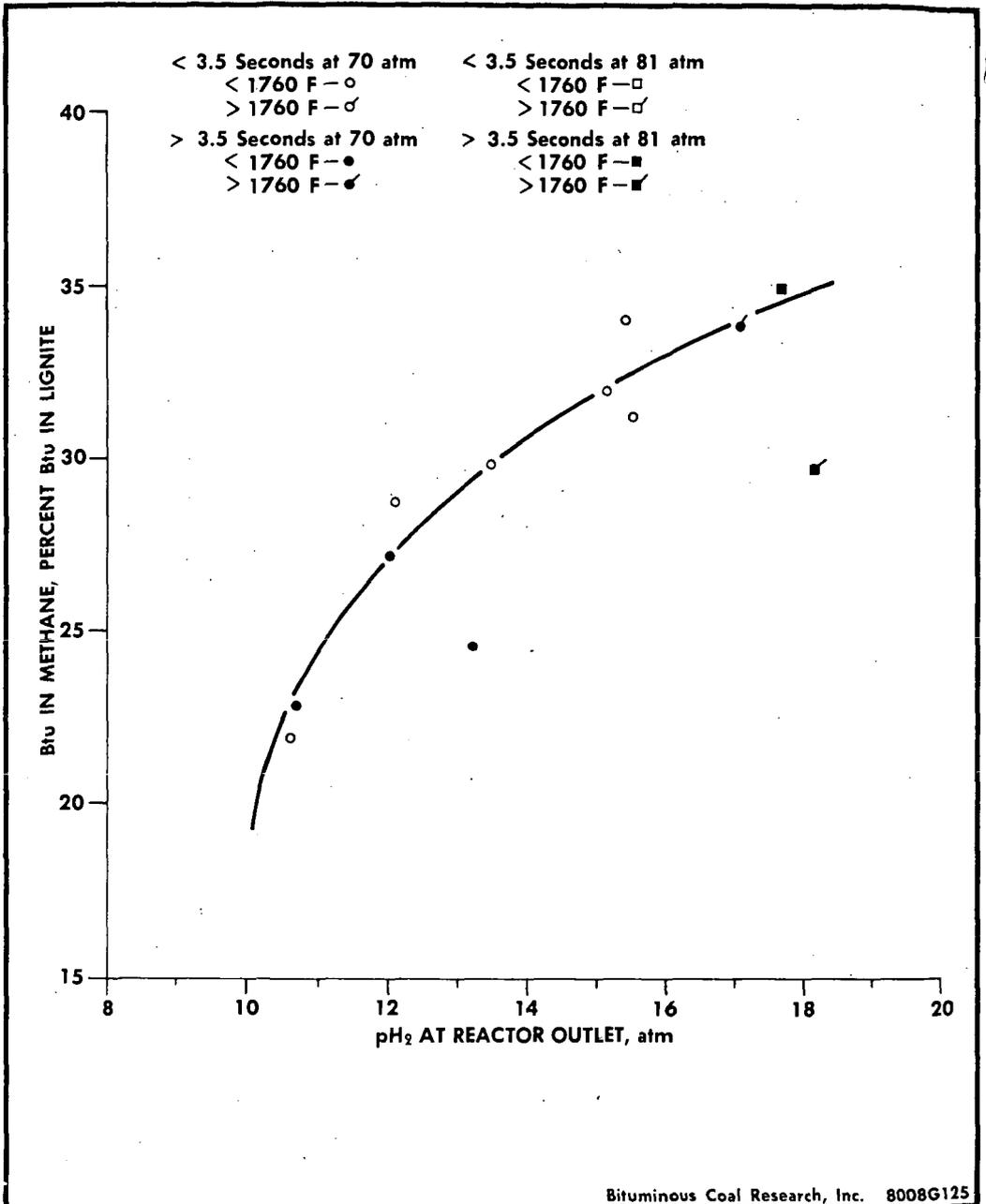


Figure 14. Effect of Hydrogen Partial Pressure at Reactor Outlet on Methane Formation in Continuous Flow Reactor Tests Using Lignite

where H_2 , CO, CO_2 , H_2O are the partial pressures of these gases in the feed stream entering the reactor--where X is the fractional increase or decrease in the partial pressure of these gases due to reaction--and, where K is the equilibrium constant. Solving this equation for X to obtain the amount of H_2 produced by the shift reaction leads to a cumbersome quadratic expression.

For use in evaluating experimental results, this complex quadratic expression may be simplified to $1/2 \sqrt{(CO)(H_2)}$; the total expression for the feed stream composition (E) then becomes:

$$E = H_2 + 1/2 \sqrt{(CO)(H_2)}$$

and is found to correlate well with hydrogen partial pressure at the reactor outlet (pH_2).

The correlation of the yield of methane with E (Figure 15) is not as good as with pH_2 (Figure 14); however, this correlation should prove useful in the evaluation of data from future experiments. Present indications are that inclusion of a term in the expression E reflecting the Stage 1 gas/coal ratio will improve the correlation significantly.

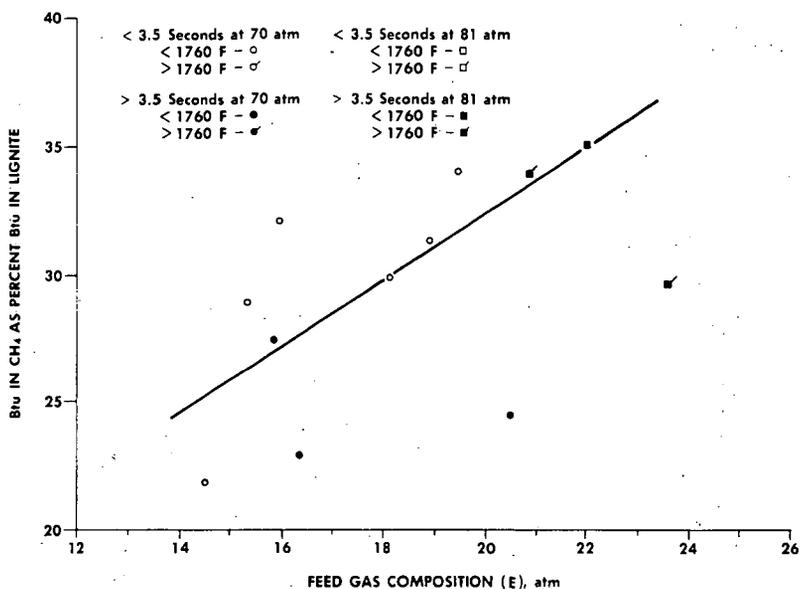
While hydrogen concentration affects mostly the methane yield the concentration of the steam/lignite ratio is most pronounced on the yield of $(CO + H_2)$; this is shown in Figure 16. In spite of the scatter, it is apparent that high steam/lignite ratio favor increased yields of $(CO + H_2)$.

In carbon gasification processes, changes in gasification rate with increased carbon "burn-off" are often observed. The quantity of "Btu in gas as percent of the Btu in lignite" increases with "burn-off"; it is plotted in Figure 17 versus the gasification rate expressed as kcal/hr/kcal inventory. This indicates that experimental conditions that lead to high conversion lead also to high lignite reactivity as expressed by the gasification rate referred to lignite inventory. The points obtained in tests with residence time between 2.3 and 4.2 seconds fall close to the curve; however, to the left of the curve, showing a lower gasification rate, are points for two tests with residence time of 8.5 and 10.4 seconds.

SUMMARY AND CONCLUSION

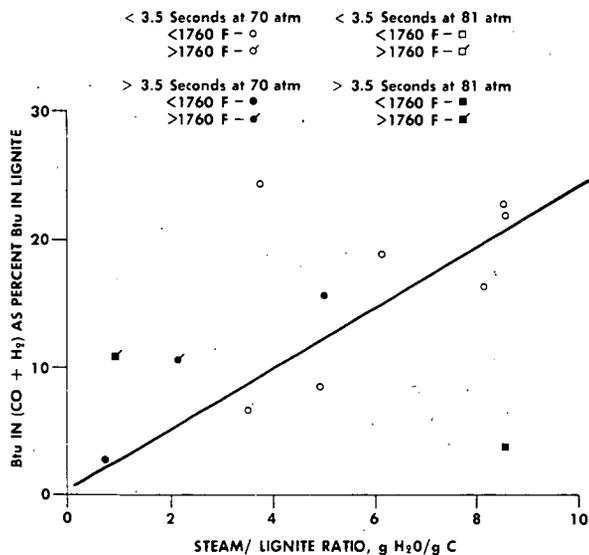
In summary, it can be stated that the experiments in bench-scale equipment have shown that methane is formed from high volatile coals at 70 atm pressure at a rate and in a yield consistent with previous assumptions for the second stage of a conceptual process for gasifying coal.

A more definitive study of the process variables is being planned by operation of a 100 lb/hr internally-heated process and equipment development unit. Shock heating by means of hot Stage 1 gas will produce a well defined Stage 2 reactor volume and a temperature gradient similar to that expected in a commercial plant. A previous economic evaluation of such a two-stage coal gasification process led to a pipeline gas manufacturing cost of about 50¢/M scf.



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Figure 15. Effect of Feed Stream Composition on Yield of Methane in Continuous Flow Reactor Tests Using Lignite



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Figure 16. Effect of Steam/Lignite Ratio on (CO + H₂) Formation in Continuous Flow Reactor Tests

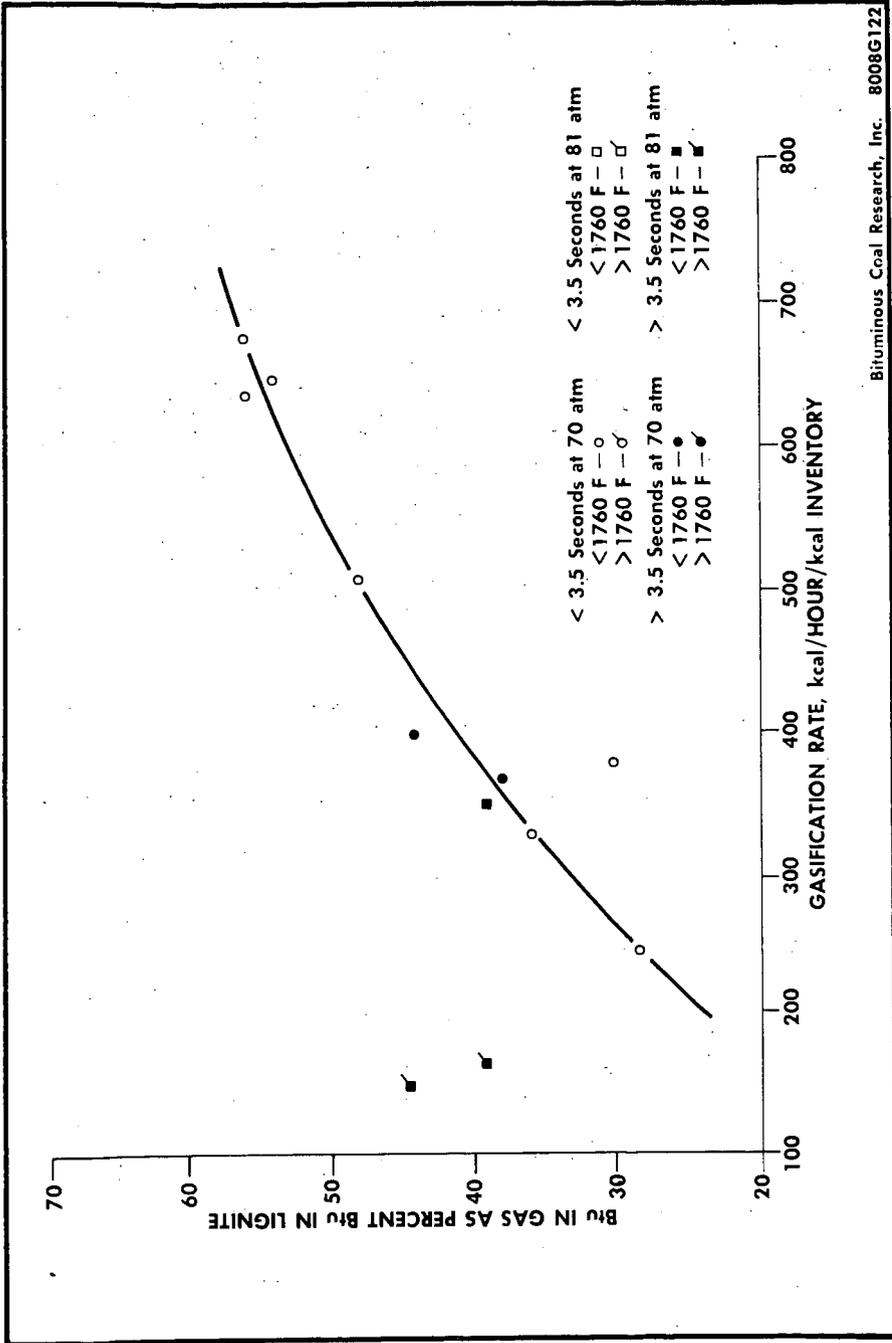


Figure 17. Effect of Conversion on Gasification Rate in Continuous Flow Reactor Tests Using Lignite

ACKNOWLEDGMENT

This paper reports results from a program of research being conducted by Bituminous Coal Research, Inc., with support from the Office of Coal Research, U.S. Department of the Interior, under Contract No. 14-01-0001-324. The authors wish to thank the Office of Coal Research for permission to publish this paper.

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Decaking of Coal in Free Fall

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INTRODUCTION

Most bituminous coals mined near Eastern populous areas are caking. Yet these are the areas which require large quantities of high-Btu pipeline gas. Our object has been to find a practical way to convert these strongly caking coals to noncaking fuel suitable for fixed-bed gasification-- a preliminary step in making pipeline gas. A fixed-bed gasifier applicable to production of synthesis gas containing methane has been used commercially in several parts of the world.

In previously reported experiments we have converted caking coals of 1/8-1/2-inch size to noncaking coal char by treating it for 3 hours in a static bed, ^{4/} coal of 18-100 Tyler mesh for 5 minutes in a fluidized bed, ^{2/} and coal of 4-8 Tyler mesh for 2 seconds in free fall. ^{3/} Nitrogen and carbon dioxide, steam, or a mixture of all three with small amounts of oxygen was the heating and treating gas in these studies.

In recent experimental work we have converted strongly caking bituminous coal from the Pittsburgh-seam of 1/4-3/8 inch size, in addition to coal of 4-8 Tyler mesh, to a noncaking form in about 2 seconds by dropping it through a countercurrent flow of steam containing oxygen. In all cases the treated or decaked coals had a free-swelling index (FSI) of 2.0 or less, which is indicative of a weakly-to-noncaking coal. Furthermore, when the treated coals were exposed to hydrogen at 600° C and atmospheric pressure for 5 minutes they showed little or no tendency to cake.

APPARATUS

The experimental work was done in the pilot plant shown in figure 1; a schematic flow diagram of the system is shown in figure 2. The system contains a steam generator, feed and receiver hoppers, a screw feeder, and a treatment vessel. This vessel, called a treater, is a 2-inch diameter, schedule 80 pipe, 20 feet long, and made of 304 stainless steel. It is surrounded by 16 individually controlled electric heaters that compensate for radiation loss and supply additional heat when needed. The main supply of heat for the treatment is from steam; a little comes from partial oxidation of the coal. Temperature is measured by thermocouples

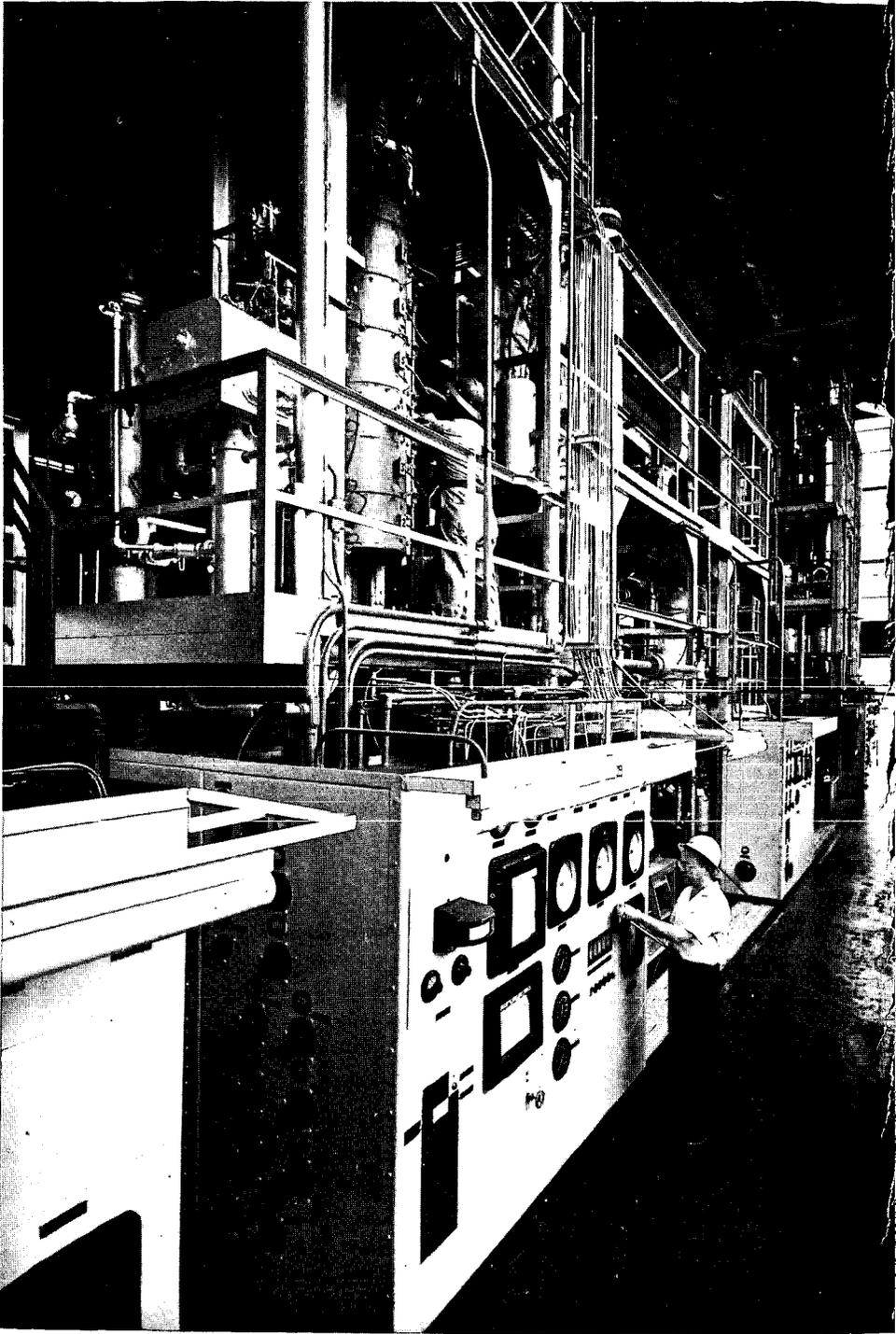


Figure 1. A View of the Pilot Plant for Decaking Coal.

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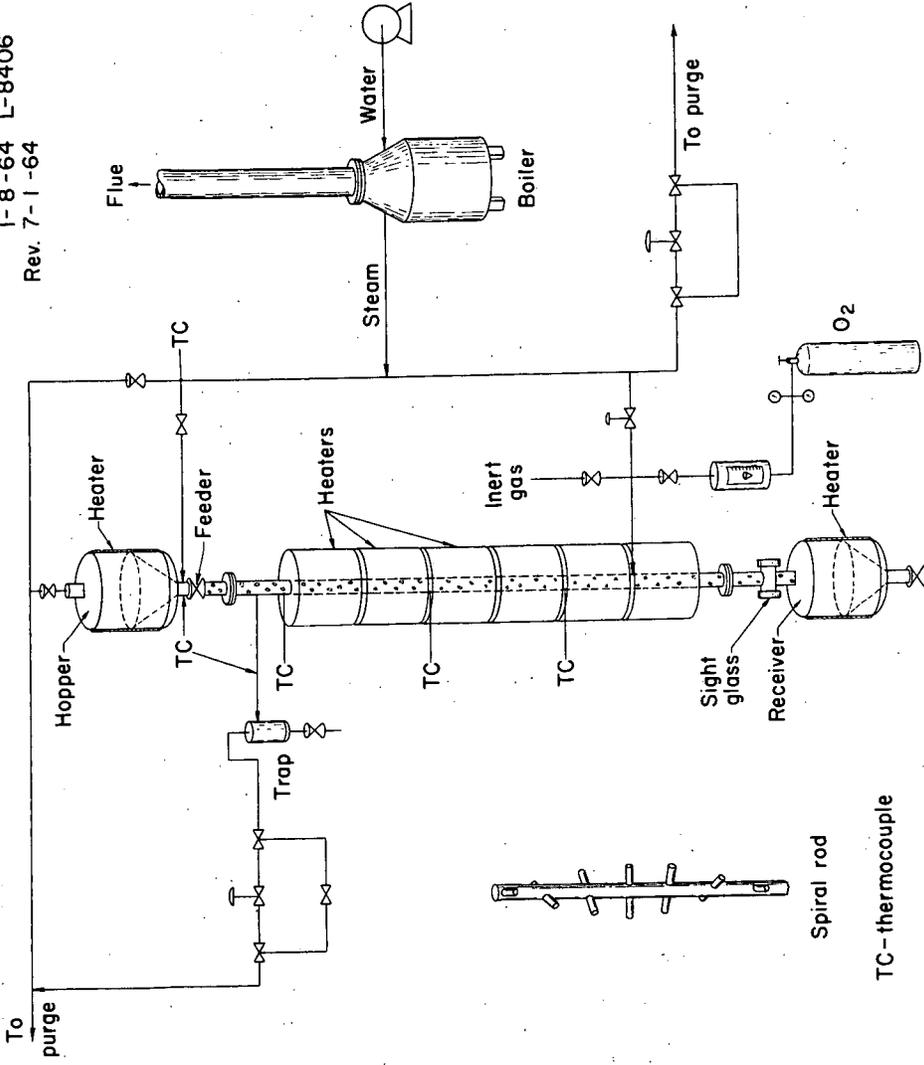


Figure 2. Schematic of Pilot Plant for Decaking Coal in Free Fall.

located at 6-, 12-, and 16-foot levels of the treater. In some early tests a spiral rod, shown in figure 2, was inserted into the treater to increase the coal-to-gas contact time, but coal particles tended to stick to the spiral rod, and it was removed.

Coal

Pittsburgh-seam coal was selected for the tests on account of its commercial importance, its reputation as a typically strong caking coal and easy access at our experimental mine at Bruceton, Pa. The maximum size of the coal treated (3/8 inch) was limited by the inside diameter of the treater (1.939 inches). During treatment the coal tends to become sticky while swelling to about 1-1/2 times its original size.

Procedure

A weighed amount of coal of 4-8 Tyler mesh or 1/4-3/8-inch size was charged to the feed hopper and heated rapidly with steam to just below the softening temperature of the coal, which for Pittsburgh-seam coal is 350° C. This temperature was previously⁴ determined as that temperature at which a fixed bed of coal offered an increase in resistance to gas flow. The heated coal was fed from the hopper at a controlled rate by a screw feeder into the 20-foot long treater where it fell freely through a countercurrent flow of steam containing oxygen to a receiver where it was quenched with inert gas. The inert gas contained about 88 percent nitrogen and 12 percent carbon dioxide. The falling coal was in contact with the steam-oxygen mixture for about 2 seconds. To determine the degree of decaking, the treated coal was exposed to hydrogen for 5 minutes at 600° C. If it did not cake during hydrogen exposure, the decaking was considered successful. Correlation of hydrogen-exposure results with free-swelling indices (ASTM Test D-720-57) indicated that decaked coal produced from coal of initial high FSI values was noncaking during the hydrogen exposure when its FSI had been reduced to 1.5 or less, and only weakly caking when its FSI was 2.0.

Results

Tests 77, 115, 917, and 1028 (Table 1) are typical of experiments performed to date. In test 77, 2 pounds of 1/4-3/8-inch coal was heated to 330° C in 10 minutes with steam. Before the coal could be treated effectively, it had to be heated to just below its softening temperature. During this preheating the coal showed only a loss of moisture. Then it dropped through the 20-foot long treater at a rate of 60 pounds of coal per hour (3,000 lb/hr-sq ft). It fell through a countercurrent flow of steam containing 5.5 mole-percent of oxygen at an average temperature of 680° C and 250 psig. The steam-to-coal weight ratio was 2.0, and the

oxygen-to-coal weight ratio was 0.21. Each coal particle expanded about 50 percent and fissured as shown in figure 3. The treated coal did not cake when exposed to hydrogen for 5 minutes. It had a FSI of 1.0 and was considered decaked. Its volatile-matter content was 24.9 percent.

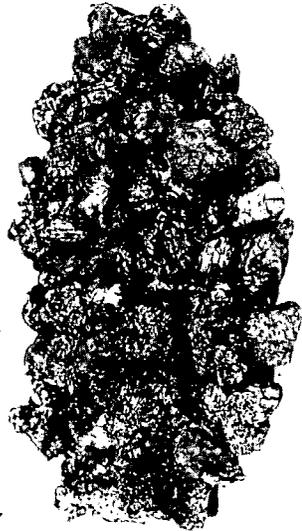
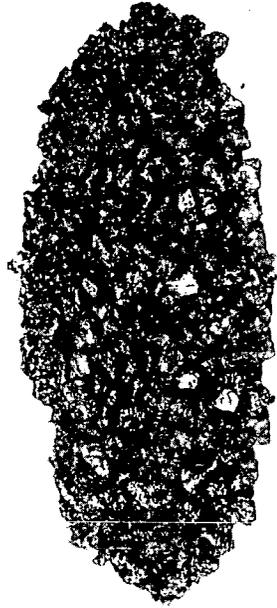
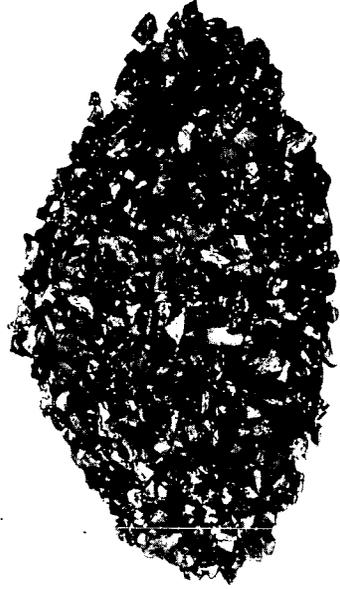
TABLE 1.- Conditions for treating a Pittsburgh-seam coal in free-fall

Test No.	Pressure, psig	Size of coal		Coal feed, lb/hr	Treating gas rate, lb/hr	
		inch	Tyler mesh		Steam	O ₂
77	250	1/4-3/8	-	60	120	12.4
115	300	-	4-8	50	40	10.4
917	300	-	4-8	40	56	10.4
1028	330	-	4-8	70	40	6.0

Test No.	Gas-to-coal ratio, lb/hr		Average reactor temp., °C	Coal heat cycle		Weight loss of coal, pct
	Steam	O ₂		Temp., °C	Time, sec	
77	2.0	0.21	680	330-430	2	15.3
115	0.8	.21	560	310-430	2	4.0
917	1.4	.26	605	310-430	2	10.2
1028	0.57	.12	605	310-430	2	6.9

In test 115, a 4-8 Tyler mesh coal was heated to 310° C in 10 minutes with steam and then dropped through the treater at a rate of 50 pounds of coal per hour through a countercurrent flow of steam containing 12.7 mole-percent oxygen at 560° C and 300 psig. The steam- and oxygen-to-coal weight ratios were 0.8 and 0.21, respectively. The treated coal caked very slightly when exposed to hydrogen at 600° C. It had a FSI of 2.0. Its volatile-matter content was 30.8 percent.

In test 917 the same size coal was similarly heated and then dropped through the treater at a rate of 40 pounds of coal per hour. Steam containing 9.4 mole-percent oxygen flowed countercurrent to the coal at 605° C and 300 psig. The steam- and oxygen-to-coal weight ratios were 1.4 and 0.25, respectively. The treated coal did not cake when exposed to hydrogen at 600° C. It had a FSI of 1.5. Its volatile-matter content was 26.7 percent.



In test 1028, a 4-8 Tyler mesh coal was similarly preheated to 310° C and then fed to and through the treater at a rate of 70 pounds of coal per hour. Steam containing 7.8 mole-percent oxygen flowed countercurrent to the coal at 605° C and 330 psig. The steam- and oxygen-to-coal weight ratios were 0.57 and 0.12, respectively. The treated coal caked only slightly when exposed to hydrogen at 600° C. It had a FSI of 2.0. Its volatile-matter content was 31.9 percent. Analyses of the coals before and after treatment are shown in Table 2.

TABLE 2.- Analysis of coal and decaked coal

Test No.	Proximate, percent			Ash	Ultimate, maf, percent					Free-swelling index
	Moisture	Volatile matter	Fixed carbon		H	C	N	O	S	
Pittsburgh-seam coal	2.0	35.6	54.4	8.0	5.6	84.3	1.7	7.0	1.4	8.0
77	0.3	24.9	67.2	7.6	4.5	85.4	1.7	7.1	1.3	1.0
115	.3	30.8	63.8	5.1	4.6	84.6	1.6	7.5	1.7	2.0
917	.5	26.7	63.8	9.0	4.9	83.9	1.8	8.2	1.2	1.5
1028	.6	31.9	62.3	5.2	4.8	84.2	1.8	7.7	1.5	2.0

DISCUSSION

To effectively alter or destroy the caking property of a strongly caking coal of small lump size in free fall, both treatment temperature and gas composition must be kept within fairly narrow limits. We decaked coal, which had been preheated to 310°-330° C, in a 20-foot treater in 2 seconds at 560°-680° C with steam containing 5.5-12.7 mole-percent oxygen. When either the preheat or reaction temperature was too low, the coal never reached decaking temperature during the 2 seconds that it took to fall 20 feet. Thus the caking property of the coal remained unchanged. When the reaction temperature was too high or the oxygen was insufficient, the coal agglomerated and plugged the treater.

Results with 4-8 Tyler mesh and 1/4-3/8 inch size coals indicate that larger size coal would require higher temperature and more oxygen.

This decaking technique offers promise as part of an integrated coal pretreatment and high pressure steam-oxygen coal gasification process which requires nonagglomerating feed.^{5/} Incorporating decaking with gasification should be simple. Both processes are at the same pressure and use the same gases. The process would be economical because the steam-to-coal weight ratio for decaking is equal to or less

than that required by the commercial Lurgi^{1/} gasifier; also the oxygen-to-coal weight ratio is less than that required in the Lurgi gasifier. Furthermore, the gases and tars produced from volatile matter in the coal during decaking can be fed directly to the gasifier as fuel, thus conserving energy and also solving the problem of effluent or off-gas from the pretreatment. The treater might serve as feed lock hoppers for pressure gasifiers, thus minimizing additional capital investment.

CONCLUSIONS

A pilot-plant study has shown that the caking property of bituminous coal of small lump size can be altered or destroyed by rapidly heating the coal to or through its plastic temperature range while it falls freely through a countercurrent flow of high-temperature steam-containing oxygen. Larger-sized particles require more severe treating conditions as evidenced by a comparison of treatment of 4-8 mesh and 1/4-3/8 inch sizes. Conditions required to decake coal could be met at commercial coal gasification plants with little additional expenditure of energy. However, gasification plants commonly use coal of particle size larger than were used in our study. We were limited to a maximum size of 3/8 inch by the swelling of the coal and the diameter of the treater. A treater of larger diameter would be required to determine the optimum conditions for larger particles.

Because with larger sized particles of 3/8 inch, the size of the expanded coal particle was an appreciable part of the free tube cross section. Additional studies should be made in a larger pretreater to determine optimum conditions of operation.

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COAL PRETREATMENT IN FLUIDIZED BED

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INTRODUCTION

During development of the IGT coal hydrogasification process for making synthetic pipeline gas,^{4,7} the most reactive part of coal for producing methane was found to correspond to its volatile matter. Therefore, research efforts were concentrated on high-volatile bituminous coals. However, when such coals were exposed to an atmosphere of hydrogen at high temperature and pressure, rapid and severe fusion of the coal particles caused caking and agglomeration in the reactor bed. To prevent this agglomeration, the coal must be pretreated to destroy its agglomerating tendency before being used as hydrogasification feed. This program was initiated to 1) establish operating conditions that would produce, with a minimum of pretreatment, a nonagglomerating material that retains maximum volatile matter, and 2) supply sufficient feed for the hydrogasification test program.

BACKGROUND

Much work has been reported on the destruction of caking properties of coal. Low-temperature carbonization, if carried far enough, drives off enough volatile matter so that the remaining char does not agglomerate. Examples of this are Consolidation Coal Company's Montour char used in much of the early hydrogasification work, and the more recent char produced by FMC Corp. by multistage pyrolysis.⁶ However, the Montour char contains only about 17% volatile matter, while the original Montour bituminous coal contained 31%.

Several investigations^{2,3,5} concluded that the agglomerating tendency is destroyed by oxidation of the surface of the coal particles. Treatment in small fluidized-bed reactors with nitrogen, steam, carbon dioxide, or helium^{2,3} all failed to destroy the caking properties. But adding a small amount of oxygen to these inert gases produced nonagglomerating coal. Minimizing pretreatment, therefore, requires minimizing the extent of such oxidation.

Investigators agree that since oxidation is involved, a fluidized bed would be necessary to dissipate the heat released and to maintain a uniform bed temperature without hot spots. However, much of the reported work was conducted in small batch reactors.^{2,3} In a large continuous unit, the uniformity of pretreatment and the residence time required would be quite different than with a batch system. In addition, batch reactors, after being charged, require a time to heat the charge up to the reaction temperature. This makes the residence time at reaction temperature uncertain. A continuous operation avoids this problem, but the backmixing in a fluidized bed leads to short-circuiting of some untreated coal. For this program, a continuous unit capable of fairly high throughput was designed and built.

EQUIPMENT AND PROCEDURE

The pretreater system is shown schematically in Figure 1. Figures 2 and 3 give actual views of some sections. The pretreater is a 10-in. Schedule 40 pipe, 15 ft long, made of A-335 alloy. The upper portion is enlarged for solids disengagement. Heat is supplied to the reactor by external electrical heaters. The bottom 76 in. of the reactor is heated by a 12-kw Huppert furnace. The next 56 in. is surrounded by four zones of heaters, each with four Hevi-Duty heating elements, providing 2.7 kw per zone. The enlarged portion of the reactor is heated by six 1-kw strip heaters. Variable voltage transformers control the power input to the heaters, which are needed primarily at start-up. Once the reaction is initiated, little external heat is required.

A 1/8-in.-thick sintered stainless steel plate serves as the gas distributor. Preheated inlet gas enters a plenum chamber and then passes through the distributor. Offgases pass through a cyclone for fines removal and then to a knockout pot for heavy tar condensation. After the gas is cooled in a water-jacketed condenser, the oils and water are collected. A final venturi water scrubber and cartridge filter remove the oil and tar mist from the gas. The gas is then metered, sampled, and vented.

The coal is crushed in a hammer mill, dried, and then screened to -16+80 mesh. About 500 lb of coal is charged to a hopper which is connected at the bottom to the pretreater by a screw feeder. The feed enters the pretreater about 6 in. above the distributor plate. Feed rates of up to 100 lb/hr can be attained. A 3-in.-diameter overflow pipe controls the bed height. The overflow collects in a receiver and is periodically dumped into drums. Fines from the bed were originally returned to the bed by an internal cyclone with a dipleg sealed in the bed, but tar tended to build up in the cyclone and caused the reactor pressure to increase. At present, a heated external cyclone with a collector pot is installed and operates much more smoothly.

Temperature is measured and recorded by a group of thermocouples in the bed at several levels, and pressure taps at various points indicate the state of fluidization. Both gases and solids are sampled and analyzed.

In addition to chemical analyses, an agglomeration test was performed on each sample to give a quick indication of the degree of pretreatment. This test is a modified version of that reported by Forney, et al.³ A sample in a stainless steel wire mesh boat is placed in a quartz tube heated by an electric furnace. Nitrogen is purged through the system while the temperature is brought up to 1400°F. Hydrogen is then passed through the system for 1/2 hr; nitrogen is again used during cooling. We found that the Bureau of Mines test³ was too mild at 600°C (1112°F) and too strong at 900°C (1652°F), and did not correspond to the hydrogasifier conditions. With our conditions, materials that are free-flowing or slightly crusted would pass through the hydrogasifier without difficulty.

DISCUSSION OF RESULTS

Of the coals to be studied in this project, attention was focused on high-volatile bituminous coal. Most of the work was devoted

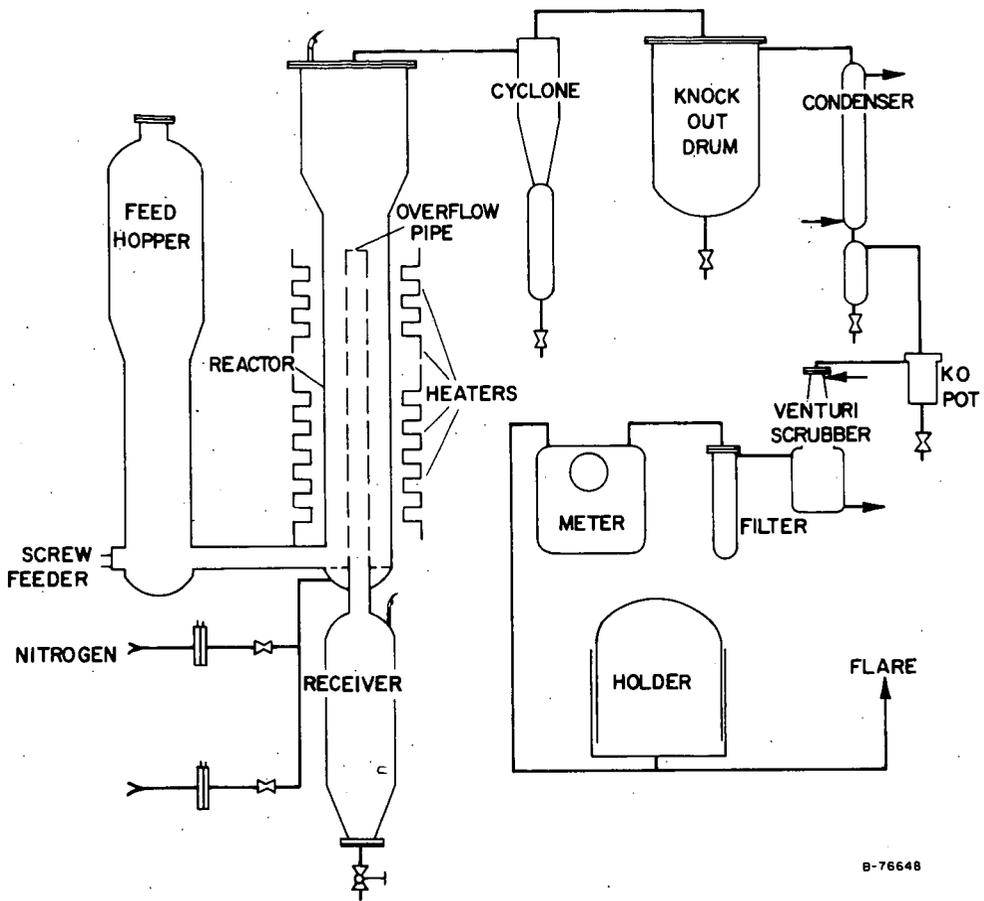


Figure 1. CONTINUOUS-FEED COAL PRETREATMENT UNIT

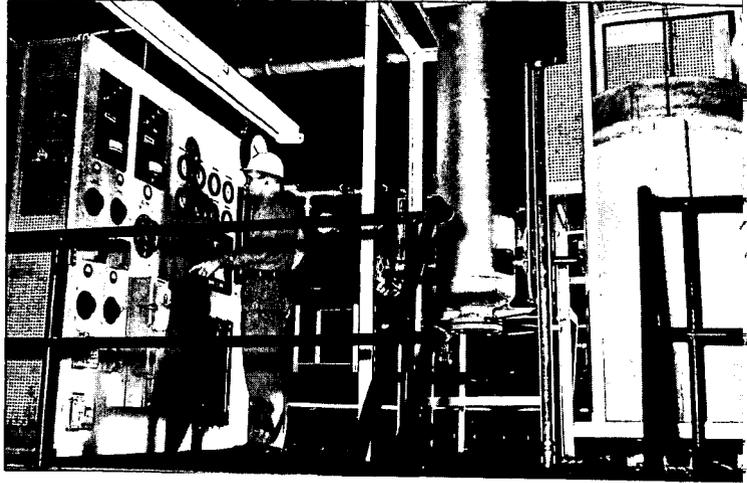


Figure 2. Fluid-Bed Pretreat
Feed Hopper, and Panel Board

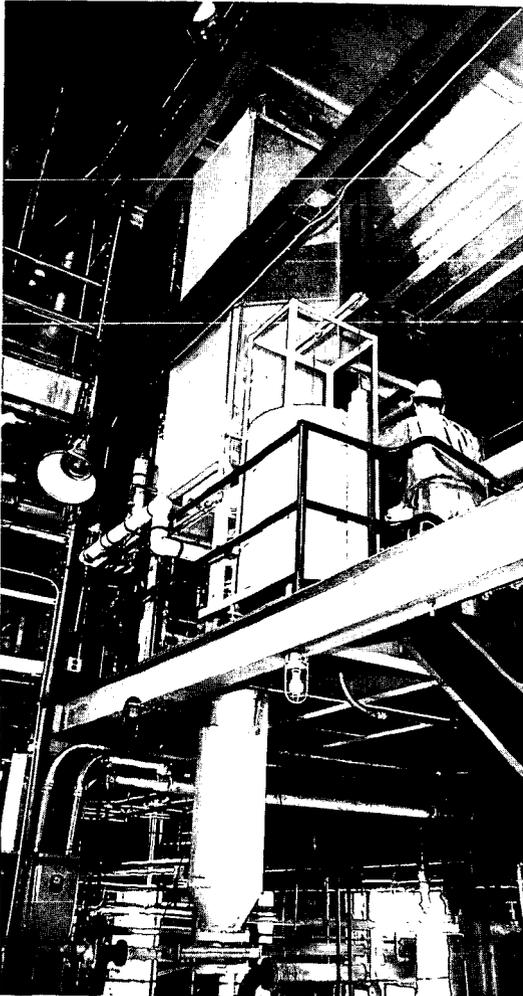


Figure 3. Fluid-Bed Pretreater
Residue Receiver.

to Pittsburgh No. 8 Seam coal from Ireland mine, with some tests on Ohio No. 6 Seam coal from Broken Arrow mine and a highly volatile West Virginia No. 5 Block coal. Proximate and ultimate analyses of these are given in Table 1. Typical run data and product analyses are shown in Table 2.

Besides the visual evaluation from the agglomeration test, the volatile-matter content was chosen as the quantitative index of pretreatment severity. Operating experience with the hydrogasifier showed that minimum coal pretreatment must reduce the volatile matter to 24-26%. Various aspects of pretreatment are discussed in more detail below.

Pretreatment Temperature

Perhaps the most critical operating variable is temperature. The coals tested have a plastic point temperature around 700°F. Below this temperature, we could not produce a free-flowing coal with a 2-hr residence time and a wide range of oxygen concentrations in the pretreatment gas. On the other hand, localized combustion begins at bed temperatures near 775°F. The heat released can not be dissipated by the bed and runaway temperature results. Similar observations were made by Agarwal, et al.¹ in operating a fluidized coal dryer. They noted that combustion occurred on the air distributor deck when stagnant pockets of coal caused by poor gas distribution reached temperatures of about 800°F. Consequently the practical pretreatment temperature range is quite narrow: between 725° and 750°F. The necessary close temperature control can be maintained with a fluidized bed.

Extent of Coal Oxidation

Since pretreatment is an oxidation process, the extent of oxidation is clearly related to the extent of pretreatment. We found that minimum pretreatment required reaction of more than 1.0 SCF of oxygen per pound of coal fed. Figure 4 shows the region of operation in terms of temperature and oxygen consumption required for successful pretreatment. Increasing the oxygen consumption would produce more and more devolatilized coal, which is contrary to our desire to preserve as much volatile matter as possible. Minimum pretreatment, therefore, requires oxygen consumption of 1.0-1.5 SCF/lb coal fed.

We investigated the effect of oxygen concentrations of from 2% to 21% (air) by volume in the pretreatment gas, by blending the correct amounts of air and nitrogen. The oxidation rate was rapid enough to consume all the oxygen fed so no oxygen breakthrough was noted in the effluent gas. Pretreatment is governed by the amount of oxygen reacted rather than by the oxygen concentration. However, at high oxygen concentration, faulty gas distribution leads to localized combustion. Moreover, with the fluidizing velocity essentially fixed by the coal particle size distribution, the coal residence time must be shortened at the higher oxygen concentration to maintain the same oxygen consumption per pound. We found 10% oxygen to be satisfactory. In large-scale operations, such a mixture can be obtained cheaply by adding air to the recycled pretreater effluent in the proper proportions. We are, however, studying the use of air (21% oxygen) in pretreatment.

Coal Residence Time

Because the rate of oxidation is very fast, there is essentially no residence time required for chemical reaction. In a plug flow reactor,

Table 1. ANALYSES OF HIGH-VOLATILE-CONTENT BITUMINOUS COALS TESTED IN PRETREATER

Coal Source	Pittsburgh No. 8		Ohio No. 6		West Virginia	
	Ireland Mine		Broken Arrow Mine		No. 5 Block	
Run No.	FP-44		FP-38		FP-48	
Proximate Analysis, wt %						
Moisture	1.1		2.4		1.1	
Volatile Matter	34.7		40.2		34.6	
Fixed Carbon	52.5		52.5		56.5	
Ash	11.7		4.9		7.8	
Total	100.0		100.0		100.0	
Ultimate Analysis (dry), wt %						
Carbon	71.1		75.3		77.1	
Hydrogen	5.01		5.63		5.25	
Sulfur	4.04		3.53		1.17	
Ash	11.88		5.00		7.86	
Screen Analysis, USS, wt %						
+20	3.2		4.5		4.0	
+30	21.7		23.8		21.0	
+40	24.6		24.3		22.7	
+60	26.4		25.4		24.4	
+80	12.4		11.3		12.6	
-80	11.7		10.7		15.3	
Total	100.0		100.0		100.0	

Table 2 OPERATING DATA AND PRODUCT ANALYSES OF SELECTED PRETREATMENT RUNS

Coal Source	Pittsburgh No. 8				Ohio No. 6			W.Va. No. 5	
	FP-11	FP-14	FP-25	FP-31	FP-33	FP-35C	FP-39	FP-48	
Run No.									
Temperature, °F									
Average	765	666	749	750	749	634	739	738	
Maximum	775	698	757	751	752	648	746	744	
Coal Feed Rate, lb/hr	49	76	37	18	28	56	47	51	
Coal Residence Time, min	53	51	111	228	120	116	98	81	
Feed Gas Rate, SCF/hr	603	590	760	584	630	574	663	619	
Oxygen Concentration, vol %	21.0	9.8	9.8	9.9	10.5	21.0	9.3	5.9	
Oxygen/Coal, SCF/lb	2.6	0.76	2.0	3.2	2.4	2.1	1.3	0.72	
Agglomeration Test Results*	C	C	F	F	F	C	F	PC	
Proximate Analysis, wt %									
Moisture	0.4	0.3	1.0	0.8	0.3	0.4	1.5	0.3	
Volatile Matter	27.4	30.3	24.7	21.3	24.6	36.6	26.6	25.2	
Fixed Carbon	58.5	55.6	65.0	63.8	68.6	58.5	66.9	67.9	
Ash	13.7	13.8	9.3	14.1	6.5	4.5	5.0	6.6	
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	
Ultimate Analysis (dry), wt %									
Carbon	69.8	69.7	72.0	69.2	75.7	74.9	74.9	77.9	
Hydrogen	4.11	4.33	3.81	3.37	3.85	4.91	3.83	4.33	
Sulfur	†	†	†	†	†	†	2.75	0.96	
Ash	13.74	13.88	9.38	14.21	6.56	4.49	5.09	6.59	

* C = caked

F = free flowing

PC = partially caked

† Not analyzed

coal feed rate would depend only on the oxygen input rate and the unit oxygen consumption. Moreover, if gas distribution is uniform, the oxidation would be uniform. In a continuous fluidized-bed reactor, however, residence time must be long enough to minimize the effect of the short-circuiting of untreated feed into the product. The solids mixing in the fluid bed results in a coal particle age distribution, and hence a distribution in the extent of oxidation. Therefore, the average residence time and unit oxygen consumption are greater for a continuous fluidized bed than for a batch unit. Also, gas of higher oxygen concentration cannot be used with a correspondingly higher coal feed rate - and hence shorter residence time - to maintain the same unit oxygen consumption, because shortened residence time leads to increased short-circuiting of untreated coal. If the residence time is not shortened, the volume of bed material required would exceed the capacity of our unit. So most of our work has been done at oxygen concentrations of 10% or less.

Figure 5 shows the region of operation for successful pretreatment in terms of coal residence time and unit oxygen consumption. The two are related in almost direct proportion. Residence times of 1/2 - 2-1/2 hr were investigated. Minimum pretreatment at reasonable feed rates requires coal residence times of between 1 and 2 hours.

Petrographic Study

To better understand the mechanism of the pretreatment reaction, samples of coal before and after pretreatment were mounted and examined petrographically.^a A skin of high reflectance was formed on the coal particles by the surface oxidation. Variation in the skin thickness was not significant, indicating rapid surface reaction and slow penetration below the skin. Short-circuited untreated coal particles can be identified as those without this skin. A free-flowing sample had fewer "skinless" particles than a sample that caked.

SUMMARY

A 10-in.-diameter continuous fluidized-bed reactor system is being operated to produce nonagglomerating coal from high-volatile bituminous coal by mild surface oxidation. Minimum pretreatment is defined by acceptability of the coal as a feed to the hydrogasifier. This corresponds to 24-26% volatile matter in the pretreated coal. The following operating variables, in the order of importance, contribute to satisfactory pretreatment: reaction temperature of 725°-750°F, oxygen reacted/coal feed ratio of 1.0-1.5 SCF/lb, and a coal residence time of 1-2 hours.

ACKNOWLEDGMENT

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COAL AND CHAR TRANSFORMATION
IN HYDROGASIFICATIOND. M. Mason
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INTRODUCTION

In the present IGT hydrogasification program we have undertaken a study of the petrographic and physical properties of the coals used and the chars produced in the various stages of the gasification process. In the past, we have attempted to study the kinetics and operation of the system without knowing what was really happening to the coal. The usual chemical analyses were conducted, but the results fell far short of indicating what was occurring within the individual coal particles. Also we believed that the identification of what made coal desirable for gasification might hinge on more than the usual coal analysis. We therefore started a study of the petrographic and physical properties of coals and chars with two objectives:

1. To find out as much as possible about what happens to the coal and how it behaves in the process.
2. To develop a correlation between the petrographic properties of coals and their suitability for hydrogasification.

Changes in the process concept as it is developed add to the complexity of the second objective. For example, if pretreatment becomes unnecessary as a result of process improvements, the assessment of a coal's suitability may be substantially modified, as will be shown in this paper. The work reported here applies mainly to the first objective, although it provides a background for the second.

For the process study, seven coals ranging in rank from low-volatile bituminous to lignite have been selected. (Progress of this work is reported in another paper of this symposium.) Of these, two strongly caking coals - Pittsburgh No. 8 and Ohio No. 6 seams - have been selected for the initial and most extensive hydrogasification study because they are the most difficult to process. The work reported here is limited to the Pittsburgh No. 8 coal.

The hydrogasification process consists of three stages that are successive with respect to the coal:

- Pretreatment to destroy the agglomerating power of the coal.
- First-stage hydrogasification, at 1200° to 1300°F, with pretreated coal as feed.
- Second-stage hydrogasification, at 1700° to 2000°F, with first-stage residue as feed.

The resultant chars from each of these stages as well as the initial coal feed have been examined.

PROCEDURES

Petrography

Petrographic work was done with a Zeiss Universal microscope. A 40X Antiflex objective and 12.5X Kpl eyepieces were used for maceral analysis. Reflectance was determined at a wavelength of 548 millimicrons, essentially as described by Schapiro and Gray⁵ and by Harrison.⁴ A 40X, 0.85 NA achromat "Aufl POL" objective and the same kind of eyepiece as above were used. The aperture in the eyepiece restricted the field to about a 2.5-micron diameter. The Photovolt 520M photometer was modified so that the recorder signal was obtained from a 2000-ohm precision potentiometer. A switch served to connect either the potentiometer or the photometer output meter to the cathodes of the two (reference and signal) tubes of the cathode follower circuits.

Glass standards obtained from Bituminous Coal Research, Inc., were used for reflectance determinations below 2%. For reflectance above 2%, a brilliant-cut diamond was used as a standard.

The fragile, hollow particles of our pretreated coal and hydrogasification residues were crushed and shattered when mounted in epoxy resin by the mounting method usually used for coal, where hydraulic pressure is applied to impregnate the coal. An apparatus and procedure for vacuum mounting was developed which will be described in a later publication.

Particle density was determined by Ergun's gas flow method.² The method was shortened by making measurements with only three rates of flow on each of two bed densities. The estimate of the standard deviation from 21 duplicate determinations was 7%.

True density was determined by helium displacement in a Beckman air pycnometer.

Feed Coal and Pretreatment

The Pittsburgh No. 8 coal was obtained from the Ireland mine of the Consolidation Coal Company. Proximate, chemical, sieve, and maceral analyses of the feed in a typical pretreatment run are given in Table 1.

Table 1. TYPICAL ANALYSES OF IRELAND MINE COAL
FED TO PRETREATER

<u>Proximate Analysis, wt %</u>		<u>Ultimate Analysis (Dry Basis), wt %</u>	
Moisture	0.9	Carbon	67.6
Volatile Matter	32.7	Hydrogen	4.62
Ash	14.1	Sulfur	4.33
Fixed Carbon	52.3	Nitrogen	1.18
Total	100.0	Ash	14.22
		Oxygen (By Difference)	8.05
		Total	100.00

Table 1. TYPICAL ANALYSES OF IRELAND MINE COAL
FED TO PRETREATER (Cont.)

<u>Petrographic Analysis, vol %</u> (Mineral-Matter Free)		<u>Sieve Analysis, USS, wt %</u>	
Vitrinite	88	20	3.7
Exinite	2	-20 + 30	22.4
Resinite	(<1)	-30 + 40	24.8
Fusinite	1	-40 + 60	25.5
Semifusinite	4	-60 + 80	11.7
Micrinite	5	-80 + 100	5.2
Total	100	-100 + 200	4.3
		-200 + 325	1.1
		- 325	1.3
		Total	100.0

The important petrographic characteristics of the coal are the content of: 1) exinite, the group of macerals having the lowest reflectance and highest hydrogen content, 2) vitrinite, the component comprising the bulk of the coal and having an intermediate reflectance and hydrogen content, and 3) inert or semi-inert components having a high reflectance and low hydrogen content. Variation of most of these components in the Pittsburgh seam can be inferred from petrographic analysis by the Bureau of Mines, though these components are reported with a different nomenclature.³

Pilot plant pretreatment of the coal to destroy its agglomeration power consists of treating the crushed coal with nitrogen-diluted air in a continuous, single-stage fluid bed at 700° to 800°F. The most striking feature of the pretreated coal particles (Figure 1) is that many have been inflated to thin-walled hollow spheroidal forms. Because of the mixing in the fluid bed and resulting variations in particle residence times, the extent of modification varies greatly from particle to particle. A few have a reflectance as low as that of the original coal and appear to be unchanged, with exinite still present in attrital areas. Appearance of vesicles, disappearance of exinite, and increase in the reflectance occur as the pretreatment progresses. Micrinite becomes difficult to distinguish. An outer zone of reflectance greater than that of the interior appears on most particles. The high reflectance of this skin is attributed to reaction with oxygen; increased reflectance in the mass of the particle may be caused only by carbonization. Reflectance of the skin ranges from 2 to 2.6%; reflectance of the interior ranges from about 0.8%, as observed on the vitrinite of the original coal, up to about 2%. The skin extends into cracks and is present in the interior of some vesicles, though usually with reduced thickness.

A quantitative measure of the swelling during the various stages is given by the average porosity determined for two sieve fractions: 66% on the -30+40 mesh fraction, and 59% on the -60+80 mesh fraction (Table 2).

Hydrogasification Residues

Residues from first- and second-stage runs that are believed to represent typical conditions for the integrated process were chosen for intensive study. In the first-stage run the reactor temperature

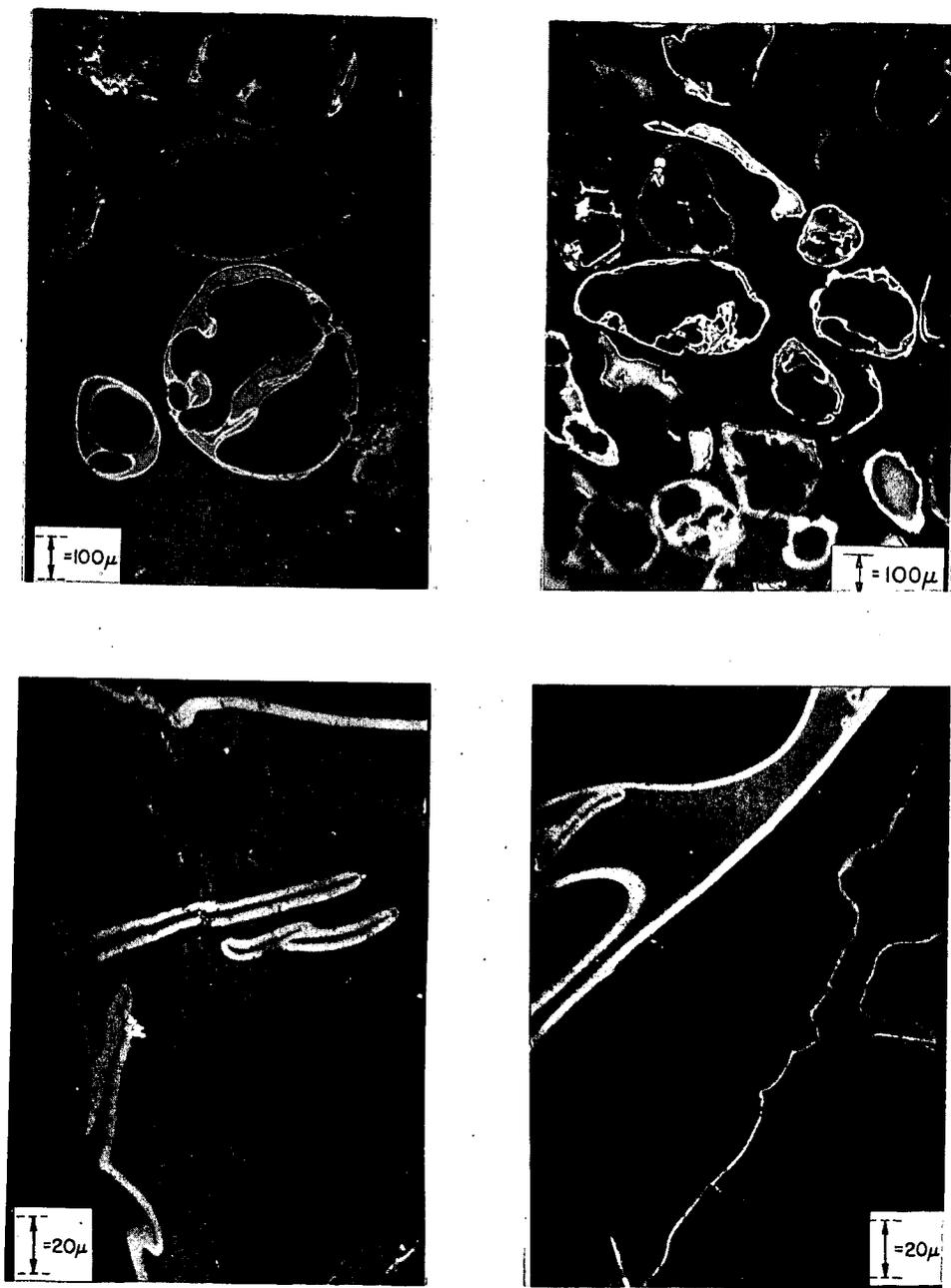


Figure 1. PRETREATED COAL

Table 2. PARTICLE AND TRUE DENSITIES OF
HYDROGASIFICATION FEED AND RESIDUE

Sample	Sieve Size, USS	Particle Density, g/cc	True Density, g/cc	Porosity, %	Ash Content (Moisture- Free), wt. %
Pretreated Coal	-30+40	0.51	1.52	66	13.7
	-60+80	0.63	1.53	59	15.6
Residue, 1st-Stage Hydrogasification	-30+40	0.48	1.80	73	17.3
	-60+80	0.54	1.77	70	19.1
Residue, 2nd-Stage Hydrogasification	-30+40	0.69	2.10	67	33.0
	-60+80	0.95	2.64	64	54.2
Residue, Free-Fall Hydrogasification	-30+40	0.26	2.13	88	--

averaged 1205°F, and the pressure was 1030 psig. About 21% of the pretreated coal (MAF) was gasified. In the second-stage run the temperature averaged 1825°F, and the pressure was 1023 psig. About 52% of the feed was gasified, equivalent to 41% of the pretreated coal.

In a petrographic examination of the first-stage residue no trace of the high-reflectance skin that is conspicuous in the pretreated coal was present in any particle (Figure 2). Occasional particles of the second-stage residue had a dark skin (Figure 3). Kinship of this dark skin with the pretreatment skin was evident from their similarity in form and in pattern of occurrence, particularly in cracks and around vesicles. While the contrast gives an appearance of darkness to this skin, measurements showed that the reflectance of this "dark" skin was actually greater than that of the skin of the pretreated coal. Evidently the reflectance of the substrate has, during the second stage, increased more rapidly and become greater than that of the skin.

Particles from both first- and second-stage runs showed great variation in both reflectance and structure. Reflectance of the first-stage residue ranged from 2.5% to 7.2%, of the second-stage residue from 3.5% to 8.6% (Figure 4). Some particles appear unchanged in structure from the pretreated coal. In others, additional vesicles, particularly small ones, have formed. In some of the particles the vesicle walls are extremely thin, or have partly disappeared to leave only a skeleton structure. In these highly inflated particles the exterior wall frequently appears more substantial than the interior vesicle walls. This may be an effect of the pretreatment skin.

Particles from a run in which untreated coal was fed were also examined. This coal was from Pittsburgh No. 8 seam but from a different mine - Consolidation Coal Company's Montour 4 mine. The hydrogasification reaction was conducted entirely in 18 feet of free fall. The run could not be completed because of agglomeration of coal in the feed tube and in the reactor. However, the structure of single particles recovered from the base of the reactor is of interest (Figure 5). They are much more uniform in appearance and reflectance than residues from runs with pretreated coal. Almost all of the particles are filled with small vesicles whose walls are perforated. The exterior walls sometimes appear thicker than interior walls, resembling, to some extent, the pretreated coal residue. However, the free-fall particles show numerous exterior wall perforations that are absent in the pretreated coal residue. Also, the particle density and porosity (Table 2) show that the particles have, on the average, swelled much more than pretreated coal.

DISCUSSION

The necessity for pretreatment strongly affects the characterization of high-volatile bituminous coal for hydrogasification. From previous work it is well known that high hydrogen-to-carbon ratio, low rank, and high-volatile matter are conducive to high reactivity and yield in hydrogasification. It is also well known that the reflectance of the vitrinite in a coal is a good indicator of its rank and volatile matter content. Thus, if pretreatment were not necessary, both high exinite content and low reflectance of the vitrinite would be very desirable. However, with the present degree of pretreatment in which

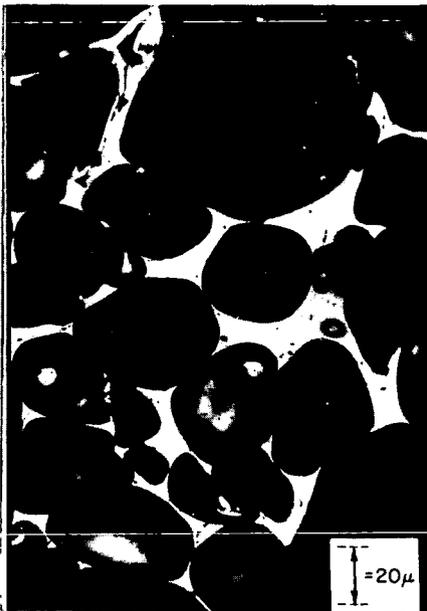


Figure 2. RESIDUE FROM FIRST-STAGE HYDROGASIFICATION

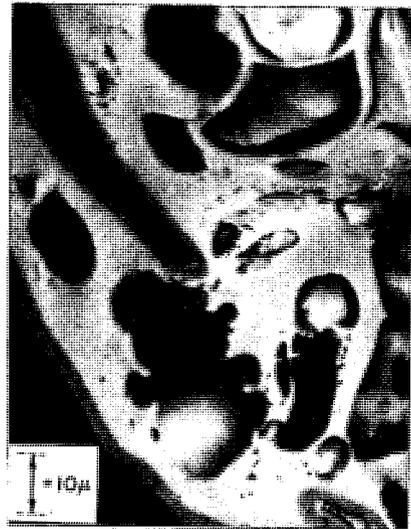


Figure 3. RESIDUE FROM SECOND-STAGE HYDROGASIFICATION

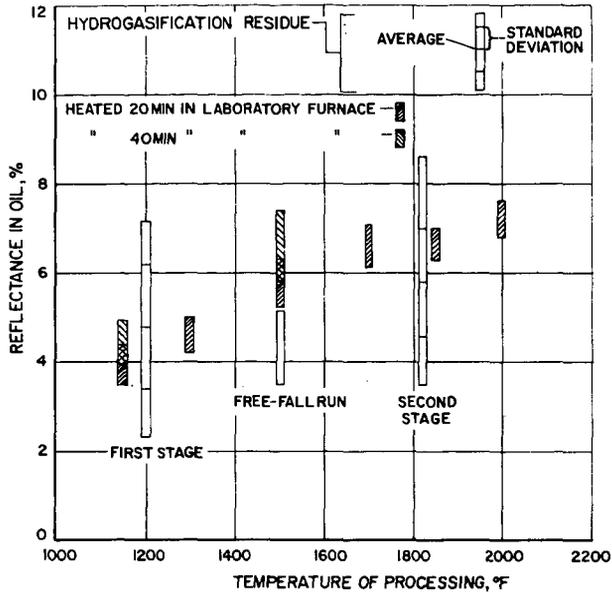


Figure 4. REFLECTANCE OF HYDROGASIFICATION CHARS

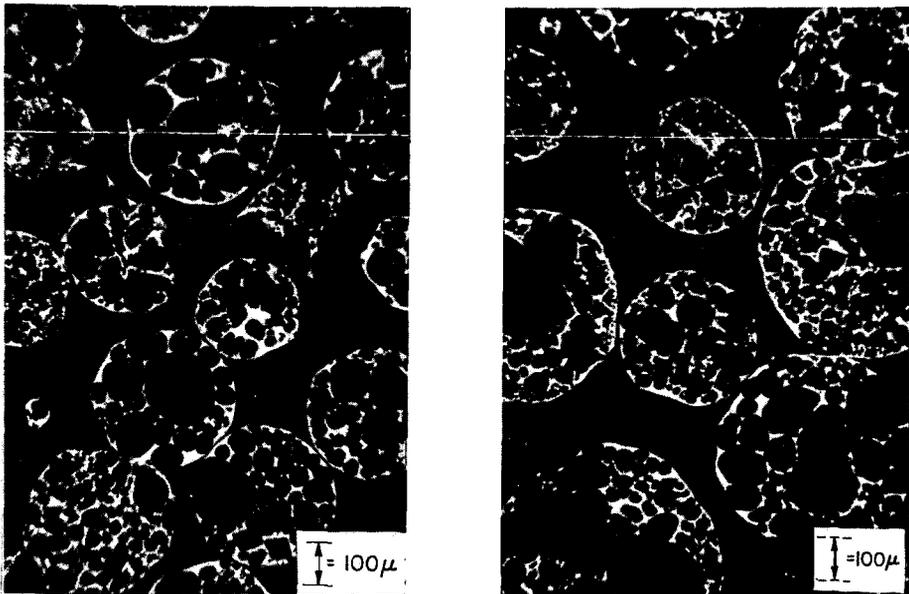


Figure 5. RESIDUE FROM FREE-FALL HYDROGASIFICATION

exinite is almost entirely destroyed, this component is of little value. Similarly, decrease of reflectance of the vitrinite below a yet undetermined level is also of little advantage, because the excess volatile matter is removed in the pretreatment. Thus our second objective - the characterization of coal with respect to its suitability for hydrogasification - is highly dependent on process development in this area. There is some likelihood that in a large commercial plant pretreatment may be avoided.

Pretreatment affects the process in other ways. Sieve analyses of residues from the first stage of hydrogasification show no increase (sometimes a small decrease) in average particle size; thus, essentially no additional swelling of the coal particles occurs in this stage, although the rate of heating is probably as high and the loss of volatiles more than in pretreatment. We attribute the dimensional stability of the particles to rigidity of the pretreatment skin. A few particles that escaped substantial pretreatment probably swell, but this may be balanced by attrition and gas-solid reaction on the exterior surface of the particles. Later runs with less severely pretreated coal show that additional swelling does occur in this stage. This is advantageous because the larger particles present a greater amount of easily accessible surface for reaction. Also, they settle or fall more slowly in free fall, thus providing a longer reaction time for such a stage.

The first-stage residue shows an increase in average porosity (Table 2), which we attribute to gasification of coal in the interior of the particle.

In the second stage of hydrogasification, particle size of the char decreases several percent. We attribute this mainly to attrition, although there may be some decrease in average diameter by way of gasification reactions on the exterior surface. Decreased porosity (Table 2) is attributed to attrition of char particles, which leaves a greater proportion of low-porosity shale particles.

The particle-to-particle variation of the residue in structure and reflectance is of interest because it probably indicates variation in reactivity. The possibility that the subclass of vitrinite in the original coal may have an effect has been considered. There is the well-known differentiation between telenite and collinite. Brown, Cook, and Taylor have suggested a different subclassification: attrital and nonattrital vitrinite.¹ However, many of our coal particles are not composed of a single subclass, while single residue particles are rather uniform in both structure and reflectance. Thus it appears that the history of the particle in the process is a likelier source of the observed variation, although the vitrinite subclass may have a minor role. Structural variation can easily be explained on the basis of variation in volatile matter content of the pretreated coal, and perhaps also in variation in the thickness of pretreatment skin.

The variation in reflectance is more difficult to explain if it is assumed that a particle's reflectance should be a function of its temperature-time history only. The reflectance variations among residue particles of the three hydrogasification runs that have been discussed are shown in Figure 4. For comparison we also show the reflectance of pretreated coal heated at different temperatures for 20 minutes and 40 minutes. The residues from the two moving-bed hydrogasification runs show much wider variation than either the heated coal or

the residue from the free-fall hydrogasification run. The bed temperature, as measured by internal thermocouple, differed by less than 100°F from the average reactor-wall temperature (the normal or reported one) throughout the 36-minute residence of the coal. However, the temperature of individual particles may rise substantially above the bed temperature, because of the heat evolved in the reaction. No explanation of the low reflectance values is available yet.

ACKNOWLEDGMENT

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THE GASIFICATION OF COAL IN A SLAGGING PRESSURE GASIFIER

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INTRODUCTION

In 1955 The Gas Council, Midlands Research Station at Solihull, began to be actively concerned in the development of a fixed bed slagging gasifier as a possible means for providing the gas industry with large gasification units to gasify a wide range of solid fuels, at high efficiency and low cost. A lean gas with a low carbon monoxide content, to be enriched with hydrocarbons to a calorific value of 500 Btu/ft³, was required. At this time the Lurgi process was well established in many parts of the world, but it used an excess of steam in the steam oxygen mixture supplied to the gasifier to prevent clinker formation in the fuel bed. As a result it was desirable to use coal of a high ash fusion temperature, and the comparatively small steam decomposition in the short contact time in the hot gasification zone limited the throughput of the gasifier and produced large volumes of phenolic liquor with its attendant disposal problem. It appeared then that better performance could be achieved by increasing the hot zone temperature of the gasifier and operating under slagging conditions.

The essence of slagging gasification is that the steam supplied per unit volume of oxygen is only that required for gasification. Under these conditions temperatures some hundreds of degrees centigrade above the fusion point of the ash are generated at the steam oxygen inlet, and the ash fuses to a liquid slag. Certain advantages follow from this, including high thermal efficiency, high throughput, a choice of fuel unrestricted by low ash fusion temperature or reactivity, and the absence of a mechanical grate. Gasification under slagging conditions does, however, introduce the hazards of high temperatures at elevated pressures.

The first slagging gasifier erected at Solihull was operated on coke at 5 atm. pressure and was used to make an assessment of the material requirements for gasification, and to investigate methods of controlling slag flow and removing slag from a pressure system⁽¹⁾. A feature of this gasifier was a flat-bottomed hearth with a side slag outlet consisting of a ¼ inch silicon carbide tube 30 inch long. Frequent blockages of the slag outlet were experienced due to the high heat loss from the slag, until an intermittent system of tapping was developed. Slag was allowed to accumulate in the hearth by directing up the tap tube hot combustion gases from a tunnel burner, and was then run off at a high rate by deflecting the burner and applying a differential pressure across the hearth. It was considered that this system of operation justified further development, but the side offtake was not satisfactory. The gasifier was therefore redesigned to take a new hearth with a short water-cooled slag tap at the centre, and was rebuilt together with the necessary auxiliary plant to provide for operation on bituminous coal at 25 atm. pressure and a gas output of 5 mill. ft³/day⁽²⁾.

DESCRIPTION OF PLANT.

Details of the gasifier and the gas cooling plant are shown in Fig. I. The fuel bed, 3 ft. diameter by 10 ft. deep, was contained within a refractory lined pressure vessel, at the top of which was mounted a water-cooled stirrer to break up any agglomerations in the fuel bed. Coal premixed with a suitable flux entered the gasifier through the fuel lock hopper, flowed by gravity through the stirrer unit, and was distributed over the top of the fuel bed as the stirrer rotated. The fuel capacity within the stirrer unit was just sufficient, when operating at the designed load, to ensure that the feed was maintained to the fuel bed during the period that the lock hopper was being recharged. Coal moved down the gasifier as it was continuously gasified by the steam oxygen mixture that was injected into

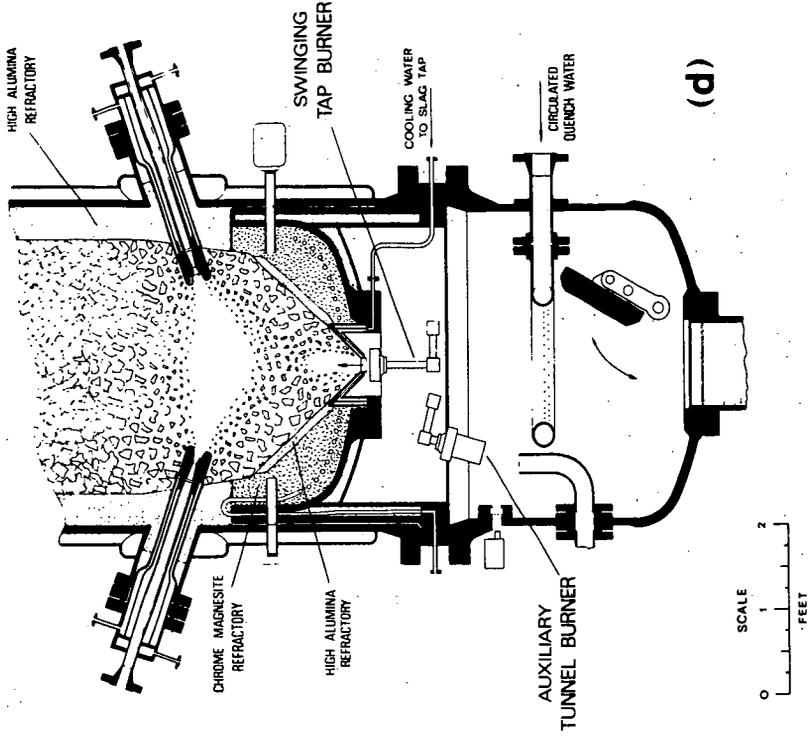


FIG. 2
Cross-Section of the Hearth and Quench Chamber

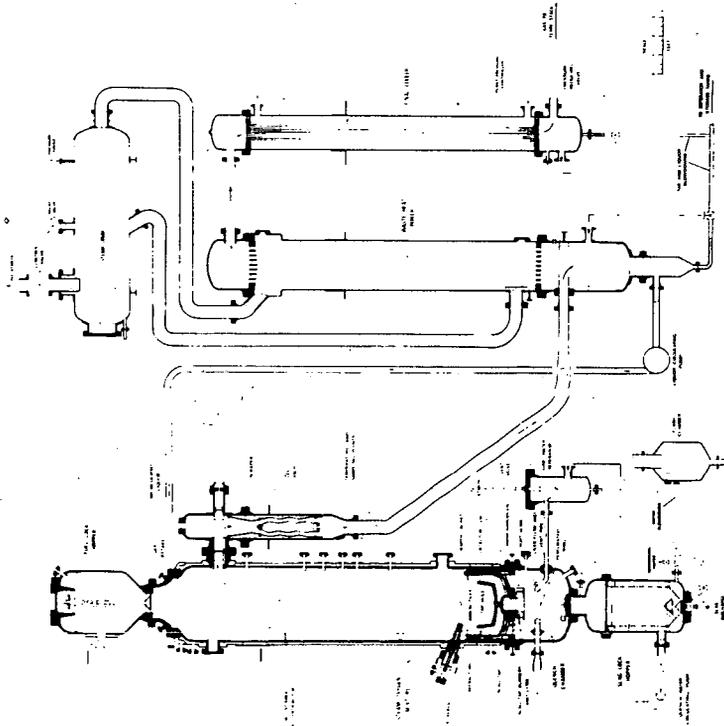


FIG. 1
The Slagging Gasifier and Gas Cooling Plant

the bottom of the fuel bed through four water-cooled tuyeres. In front of the tuyeres the temperature generated by the combustion of the fuel with the oxygen melted the ash which drained into the hearth below. The hot zone was confined to the centre of the gasifier away from the refractory walls by projecting the tuyeres 6 inch into the fuel bed, and using a blast velocity of about 200 ft/sec.

The hearth of the gasifier was contained within a water jacket supported from a carrier ring fitted between the main flanges of the gasifier and the quench chamber. Slag was discharged vertically downwards into water in the quench chamber where it formed a glassy black frit that settled in the slag lock hopper. Water was circulated at a high rate, from the slag hopper through a cooler and back into the quench chamber via a perforated ring, to create highly turbulent conditions that avoided stratification and helped to quench and break up the slag.

The product gases left the gasifier through an offtake fitted with a scraper that kept it free from deposits of tar and dust, and were quenched by liquor recirculated from the base of the waste heat boiler. After leaving the waste heat boiler the gases passed through a final cooler to a reducing valve that controlled the plant pressure. Tar and liquor condensate from the gas was blown down through valves controlled by the level of liquid in the sumps of the waste heat boiler and final cooler, and passed into a large storage tank where separation of the two phases occurred.

The cooled gases from the plant were burnt at ground level within an acoustically lined enclosure at the base of a 120 ft. high chimney stack.

DEVELOPMENT OF THE SLAG TAP.

In small slagging gasifiers the heat capacity of the slag stream even when the ash content of the fuel is increased artificially by fluxing is low in proportion to the high rate of heat loss, and problems with viscous slag, solidifying slag, and stalaicite formation are common when continuous tapping is attempted. To avoid these difficulties the tapping system for the experimental gasifier was based on intermittent tapping from a reservoir of slag contained in the hearth. This gave a homogeneous slag with consistent flow properties and enabled gasifying media to be introduced through the tap hole in an attempt to control the slag temperature independently of the main gasification reactions, but the increased slag residence time in the hearth encouraged the separation of liquid iron.

The fuels used in the slagging gasifier had a high iron content. In fact it was the presence of the iron compounds that gave the ash the low melting point and good flow properties for which the fuels were originally chosen. The strongly reducing conditions in the hearth inevitably led to the formation of iron, although the degree of reduction was greatly reduced by introducing oxygen through the tap hole. In the absence of a suitable refractory it was necessary to develop a water cooled metal slag tap that was compatible with the slag under the conditions existing in the hearth and that would also withstand liquid iron, which at temperatures above 1500°C has a very high heat capacity. To preserve the slag tap it was necessary to have a very high heat transfer rate to the cooling water to form a protective layer of solidified slag and to freeze any iron before it damaged the slag tap. It was therefore desirable to construct the slag tap with metal having a high thermal conductivity, use high cooling water rates, and avoid any accumulations of iron in the hearth. Originally austenitic stainless steels were used for the slag tap because of the type of slag tap burner employed, but later carbon steel was found to be satisfactory.

As a consequence of iron attack the hearth, slag tap and slag tap burners went through several stages of development, and these have been described in details by Hebden⁽²⁾ et al. The hearth depicted in Fig. 1 was abandoned at an early stage. It was unsatisfactory because of the erosion of the carbon tiles in the vicinity of the tap hole by the slag tap gases, and its shape permitted iron to collect. The slag tap withstood small quantities of iron, but it was found that masses of

10 to 30 lb. iron accumulated and destroyed the slag tap as they flowed uncontrollably from the hearth. Experience indicated that the hearth should slope steeply towards the tap hole with the minimum opportunity for iron to collect at any point. Thus, the hearth and slag tap were made funnel shaped, and the slag tap was tapped as frequently as possible to limit the quantity of iron that could collect.

The hearth and slag tap that proved reliable for more than 100 hours operation, and which were used for the performance tests, are shown in Fig. II. The floor of the refractory hearth sloped downwards at 45° to a carbon steel slag tap assembly, at the centre of which was the slag tap tube $1\frac{1}{2}$ inch diameter by 2 inches long. Very little erosion of the refractory hearth occurred for it was found that the high temperature gases and slag were confined to a zone about 20 inches diameter in the centre of the gasifier, and the refractory walls at the side were protected by unburnt fuel. Below the slag tap two swinging burners were mounted. The tap burner controlled the slag tapping and was used to introduce air, oxygen and town gas into the slag tap tube, where combustion occurred, giving a linear gas velocity sufficiently high to hold back the slag in the hearth. The auxiliary burner which had a refractory tunnel was normally in the retracted position and was installed to clear the tap hole in the event of a blockage a purpose for which the tap burner was unsuited. It was necessary to use this burner only on very rare occasions.

The slag tap shown in Fig. II was not completely immune from iron attack, which when it did occur, was invariably confined to an area at the outer edge of the tap cone entrance that was most difficult to cool effectively. To give this vulnerable area added protection water-cooled coils of copper tubing were installed in the hearth. The high heat transfer rates possible with the copper tubing enabled it to withstand large amounts of iron without suffering any damage. It is considered that copper is a very promising material for the construction of the slag tap, and the slag tap has been redesigned to enable it to be fabricated from this material.

SLAG TAPPING.

The intermittent slag tapping system proved to be so easy to operate and trouble free that it was possible to adopt an automatic tapping system. Initially the tapping was controlled on a time basis, but later it was controlled by the slag level in the hearth. With the slag tap burner directing the hot gases up through the tap hole the slag level in the hearth increased. On reaching the level of a collimated beam of gamma rays from the level detector, about 12 inches above the tap hole, a sequence of operations was started to tap the slag. The tap burner was swung away from the tap hole, and on reaching its fully retracted position a control valve on a vent line from the quench chamber was opened to reduce the pressure in the quench chamber below that of the gasifier. A controlled differential pressure across the hearth was maintained for a pre-set time period to force the slag to flow from the hearth, and the control valve was then closed. As the pressure in the slag quench chamber built up, due to the gases supplied to the burner, the slag flow stopped, and the tap burner was swung back to the tap hole. In a typical tapping cycle the slag was tapped for 20 seconds every 4 to 6 minutes.

During the development work on coke the slag was tapped at differential pressures of 5 to 15 lb/in.². When coal was tested it was found that at these differential pressures fuel was entrained in the slag stream. The differential tapping pressures were gradually reduced and it was possible to drain slag from the hearth at a rate of more than 10,000 lb/hr. with a pull of 1 lb/in.². At these low differentials carbon could not be detected in the slag, and the temperature of the slag stream was more uniform than at the higher differential pressures.

While the arrangement of swinging burners worked well on the pilot plant mechanical devices of this type would not be a practical proposition in a large plant. They could be replaced by a fixed burner arrangement mounted below the slag tap which would allow iron to pass out through the tap hole at any time while the

slag was retained and intermittently tapped to maintain a constant level, or reservoir, in the hearth.

GASIFIER PERFORMANCE

The first phase of the experimental programme was to develop the hearth design and the slag tapping system, and for this purpose a free flowing slag was required. Avenue coke was selected as a suitable fuel on the basis of its silica ratio, a parameter of chemical composition that gives a good correlation between the viscosity and temperature of slags⁽³⁾. The coke was mixed with blast furnace slag in the proportion 2 parts slag to 1 part ash to increase the volume of slag to be tapped. This simplified plant operation and avoided any complications that might arise with coal, so that attention could be concentrated on the hearth and slag tap. When the design of the hearth and slag tap had progressed sufficiently to enable the plant to be operated continuously for 4 days the changeover was made from coke to coal.

The first experimental runs with coal were made with Donisthorpe washed doubles, a weakly caking coal that was known to behave well in slagging boilers. It was mixed with blast furnace slag to increase its ash content and was successfully gasified at 300 p.s.i. and an oxygen rate of 40,000 ft³/hr. Using the same fuel the gasifier was next operated at its designed gas output of 5 mill. ft³/day for a test period of 81 hours to obtain data from which the performance of the gasifier could be accurately assessed.

The next run was to attempt to gasify a smaller and dirtier coal with a high proportion of adventitious ash, i.e., untreated singles with an ash content of 11%. With the higher ash content it was no longer necessary to ballast the fuel, but to preserve approximately the same silica ratio a flux of dolomite was added in the ratio 0.3 lb/lb. ash. The gasifier worked well on the dirtier coal without any difficulty with the fuel bed, or with tapping the slag.

It was then considered of interest to establish the limit of the gasifier output, and a run was made at an output of 7½ mill. ft³/day, i.e., 50% above the designed output. The gasifier operated smoothly and slag tapping was consistent, but as the run progressed difficulties were experienced with the gas cooling system and run was terminated after 10 hours. The factor that limited the output was the lock hopping of the fuel. At this output the distributor was empty before recharging and repressurising of the lock hopper could be completed. This resulted in a widely fluctuating gas outlet temperature which was normally fairly steady at 350 to 400°C, it now fluctuated between 200 and 800°C. A greater capacity in the distributor and another lock hopper would be required before any material increase in output could be attempted.

The final run made with the slagging gasifier was to test its ability to handle a coal with a high fusion point, and a coal in the highest range of silica ratios was selected from Newstead Colliery in the East Midlands coalfield. The ash content of 6% was fluxed by the addition of dolomite to reduce the silica ratio to 65 and, in a run of 10 hours, no difficulty was experienced in tapping the slag which was in fact remarkable for its free flowing character. The indications were that a lower flux:ash ratio or steam:oxygen ratio could have been employed.

a) Fuel.

The details of the fuel and the chemical composition of the fuel ash and flux used in the performance tests are given in Tables 1 and 2.

TABLE 1. Fuel Analysis

Test No.	54	67	70	71	72
<u>Fuel</u>	Avenue No.2 Coke	Donisthorpe D.S. Nuts	Donisthorpe Untreated Singles	Donisthorpe D.S. Nuts	Newstead Doubles
Nominal size (in.)	1½ - 1	1½ - 1	1 - ½	1½ - 1	2 - 1
Rank	-	902	902	902	802
<u>Ultimate Analysis</u>					
Carbon wt. %	88.0	71.3	68.7	74.6	73.8
Hydrogen "	0.75	5.0	4.75	5.0	4.7
Nitrogen "	1.05	1.55	1.5	1.55	1.55
Sulphur "	1.15	1.45	1.8	1.3	0.7
Chlorine "	0.05	0.15	0.05	0.2	0.3
Oxygen, errors, etc.	1.45	13.2	11.75	11.7	11.15
Ash "	7.55	7.35	11.45	5.65	7.6
	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>
Moisture as charged	9.45	12.7	15.1	13.8	12.6

TABLE 2. Ash and Flux Compositions

Composition wt. %	Avenue No. 2 Coke	Donisthorpe D.S. Nuts	Donisthorpe Untreated Singles	Newstead Doubles	Blast Furnace Slag	Dolomite
Al ₂ O ₃	26.81	28.50	27.52	32.40	20.6	2.18
SiO ₂	44.18	38.60	44.53	47.0	33.40	0.86
Fe ₂ O ₃	15.24	15.60	15.49	4.52	1.63	1.07
TiO ₂	1.03	1.22	1.17	0.95	0.73	0.04
Mn ₃ O ₄	0.17	0.22	0.23	0.20	1.26	0.18
P ₂ O ₅	0.45	0.49	0.32	1.25	0.12	0.17
Na ₂ O	2.36	1.09	0.55	2.14	0.53	0.08
K ₂ O	2.11	1.38	2.17	0.80	1.26	0.12
CaO	5.14	5.71	4.75	5.95	33.10	30.2
MgO	1.05	2.06	2.17	1.70	6.15	21.6
SO ₃	1.46	6.21	2.59	3.49	1.0	0.01
Ash Properties						
Silica Ratio*	67	62	69	80	46	-
Fusion Temps., °C						
Initial Reformation	1110	-	1165	1235	1230	-
Hemisphere Point	1215	1250	1350	1355	1250	-
Flow Point	1330	1345	1470	1545	1320	-

* Silica Ratio =
$$\frac{\text{SiO}_2 \times 100}{\text{SiO}_2 + \text{Equiv. Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}}$$

b) Performance Data.

The performance data obtained during one test on coke and four tests on coal are summarised in Table 3 and cover changes in fuel, fuel size, gasifier output and ash fusion properties. The fuel quantities are expressed as dry and ash free and all product gas volumes are given on the nitrogen free basis to simplify comparison. The greater part of the nitrogen content of the gas produced originated from the air supplied to the slag tap burner and varied between 5 and 7 per cent depending on the operation of the slag tap and the gasifier output. To obtain a product gas with a low nitrogen content suitable for synthesis gas the slag tap burner could be run on a mixture of make gas, oxygen and steam.

The steam oxygen ratio was maintained almost constant. A ratio of 1.1 vol./vol. gave satisfactory slagging conditions on coal, being slightly reduced when operating with the higher melting point ash (Test 72). Similarly, the rates of supply of gas, air and oxygen were not varied by significant amounts.

The gas compositions are characterised by low carbon dioxide and high carbon monoxide contents. It is interesting to note that in the high output run (Test 71) the calorific value of the gas was unaffected. The organic sulphur content was rather higher than expected; Lurgi gas usually contains less than 10 grains/100 ft.³.

During the tests on coal the rate of slag flow through the tap hole, calculated from the slag tapping times, was between 10,000 and 14,000 bl./hr. whereas the rates were as high as 30,000 lb./hr. with coke. This was not due to any difference in the rheological properties of the slags, but to the use of lower differential pressures across the hearth when tapping coal slag.

The absence of volatile matter and the lower reactivity result in coke having a higher oxygen consumption than coal. The variation in the oxygen consumption figures for coal are hardly significant, but they reflect the increase which can be expected with higher ash contents and the use of a flux. The specific throughput figures are noteworthy in that for these conditions a gasification rate of 1,000-1,500 lb. d.a.f. coal/hr. ft.² would appear to be readily attainable without any undue sacrifice in performance. Gas output from the fuel bed is extremely high and is equivalent to more than 30,000 to 42,000 ft.³/hr. per ft.² of fuel bed.

c) Mass and Heat Balances.

Due to the scale of operations it was difficult to accurately measure the make gas, and a carbon balance was used to obtain this major item. A typical mass balance is given in Table 4. The hydrogen and oxygen items show differences which are relatively small and can be attributed to the loss of flash steam during the blowing down of liquor from the waste heat boiler.

A heat balance for the same test is given in Table 5. It shows that 1.5 per cent of the total heat supplied is lost as high grade heat from the hearth 0.3 per cent being in the slag stream and 0.7 per cent being in the cooling water from the tuyeres and slag tap. The heat lost from the jacket and stirrer amounts to a similar quantity but in a commercial gasifier this would be recovered as gasification steam. Of the total heat supplied 80.3 per cent appears as potential heat in gas and 90.3 per cent as potential heat in gas plus by-products.

TABLE 3. Performance data obtained on the slagging gasifier operated at 300 lb/in.²
(Fuel figures are on dry and ash-free basis)

Test No.	54	67	70	71	72
Duration, (hr.)	54	81	30	12	14
<u>Supplied</u>					
Fuel	Avenue Coke	Donisthorpe D.S. Nuts	Donisthorpe Untreated Singles	Donisthorpe D.S. Nuts	Newstead Singles
Size Feed rate (in.) (lb./hr.)	1½ - 1 3,640	1½ - 1 6,930	1 - ½ 6,520	1½ - 1 10,150	2 - 1 6,560
Flux	Blast Furnace	Blast Furnace	Dolomite	-	Dolomite
Flux:ash ratio (lb./lb.)	Slag 0.83	Slag 0.75	0.3	0.0	0.32
Steam:oxygen ratio (vol./vol.)	1.17	1.10	1.10	1.10	1.06
Steam rate (lb./hr.)	1,650	2,038	2,040	2,965	2,045
Oxygen rate (ft. ³ /hr.)	30,100	39,650	39,640	57,615	41,240
Slag tap burner					
Gas rate (ft. ³ /hr.)	3,000	3,000	2,735	3,000	3,000
Air rate (ft. ³ /hr.)	16,050	16,050	12,590	16,050	16,050
Oxygen rate (ft. ³ /hr.)	1,200	900	1,120	1,200	1,200
<u>Produced</u>					
Gas (N ₂ free basis)					
CO ₂	1.85	2.55	3.5	2.7	2.35
C _n H _m	0.0	0.45	0.7	0.55	1.05
H ₂	27.25	28.05	29.25	28.1	28.65
CO	70.45	61.3	60.05	60.85	60.55
C _n H _{2n} + 2	0.45	7.65	6.5	7.7	7.25
	100.0	100.0	100.0	100.0	100.0

TABLE 3. (Contd.)

Test No.	54	67	70	71	72
Value of 'n'	1.0	1.123	1.128	1.129	1.114
Calorific value	315	374	366	375	379
H ₂	-	250	233	-	144
Organic sulphur	-	206	126	-	-
Rate	3.7 x 10 ⁶	5.1 x 10 ⁶	5.0 x 10 ⁶	7.23 x 10 ⁶	5.09 x 10 ⁶
(Btu.ft. ³)					
(gr./100 ft. ³)					
(ft. ³ /day)	542	938	1,026	534	602
(lb./hr.)	1.1	4.0	5.3	3.1	3.6
(min./hr.)	19.7	77.5	69	229	63
Dust Carry-over	-	508	501	-	453
(lb./hr.)	-	1,609	1,807	-	1,413
Ter	-	30,100	34,700	-	35,600
Liquor	-			-	
Permanganate value	-			-	
(p.p.m.)					
<u>Specific Data</u>					
Consumption					
Fuel	516	981	924	1,440	930
(lb./hr.ft. ²)					
(lb./therm)	3.40	2.56	2.66	2.62	2.54
(ft. ³ /therm)	71.4	55.2	56.2	54.7	56.6
Production					
Gas	94,800	68,800	71,900	66,500	72,400
(ft. ³ /ton)					
(therms/ton)	299	258	263	250	274
(therms/hr.ft. ²)	69	113	109	153	114
(per cent fuel charged)	0.45	0.9	0.8	1.84	0.8
Dust	-	15.4	16.2	-	15.5
(gal./ton)	-	2.0	2.35	-	1.76
Tar					
Liquor					
(lb./therm)					

TABLE 4. Mass Balance for Test 67 - lb./hr.

		Carbon	Hydrogen	Oxygen
IN	Coal	5,323	373	993
	Moisture	-	121	972
	Steam and Oxygen	-	226	5,106
	Slag Tap Burner	41	15	378
		<u>5,364</u>	<u>737</u>	<u>7,449</u>
OUT	Gas	4,896	509	5,925
	Dust	48	2	6
	Tar	406	38	45
	Liquor	14	176	1,376
	Difference	0	12	97
		<u>5,364</u>	<u>737</u>	<u>7,449</u>

TABLE 5. Heat Balance for Test 67.

		Therm/h.	%
IN	Coal (potential)	958	15.8
	Town gas (potential)	13.5	1.35
	Steam and Oxygen (latent and sensible)	28.5	2.85
		<u>1000.0</u>	<u>100</u>
OUT	Gas (potential)	803.0	80.3
	Gas and vapours (latent and sensible)	55.5	5.55
	Tar (potential)	84.4	8.44
	Dust (potential)	8.6	0.86
	H ₂ S ammonia, etc. (potential)	4.6	0.46
	Slag (sensible)	8.0	0.8
	Cooling water from tuyeres and hearth (sensible)	6.6	0.66
	Cooling water from gasifier jacket and stirrer (sensible)	15.2	1.52
	Unaccounted for losses, etc.	14.1	1.41
	<u>1000.0</u>	<u>100.0</u>	

d) Ash and Slag Balances.

By making a mass balance of constituents in the fuel ash, flux and slag and assuming a quantitative recovery of such refractory oxides as alumina lime, magnesia and titania the loss of the other constituents were evaluated. As was expected the losses increased as the temperature in the tuyere zone increased, and the percentage loss of each constituent would be correlated with the steam oxygen ratio. Actual temperatures measured by sighting an optical pyrometer through the tuyeres ranged from 1800°C at a steam oxygen ratio of 1.3 v/v to more than 1950°C at 1.10 v/v.

In addition, to the loss of the more volatile constituents such as sulphur phosphorus, chlorine and oxides of sodium and potassium there was a loss of iron oxides due to the formation of metallic iron, and also of silica. Loss of silica was due to its reduction to volatile silicon monoxide, which was subsequently reoxidised and carried away in the gas stream as silica fume. With coke the loss of silica was 5% at a steam oxygen ratio of 1.3 but this increased very rapidly at a ratio of about 1.10 v/v to more than 15%. Typical losses of sodium oxide, potassium oxide and sulphur were 5, 5 and 40% respectively at 1.3 v/v, increasing to 40, 40 and 80% at a ratio of 1.10 v/v. These materials were deposited in varying degrees in the gas offtake and in the sumps of the waste heat boiler and final cooler. The deposits in the gas offtake were enriched with alkali metal oxides and had a silica concentration of more than 50%. Most of the material was removed in the bottom of the waste heat boiler, but finely divided solids with an ash content greater than 90%, of which 75% was silica, separated from the gas in the final cooler and was removed in the blow down.

The loss of ash constituents from the coals tested were significantly lower than for coke, with the exception of chlorine and sulphur. Silica losses were negligible apart from the test with untreated coal that contained a high proportion of shale.

The loss of iron oxides is of considerable importance in the operation of a slagging gasifier due to the hazard presented by liquid iron, and to the effect upon the flow properties of the slag. Iron oxide acts as a flux and its loss raises the melting point, and by increasing the silica ratio produces an increase in the slag viscosity. A controlled series of experiments with coke showed that there was little effect on the reduction of iron oxides by decreasing the steam oxygen ratio from 1.40 to 1.20 v/v, but a further decrease to 1.10 v/v almost doubled the iron formation. However, it was found that this trend could be reversed by supplying extra oxygen to the gases passing through the tap hole, and reduction of the iron oxides was decreased to 15%. Although in the experiments with coal between 20 and 30% reduction occurred it is considered that this could have been much improved by supplying a larger proportion of the gasifying media through the tap hole.

e) Tar and Liquor.

Although the tar and liquor condensates from the gas were separated in two stages they were discharged into a common separating tank for ease of handling. This, together with the high liquor circulation rate from the sump of the waste heat boiler to provide the gas quench, produced a tar water emulsion. However, the emulsion was not persistent and three phases that could be separated without much difficulty were formed; a lower layer of solids, a middle layer of tar and an upper layer of liquor.

The liquor originated almost entirely from the moisture in the coal and had a permanganate value of 30,000 p.p.m., i.e., more than twice that from a Lurgi gasifier. Its smaller volume and, hence its reduced capacity to take into solution oxygen absorbing agents means, however, that its total oxygen absorbing potential per therm of gas is only half that of Lurgi liquor.

The tar, even after prolonged standing, retained about 20 to 25% water and about 4% suspended solids. It has been analysed by the Coal Tar Research Association⁽⁴⁾ and found to have the general characteristics associated with a vertical retort tar, i.e., a similar pitch yield and contents of naphthalene and tar acids. The high ratio of 2 to 1 methyl naphthalene and the high content of light oil, which was greater than that normally found in a carburetted water gas tar, indicated a high temperature of formation.

f) Behaviour of the Fuel Bed.

There was no evidence of channelling as a result of blockage of part of the fuel bed with fines, or any other abnormal behaviour during the operation of the slagging gasifier for a total of 500 hours with coke and 300 hours with coal. Screen analysis of the fuel bed at the end of the experimental tests with coal indicated that degradation increased as the fuel moved down the bed, but there were two main zones where this occurred, in the caking zone at the top of the bed due to the action of the stirrer, and in the tuyere zone due to the highly turbulent motion of the fuel. Table 6 shows the size distribution in the fuel bed immediately below the stirrer, and at the tuyere level, when the fuel charged to the gasifier was $\frac{1}{2}$ inch to 1 inch and 1 inch to $\frac{3}{4}$ inch. The proportion of fuel below $\frac{1}{2}$ inch at the tuyere level showed little variation in the tests on coal and averaged 30%

TABLE 6.

Fuel Size Inch	Test 67			Test 70		
	As Charged	Below Stirrer	At Tuyere Level	As Charged	Below Stirrer	At Tuyere Level
$\frac{1}{2}$ to 1	24.6	-	-			
1 to $\frac{3}{4}$	40.0	-	-	21.0	-	-
$\frac{3}{4}$ to $\frac{1}{2}$	21.0	59.1	10.9	15.6	21.4	9.2
$\frac{1}{2}$ to $\frac{1}{4}$	9.7	29.9	49.3	53.0	57.0	29.2
$\frac{1}{4}$ to $\frac{1}{8}$	1.4	3.1	8.1	2.2	8.6	30.1
below $\frac{1}{8}$	3.3	3.7	29.7	8.2	14.0	30.6

The fuel below $\frac{1}{2}$ inch entering the gasifier in Test 70 was more than double that in Test 67 but there was no significant change in the amount of dust carryover. In each of these tests the gas output was equivalent to four times that of a typical Lurgi gasifier but the fuel carryover was less than 1% of the fuel charged. However, on raising the gas output by 50% (Test 71) the carryover was doubled. With coke the carryover was only half that associated with coal, due to the absence of any mechanical breakage by the stirrer and the lower gas velocity above the fuel bed. There is little doubt that the carryover could be reduced by giving attention to stirrer design and perhaps by adopting the recirculation of tar dust mixtures as practised on the commercial Lurgi gasifier.

h) Comparison with a Lurgi Gasifier.

The Donisthorpe coal used in the slagging gasifier for Test 67 and 71 is similar to the coal used at the Lurgi gasification plant at Westfield, so that it is possible to make a direct comparison between the performances of the two types of gasifier. In Table 7 the performance data from Test 67 is compared with data given by Ricketts⁽⁵⁾.

Recent developments in the Lurgi process have resulted in lower steam consumptions and corresponding increases in gasifier output, but the output is still much lower than a slagging gasifier. At Westfield it has been possible to obtain nearly 20% more crude gas than the guaranteed maximum of 12 mill. ft.³/day, although at the higher loads more exacting operating conditions are required to avoid clinker formation. This compares with an output from the slagging of 5.2 mill. ft.³/day of

gas having a higher calorific value, which can be increased by 50% to 7.3 mill. ft.³/day without any significant loss of performance. The output of the experimental slagging gasifier when operating at a lower pressure is therefore more than half that of the commercial Lurgi gasifier. When expressed as the weight of fuel gasified or the volume of synthesis gas ($\text{CO} + \text{H}_2$) per unit cross sectional area of shaft the output of the slagging gasifier is at least four times greater than the Lurgi gasifier.

In Table 7 the material requirements of the two gasifiers are compared for the production of a therm of crude gas and for 1,000 ft.³ of synthesis gas. Steam requirements show the greatest difference; that of the slagging gasifier being about one fifth of the Lurgi gasifier. However, the composition of the crude gases should be considered when comparing steam consumption if the gas is to detoxified or if synthesis gas is required. In the Lurgi crude gas there is sufficient undecomposed steam to carry out the required reduction in carbon monoxide content without added steam or liquor, but extra steam would be needed with the slagging gasifier because of its high carbon monoxide content, small volume of undecomposed steam and lower outlet temperature. Under these conditions the slagging gasifier loses some of its advantage in steam consumption.

The oxygen consumption per therm of crude gas from the slagging gasifier is about 10 to 12% higher than that of the Lurgi gasifier. This is due to the formation of a smaller proportion of the exothermic products carbon dioxide and methane, and to the loss of high grade heat to the hearth slag tap and tuyere cooling water. The oxygen consumption per unit volume of synthesis gas shows little difference between the two gasifiers.

TABLE 7. Comparison of the results from the slagging gasifier and a commercial Lurgi Plant.

	Lurgi Gasifier	Slagging Gasifier
Operating pressure (lb./in. ²)	355	300
Fuel:		
Rank	902	902
Size range (in.)	1¼ to ¾	1½ to ¼
Ash, including flux (%)	14.6	11.4
Moisture (%)	15.6	14.7
Steam/oxygen ratio (vol./vol.)	5.4	1.10
Crude Gas Composition, (% Vol.)		
CO ₂	24.6	2.5
C _n H _m	1.1	0.45
CO	24.6	60.5
H ₂	39.8	27.75
C _n H _{2n+2}	8.7	7.6
N ₂	1.2	1.0
	<u>100.0</u>	<u>100.0</u>
Calorific value (Btu/ft. ³)	309	371
Steam consumption (lb./therm crude gas)	11.6	2.56
Steam consumption (lb./1000 ft. ³ (CO + H ₂))	56.1	10.7
Oxygen consumption (ft. ³ /therm crude gas)	49.5	55.2
Oxygen consumption (ft. ³ /1000 ft. ³ (CO + H ₂))	238	236
Synthesis gas (CO + H ₂) output (ft. ³ /hr. per ft. ²)	4,930	26,700
Gasification rate (lb. d.a.f. coal/hr. per ft. ²)	210	981
Efficiency $\frac{\text{(Potential heat gas)}}{\text{(Potential heat coal)}}$	81	82.5

CONCLUSIONS.

A pilot scale slagging gasifier has been developed that will gasify coke and weakly caking coals, and performance data have been obtained at 20 atm. pressure. The gasifier had a low steam consumption, high output, high thermal efficiency and handled coal with a wide range of ash fusion temperatures provided that dolomite was used to flux the more refractory ashes. A crude gas output of $7\frac{1}{2}$ mill. ft.³/day equivalent to 42,000 ft.³/hr. per ft.² of fuel bed was obtained without any limitation by the fuel bed.

Comparison of the results with those of a Lurgi installation showed that the steam consumption and liquor volume were one fifth, and the gas output per unit area of the fuel bed was from four to seven times greater than the Lurgi gasifier. The slagging gasifier produced a gas with a high carbon monoxide content and there was little undecomposed steam to convert it. However, with the added steam necessary to convert the carbon monoxide to the level required for synthesis gas the overall steam consumption would be lower than for the Lurgi gasifier. For detoxification to the level required in the United Kingdom it would be logical to convert part of the carbon monoxide and use methane synthesis to remove the remainder, at the same time increasing its calorific value.

The system of intermittent tapping, in which a reservoir of slag was maintained in the hearth, and enabled the slag to be run off at a high rate by the application of a controlled differential pressure, proved to be very satisfactory. Coal with a low ash fusion temperature, uncleaned coal with a high proportion of adventitious ash and coal with a refractory ash when suitably fluxed, gave a homogeneous slag that was tapped without blocking the slag tap. This tapping system could be used for scale up to a commercial size, by making modifications to the slag tap burner design to allow the free drainage of iron from the hearth.

Experience with the slagging gasifier indicated that water cooled metal surfaces were essential for the slag tap and areas of the hearth exposed to hot slag, but were prone to attack by liquid iron. Iron attack was greatly reduced by maximising heat transfer through the metal surfaces, by preventing iron from accumulating in the hearth, and by introducing oxidising gases through the tap hole to retain the bulk of the iron in solution in the slag. The water cooled steel slag tap used in the gasifier proved capable of withstanding hot slag and iron for long periods, but occasionally suffered some damage from iron attack. Complete resistance to iron attack is an obvious design requirement, and recent experiments suggest that this can be achieved by the use of copper.

The development of the slagging gasifier has now reached a stage that requires the proving of designs and materials for longer periods of time, possibly on a prototype gasifier. However, in the United Kingdom the gasification of solid fuels, even with the improvements offered by operation under slagging conditions, cannot at present compete on economic grounds with the new oil gasification processes now available. An alternative route for producing gas from coal, by hydrogenation and gasification in a fluidised bed, is therefore being investigated on the pilot plant scale.

Acknowledgments.

This paper is published by permission of The Gas Council, and the work described was carried out under the Direction of Dr. F. J. Dent and Dr. D. Hebden.

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A KINETIC STUDY
OF THE REACTION OF COAL CHAR
WITH HYDROGEN-STEAM MIXTURES

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INTRODUCTION

The gasification of coal with hydrogen-steam mixtures for the production of a gaseous product of high heating value in a practical continuous reactor is of paramount importance to the gas industry. A number of research programs are now under way to develop an efficient and economically feasible process for the production of high-heating-value gas from coal. One of these, a study at the Institute of Gas Technology, has led to the work reported here.

The reaction of coal with a steam-hydrogen mixture represents a system of heterogeneous reactions in which solid and gas phases are present. The study and interpretation of two such phase reactions is inherently more complex than those of homogeneous reactions in which only a single phase is present. For a reaction to proceed between a fluid and a solid, a combination of diffusional and kinetic processes with adsorption and surface-reaction steps are considered to occur.

The literature contains a number of papers^{2, 4, 13, 14, 18, 19, 21, 23-25, 27, 30, 31, 33-36} concerned with the kinetics of these reactions. The carbon studied in these papers ranges from coal to graphite.

Because it requires a large number of possible variables, such as temperature, pressure, the nature of chemical reaction, and the character of the solid surface, and because it incorporates a large number of constants which require experimental evaluation, the general mathematical model to estimate the product gas distribution for different levels of carbon conversion can become exceedingly complicated. Practical application of this model is particularly difficult when a choice has to be made between reaction mechanisms, each of which can generate complex functions with a sufficient number of arbitrary constants to fit any given experimental curve. The purpose of the work discussed in this paper was to study the influence of temperature and the partial pressure of hydrogen and steam on the rate of steam-hydrogen and coal char reactions and to develop a correlation to estimate the performance of a hydrogasification reactor in terms of its product gas distribution for different levels of carbon conversion.

GENERAL CONSIDERATIONS

Most coals are made up of a number of macerals. Carbons derived from different macerals differ in reactivity. As gasification proceeds, a decline in rate is expected since carbon of progressively lower reactivity remains. Differences in the chemical reactivity of macerals have been reviewed by Brown³ and Channabasappa and Linden,⁵

who found, in increasing order for hydrogenation, that fusain, durain, and vitrain have different reactivities.

In their study of coal pyrolysis, Chermin and Van Krevelen⁶ showed that, upon heating, coal first becomes metaplastic and then gives off volatile matter, leaving a rather stable coke. Thus coal char consists of two portions which differ greatly in reactivity. The highly reactive portion is related to the amount of volatile matter characterized by the aliphatic hydrocarbon side chain and to the oxygenated functional groups present. The low reactivity portion is the residual carbonaceous stable coke. Thus the gasification of coal by simultaneous reactions with steam and hydrogen at elevated temperatures is divided into first- and second-phase reactions, each reaction representing one of the two distinctly different reactivities of carbon present in coal.

FIRST-PHASE REACTION



where C^* is the reactive carbon present in the first phase.

Of course, the actual reactions are much more complex than indicated by the above simple schemes. It has been demonstrated¹⁰ that the gaseous products due to the first-phase reactions are predominantly methane, carbon monoxide, and hydrogen. The experimental data of the same investigations show that the hydrogen and steam reactions in the first phase are taking place independently of each other and are probably undergoing pyrolysis followed by the vapor-phase reaction of hydrogen and steam. The rates of the two first-phase reactions, therefore, are assumed to be additive. Let X_{H_2} and X_{H_2O} be the conversions of carbon due to hydrogen and steam respectively, then the overall conversion of carbon is simply:

$$X = X_{H_2} + X_{H_2O} \quad (3)$$

Hydrogen-Char Reaction

The hydrogen-char reaction in the first phase may be represented by:

$$\left[\frac{dX_{H_2}}{d\theta} \right]_1 = k_1(f-X) (P_{H_2} - P_{H_2}^*) \quad (4)$$

or

$$\frac{[dX_{H_2}]_1}{(1-X)d\theta} = \frac{k_1(f-X)}{1-X} (P_{H_2} - P_{H_2}^*) \quad (5)$$

where k_1 is the rate constant obtained, which has the unit of $(\text{atm}\cdot\text{hr})^{-1}$, and f is the fraction of carbon that reacts according to the first-phase reaction. This mechanism states that the first-phase reaction occurs in such a way that the rate of reaction at any time is proportional to the mass (or volume) of the unreacted portion of the volatile carbon still present in the particle and to the effective partial pressure of hydrogen. Figures 1, 2, and 3 compare the proposed rate equation with the experimental results obtained from a semiflow system¹⁰ at three temperature levels.

Equilibrium of Coal Char Hydrogen Reaction

The coal-hydrogen reaction has been shown to exceed the carbon-hydrogen-methane equilibrium at low conversion and to reach the carbon-hydrogen equilibrium at nearly complete conversion.^{35,36} From the equilibrium composition of the hydrogen-char system, a pseudo-equilibrium constant, K_p , is defined as:

$$K_p = \frac{P_{CH_4}^*}{(P_{H_2}^*)^2} \quad (6)$$

which has been calculated as a function of the carbon conversion level.

Figure 4 indicates the general trend of the K_p values at 1300°F with respect to the fraction of carbon converted. An empirical relationship was developed to convert the equilibrium constant from one temperature to another. The relationship is:

$$(K_p)_T = \frac{(K_p)_{1300^\circ F}}{34,713} \exp\left(\frac{18,400}{T}\right) \quad (7)$$

where T is in degrees Rankine.

Effect of Hydrogen Partial Pressure

Apart from the equilibrium hindrance, the rate of gasification is affected by the partial pressure of hydrogen. The rate of reaction of coal with hydrogen in the first phase is shown by Figures 1, 2, and 3 to be roughly proportional to the partial pressure of hydrogen. A similar type of reaction was proposed for hydrogen-char reactions.^{35,36} This has been shown to agree with the majority of previous investigators who found that the reaction is approximately a first-order one with hydrogen. Gorin et al.,¹⁶ showed that the methane formation rates with pure hydrogen and hydrogen-steam mixtures at the same partial pressure as hydrogen are a strong function of the partial pressure of hydrogen. Wen and Huebler^{35,36} demonstrated that the rate of methane formation is roughly proportional to the difference between the partial pressure of hydrogen and the hydrogen partial pressure in equilibrium with the char. Von Fredersdorff³² observed that an increase in hydrogen partial pressure would increase the rate of hydrogenolysis. This relationship is further confirmed by Moseley and Paterson,²⁸ who reported that the rate of hydrogenation of coal to methane is directly proportional to the hydrogen partial pressure even in the very early stages of the reaction.

Effect of Temperature

Figures 1, 2, and 3 show that the fraction of the carbon that reacts according to the first phase, f , increases with the temperature. Moseley and Paterson²⁸ pointed out that the fraction of carbon that reacts according to the first phase is a function of both temperature and pressure. Since the total pressures employed in the present investigation were nearly constant at approximately 70 atm, total pressure had no significant effect on the value of f . Previous investigators¹¹ observed that an increase of pressure broadens the range of the initial high-rate period. But, for a small range of pressures, the fraction of carbon that goes into the first-phase reaction can be assumed to be a function of only the temperature.

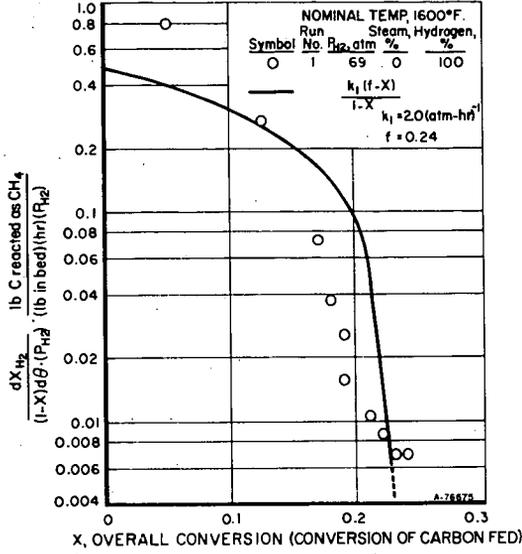


Figure 1. RATE OF HYDROGEN-CHAR REACTION DURING FIRST-PHASE REACTION AT 1600°F

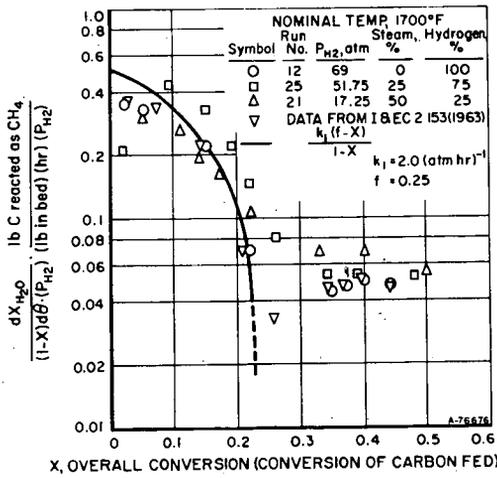


Figure 2. RATE OF HYDROGEN-CHAR REACTION DURING THE FIRST-PHASE REACTION AT 1700°F

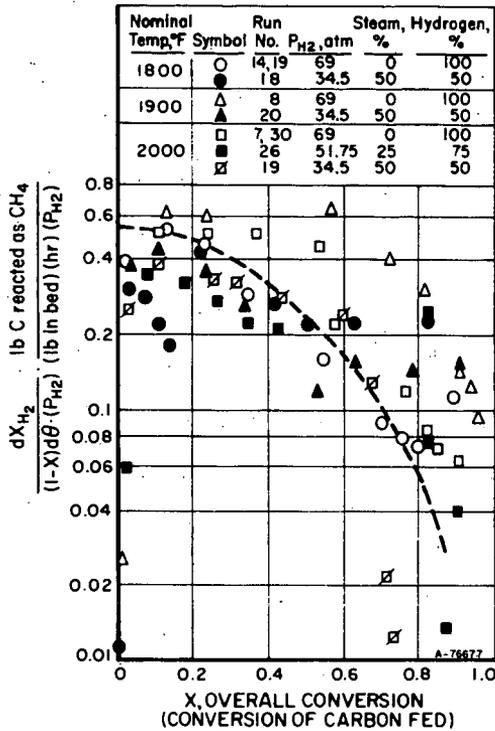


Figure 3. RATE OF HYDROGEN-CHAR REACTION DURING THE FIRST-PHASE REACTION ABOVE 1800°F

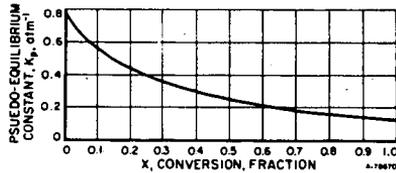


Figure 4. APPROXIMATE TREND OF THE EQUILIBRIUM CONSTANT AS A FUNCTION OF CONVERSION FOR THE HYDROGEN-CHAR REACTION AT 1300°F AND 2000 PSIG TOTAL PRESSURE

The values of f for various temperatures are tabulated as follows:

Temperature, °F	f
1300	0.22
1500	0.23
1700	0.25

Above 1800°F, the rate of the hydrogen reaction is not substantially affected by the temperature, as shown in Figure 3. This is probably because, at these high temperatures (1800°-2050°F), the chemical reaction is so rapid that the rate becomes controlled by diffusion. In addition, at such high temperatures, the reaction rate for the remainder of the relatively stable carbon is no longer small enough to be neglected. Thus differentiation of the first-phase reaction from the second-phase reaction becomes so difficult that an accurate value of f cannot be obtained.

Steam-Char Reaction

The steam-char reaction in the first phase is represented by:

$$\left[\frac{dX_{H_2O}}{d\theta} \right]_1 = k_2 (f-X) \quad (8)$$

and

$$\frac{[dX_{H_2O}]_1}{(1-X)d\theta} = \frac{k_2 (f-X)}{1-X} \quad (9)$$

where k_2 is the rate constant having the unit of hr^{-1} , and f is the fraction of carbon that will react according to the first-phase reaction. As in the hydrogen-char reaction, the first-phase reaction of steam-char is a volume reaction, the rate of which is proportional to the amount of the unreacted portion of the volatile carbon still present in the particle.

Effect of Partial Pressure of Steam

Contradictory conclusions have been reported in the literature regarding the effect of the partial pressure of steam. The reaction has been variously reported to be of the zero order,³⁰ fractional order, first order,^{12, 15, 17, 18, 20} and between first and second order^{20, 30} with respect to steam. As shown in Figures 5, 6, 7, and 8, the rate of the steam-char reaction is not affected by the partial pressure of steam, so far as detectable by the experiment. This is in agreement with the previous investigators.^{13, 25, 28, 29}

Effect of Temperature

The fraction of carbon that will react according to the first-phase mechanism for steam also increases with increasing temperature. As shown in Figures 5, 6, 7, and 8, the temperature dependency of f and k_2 can be evaluated by the proposed mechanism. However, these correlations must be treated with caution since the second-phase reaction may become so rapid at temperatures above 1900°F that the isolation of the first-phase reaction from the second-phase reaction would become difficult; thus the evaluation of f might no longer be accurate.

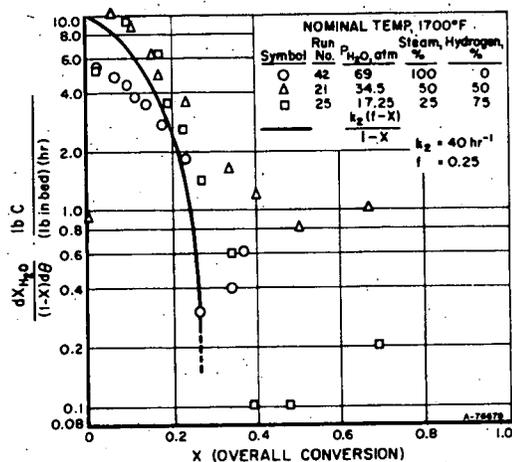


Figure 5. RATE OF STEAM-CHAR REACTION DURING THE FIRST-PHASE REACTION AT 1700°F

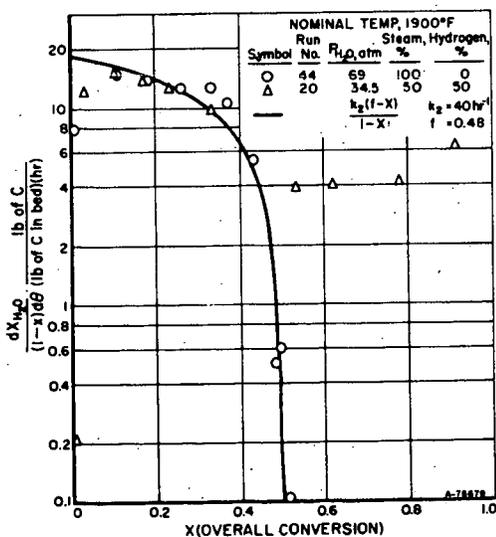


Figure 6. RATE OF STEAM-CHAR REACTION DURING THE FIRST-PHASE REACTION AT 1900°F

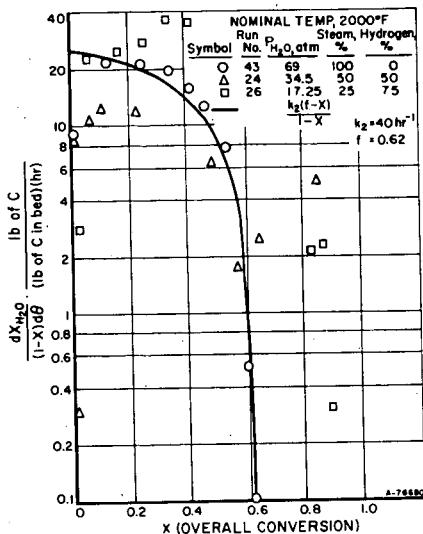


Figure 7. RATE OF STEAM-CHAR REACTION DURING THE FIRST-PHASE REACTION AT 2000°F

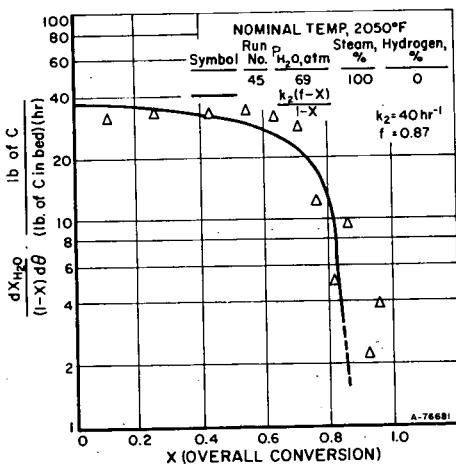


Figure 8. RATE OF STEAM-CHAR REACTION DURING THE FIRST-PHASE REACTION AT 2050°F

SECOND-PHASE REACTION

The second-phase reaction is a heterogeneous reaction which occurs at the surface of the particle. The reaction causes the reacting surface to shrink and leaves an ash layer as the particle moves through the reactor. Unlike the first-phase reaction which is only slightly affected by temperature, the second-phase reaction is quite sensitive to variations in temperature. At temperatures below 1700°F, the first-phase reaction rate is an order or two larger than the second-phase reaction rate, but as the temperature approaches 2000°F, the two rates become comparable. This is, of course, true only when the reaction is controlled by the chemical step.

Hydrogen Reaction

As discussed previously,^{35, 36} if this reaction under experimental conditions in the continuous flow reactor is controlled by gas diffusion, the reaction rate may be characterized by:

$$\left[\frac{dX_{H_2}}{d\theta} \right]_2 = \frac{(K_g)_{H_2}}{D_p} (1-f) (P_{H_2} - P_{H_2}^*) \quad (11)$$

where $(K_g)_{H_2}$, the effective mass transfer coefficient for hydrogen, is defined as:²²

$$(K_g)_{H_2} = \frac{3kg}{\rho_c} \quad (12)$$

and can be obtained from the moving-bed data by the relation:

$$(K_g)_{H_2} = \frac{x_{H_2} D_p}{\left(\frac{W}{F}\right) (\Delta P_{H_2})_{avg}} \quad (13)$$

In the above equation x_{H_2} differs from X_{H_2} and is the fractional conversion of carbon present in the second-phase reaction, i.e. based on $(1-f)$. $(\Delta P_{H_2})_{avg}$ is the mean hydrogen partial pressure difference, $(P_{H_2} - P_{H_2}^*)$, at the gas inlet and at the point where X equals f in the moving-bed reactor.

Since in the flow reactor the reaction in the second phase has been proved to be controlled by the diffusion,^{35, 36} the rate is less sensitive to the change in temperature than to the change in gas velocity.

The values of $(K_g)_{H_2}$ from the moving-bed reactors using both pure hydrogen feed and hydrogen-steam mixture feed are calculated and are plotted in Figure 9 as a function of average particle Reynold's number, at the operating conditions listed. Two correlation lines are obtained: one at an average temperature of 1300°F and the other at temperatures above 1500°F. At the higher temperatures, coal particles may crack due to sudden and severe heating immediately after being fed to the reactor. This heating results in rather violent devolatilization and the subsequent first-phase reaction. However, the particle disintegration due to devolatilization can reach only a certain magnitude. Between 1500° and 1800°F, $(K_g)_{H_2}$ is affected less by the temperature. The two correlations may be written as:

$$(K_g)_{H_2} = \frac{D_p x_{H_2}}{W (\Delta P_{H_2})_{avg}} = 1.2 \times 10^{-5} (N_{Re})^{1.11} \text{ for } T > 1500^\circ F$$

$$= 0.35 \times 10^{-5} (N_{Re})_{IM}^{1.11} \text{ for } T = 1300^\circ F \quad (14)$$

Figure 9 includes the data from the char feed that contains approximately 17% volatile matter and the spent char feed that contains less than 5% volatile matter. Because of the complexity of the process, the scattering of the data points may be attributed to many causes. Among them, the temperature uniformity and the particle size distribution can be considered significant. Because it was difficult to maintain a uniform temperature throughout the bed, an average temperature (nominal) is used in the correlation. In addition solid feed contains a fraction of particles that are so small that during their migration through the reactor they must be in a state of semifluidization. Since these factors can make the mass transfer characteristics extremely complex and since many variables are involved, the correlations obtained in Figure 9 must be regarded as satisfactory.

Steam-Char Reactions



The steam-char reaction during the second phase is probably very similar to the carbon-steam reaction occurring at the char surface. Analogous to the hydrogen-char reaction in the second phase, the rate of the steam-char reaction in the continuous-flow moving-bed reactor is probably controlled by gas diffusion and may be characterized as:

$$\left[\frac{dx_{H_2O}}{d\theta} \right]_2 = \frac{(K_g)_{H_2O}}{D_p} (1-f) (P_{H_2O} - P_{H_2O}^*) \quad (16)$$

$$\text{where } (K_g)_{H_2O} = \frac{x_{H_2O} D_p}{W (\Delta P_{H_2O})_{avg}} \quad (17)$$

x_{H_2O} and $(\Delta P_{H_2O})_{avg}$ are defined as analogous to those for the hydrogen-char reaction. $P_{H_2O}^*$ is calculated based on unit carbon activity.^{38,37} The amount of carbon conversion due to steam is evaluated from the experimental product gas analysis based on carbon oxides. Figure 10 shows the relationship between $(K_g)_{H_2O}$ and $(N_{Re})_{IM}$. As is evident from the figure, at temperatures above 1500°F, the effective mass transfer coefficients are functions of the particle Reynold's number and are insensitive to the temperature variations. At 1300°F, the steam-char reaction is very slow and probably controlled by the chemical step at the reaction surface of the char particles. Reasons similar to those given for the hydrogen-char reaction can be given here to account for the scattering of the data points. The correlation line for temperatures above 1500°F can be given as:

$$(K_g)_{H_2O} = \frac{D_p x_{H_2O}}{W (\Delta P_{H_2O})_{avg}} = 1.7 \times 10^{-5} (N_{Re})_{IM}^{1.20} \quad (18)$$

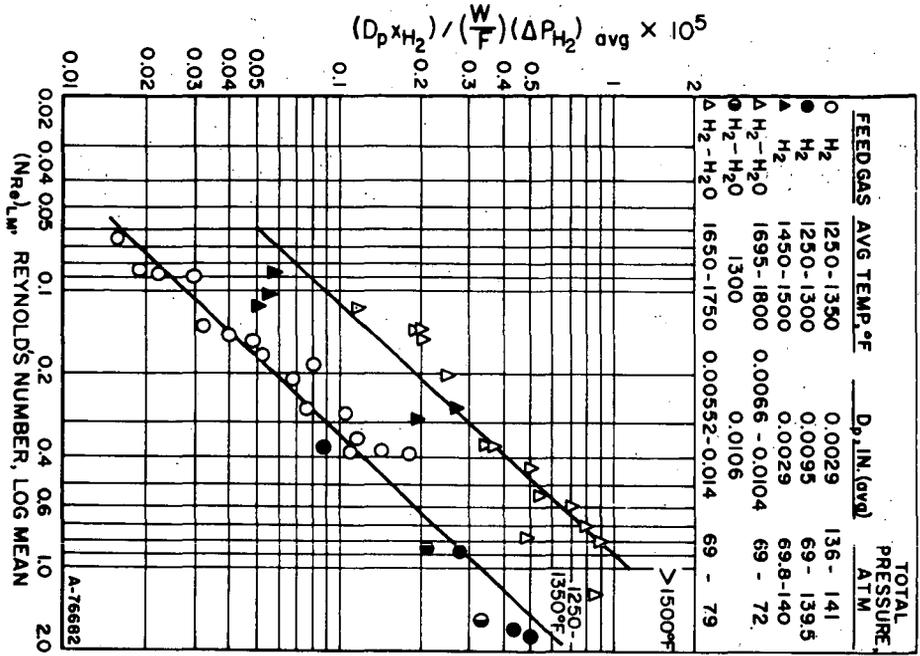


Figure 9. EFFECTIVE MASS TRANSFER COEFFICIENT FOR HYDROGEN-CHAR REACTION AND REYNOLD'S NUMBER RELATION INDICATING DIFFUSION CONTROL MECHANISM

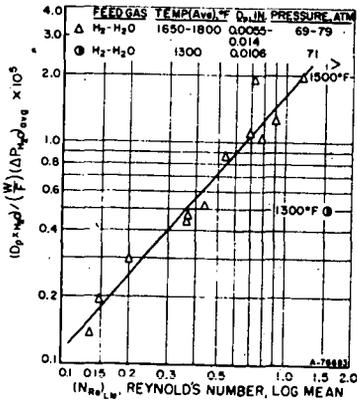


Figure 10. EFFECTIVE MASS TRANSFER COEFFICIENT FOR STEAM-CHAR REACTION IN SECOND PHASE INDICATING DIFFUSION CONTROL

The overall reaction, including both the first phase and the second phase, may now be written as:

Overall Reaction Rate:

$$\frac{dX}{d\theta} = \frac{dX_{H_2}}{d\theta} + \frac{dX_{H_2O}}{d\theta} \quad (19)$$

Hydrogen-Char Reaction Rate:

$$\frac{dX_{H_2}}{d\theta} = [k_1(f-X) + \frac{(K_g)_{H_2}}{D_p}(1-f)] (P_{H_2} - P_{H_2}^*) \quad (20)$$

for $X < f$

$$\frac{dX_{H_2}}{d\theta} = \frac{(K_g)_{H_2}}{D_p} (1-f) (P_{H_2} - P_{H_2}^*) \quad (21)$$

for $X > f$

Steam-Char Reaction Rate:

$$\frac{dX_{H_2O}}{d\theta} = k_2(f-X) + \frac{(K_g)_{H_2O}}{D_p} (1-f) (P_{H_2O} - P_{H_2O}^*) \quad (22)$$

for $X < f$

$$\frac{dX_{H_2O}}{d\theta} = \frac{(K_g)_{H_2O}}{D_p} (1-f) (P_{H_2O} - P_{H_2O}^*) \quad (23)$$

for $X > f$

WATER-GAS SHIFT REACTION

CO_2 is assumed to be produced solely by the water-gas shift reaction:



This reaction, which occurs simultaneously with the gasification of carbon by steam and hydrogen, can proceed either heterogeneously on the char surface or homogeneously in the gas phase, or by a combination of both, depending upon the reaction and operation conditions. The water-gas shift reaction probably occurs predominantly on the char surface^{1, 7-9} and is catalyzed by the inorganic ashes present in char.

The water-gas shift reaction may account for a substantial fraction of the steam produced. Opinions concerning the extent of this reaction differ greatly from investigator to investigator. Some¹⁹ have pointed out that it appears to be fast enough to reach equilibrium in a reacting steam-carbon system. The data reported by others^{25, 31} support the view that quasi-equilibrium is reached between char and product gas.

In calculating the product gas distribution for the moving-bed reactor in the present work, water-gas shift equilibrium at the exit is assumed.

APPLICATION TO MOVING-BED REACTOR DESIGN

For a small-diameter, long-length shaft-type reactor, the assumption of plug flow for both solids and gases is valid. Below is a carbon balance for the differential volume, dV :

$$F dX = \left[\frac{dX_{H_2}}{d\theta} + \frac{dX_{H_2O}}{d\theta} \right] \rho_B dV \quad (25)$$

Substituting Equations (20) through (23) in Equation (25) and integrating, we get:

$$\begin{aligned} \frac{V\rho_B}{F} = & \int_0^f \frac{dX}{\left\{ \left[k_1(f-X) + \frac{(K_G)_{H_2}(1-f)}{D_p} \right] (P_{H_2} - P_{H_2}^*) + k_2(f-X) + \frac{(K_G)_{H_2O}(1-f)}{D_p} (P_{H_2O} - P_{H_2O}^*) \right\}} \\ & + \int_f^X \frac{dX}{\frac{(K_G)_{H_2}}{D_p} (1-f) (P_{H_2} - P_{H_2}^*) + \frac{(K_G)_{H_2O}}{D_p} (1-f) (P_{H_2O} - P_{H_2O}^*)} \end{aligned} \quad (26)$$

Numerical or graphical integration of Equation (26) may be performed to obtain the reactor volume necessary for a carbon conversion of X :

$$dX = \left[1 + \left(\frac{dX_{H_2O}}{dX_{H_2}} \right) \right] dX_{H_2} \quad (27)$$

The fraction of carbon converted by hydrogen can be found by:

$$\begin{aligned} \int_0^{X_{H_2}} dX_{H_2} = X_{H_2} = & \int_0^f \left[1 + \frac{\frac{dX}{k_2(f-X) + \frac{(K_G)_{H_2O}}{D_p} (1-f) (P_{H_2O} - P_{H_2O}^*)}}{\left[k_1(f-X) + \frac{(K_G)_{H_2}}{D_p} (1-f) \right] (P_{H_2} - P_{H_2}^*)} \right] dX \\ & + \int_f^X \left[1 + \frac{\frac{dX}{\frac{(K_G)_{H_2O}}{D_p} (1-f) (P_{H_2O} - P_{H_2O}^*)}}{\frac{(K_G)_{H_2}}{D_p} (1-f) (P_{H_2} - P_{H_2}^*)} \right] dX \end{aligned} \quad (28)$$

and the fraction of carbon converted by steam is given by:

$$X_{H_2O} = X - X_{H_2} \quad (29)$$

Then, knowing the fractions of carbon converted by hydrogen and steam and assuming water-gas shift equilibrium at the exit, product gas composition can be calculated. The evolution of gases from coal is neglected in making this calculation. However, this evolution can easily be accounted for by assuming that the gases H_2 , H_2O , H_2S , and N_2 are evolved instantaneously at $X = f$ and by adding corresponding amounts to the gas stream at that point.

As an approximation, the second-phase reactions may be neglected for carbon conversions less than f . This will simplify Equations 26 and 28 considerably.

CONCLUSION

The gasification of coal char with a hydrogen and steam mixture at high temperatures and high pressures can be satisfactorily represented by the proposed mechanism to estimate the product gas distribution for different levels of carbon conversion.

The coal char reaction with a hydrogen and steam mixture is represented by the first-phase and the second-phase reactions. The first-phase reaction is related to the amount of volatile matter and may be regarded as a volume (or mass) reaction. The second-phase reaction is characterized by the heterogeneous reaction at the carbon surface, a reaction which is controlled by gas diffusion for the range of operating conditions in the continuous moving-bed reactor.

The char-hydrogen reaction and the steam-char reaction are considered as taking place independently so that the rates of the reactions are additive.

NOMENCLATURE

D_p = average char particle diameter, ft

f = fraction of carbon in the coal char which potentially can react with hydrogen and/or steam according to the first-phase reaction

F = coal char feed rate, lb/hr

G = mass velocity of the gas, lb/sq ft-hr

k_1 = hydrogen reaction rate constant in the first phase, (atm-hr)⁻¹

k_2 = steam reaction rate constant in the first phase, hr⁻¹

k_g = mass transfer coefficient, lb/sq ft-hr

$(K_g)_{H_2}$ = effective mass transfer coefficient for hydrogen, ft/hr-atm

$(K_g)_{H_2O}$ = effective mass transfer coefficient for steam, ft/hr-atm

$N_{Re, LM}$ = $\frac{DG}{\mu}$, the particle Reynold's number log-mean

$P_{CH_4}^*$ = partial pressure of methane, atm

P_{H_2} = partial pressure of hydrogen, atm

$P_{H_2}^*$ = partial pressure of hydrogen in equilibrium with coal char and methane, atm

P_{H_2O} = partial pressure of steam, atm

$P_{H_2O}^*$ = partial pressure of steam in equilibrium with C, CO, CO₂, and H₂, atm

T = temperature, °F

V = volume of the reactor, CF

W = weight of coal char in bed, lb

X = fraction of carbon converted

X_{H_2} = fraction of carbon converted by hydrogen

X_{H_2O} = fraction of carbon converted by steam

x_{H_2} = fraction of carbon converted in the second phase by hydrogen,

x_{H_2O} = fraction of carbon converted in the second phase reaction by steam

ρ_C = density of carbon in coal char, lb/CF

ρ_B = bulk density of coal char in bed, lb/CF

θ = time, hr

μ = viscosity of the gas, lb/ft-hr

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HIGH BTU GAS BY THE DIRECT CONVERSION OF COAL

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INTRODUCTION

Processes for the production of high-Btu gas from coal are being developed for future use when there is an economic need for manufactured gas. (2,5)¹ A number of processes based on both coal and petroleum are available, and various estimations of production costs or selling price have been published. (1,3,4,6) Those processes based on coal can be divided into two general categories: indirect and direct. Indirect processes are those requiring the coal carbon to be converted into synthesis gas (hydrogen and carbon monoxide) which, after adjustment of the gas composition and removal of impurities, is reacted catalytically at moderate pressure and temperature to produce methane. Direct processes are those in which the coal carbon is combined with hydrogen to produce methane in a noncatalytic operation taking place at high pressure and high temperature. Each approach to the production of high-Btu gas has advantages as well as disadvantages, and thus far, a clear-cut superiority has not been demonstrated for one or the other. This paper reports the progress made by the Pittsburgh Coal Research Center of the United States Bureau of Mines in developing a direct process for converting coal to high-Btu gas.

The Bureau's conception of hydrogenating coal to methane in dilute-phase concurrent flow originated from an earlier attempt to produce hydrocarbon gases by entraining feeds of strongly caking and noncaking coals in a stream of hydrogen which passed through a hot reactor in turbulent flow. Even though the gas velocity was high, carbonization of coal in the reactor always stopped the flow. These experiments indicated the possibility of devolatilizing the coal to dry char providing the coal particles were small and dispersed throughout a stream of hot gas. Under these conditions the coal particles would be heated very rapidly, and, if the diameter of the reactor was large relative to the entering feed stream, the coal would pass through its plastic range without agglomerating into a large mass or sticking to the wall of the reactor. This was successfully demonstrated experimentally several years ago using strongly caking coal, hvab Pittsburgh seam, and hydrogen at 1,000 psig. The reactor had a diameter of 3 inches, and was heated to a nominal temperature of 800° C while the entering stream of coal had a diameter of 5/16 inch. A dry, free-flowing, nonagglomerated char was produced during free-fall through a heated zone 4 feet in length.

Since that time, a dependable system for hydrogasifying coal in dilute-phase has been developed, and experimental data are being obtained. In addition, some data have been obtained for the hydrogenation of dilute-phase char. These experimental results are presented, and a conceptional process is discussed wherein these two operations are integrated for the production of high-Btu gas on a commercial scale.

DILUTE-PHASE HYDROGENATION

The reaction of coal with hydrogen in dilute-phase is intended to be a means whereby strongly caking coals can be reacted at high temperatures in the "as received" condition without incurring agglomeration. The primary products are hydrocarbon gases

^{1/} Underlined numbers in parentheses refer to items in the list of references at the end of this report.

and a solid residue of coal which is a dry, free-flowing, nonagglomerated char that can be processed further by hydrogenation, gasification, or burned as fuel; in addition, a minimal amount of hydrocarbon liquids might be produced. One anticipated application of dilute-phase hydrogasification is the direct conversion of coal to high-Btu gas.

Until recently, a major portion of the work was concerned with the development of means for feeding strongly caking coal into gas mixtures at high temperatures and high pressures. When this problem was solved, experiments were made with the objectives of determining the operability limits of the system with respect to coal throughput and to explore the effects of hydrogen-to-coal ratio on the quality of the product gas and char.

All experiments in dilute-phase hydrogasification used a feed of Pittsburgh seam coal having a free-swelling index of 8 and a volatile content of 41 percent, moisture-ash-free basis. Ultimate and proximate analyses are given in table 1. This choice

TABLE I
ANALYSES OF HIGH-VOLATILE A BITUMINOUS COAL

	As received, percent	Maf, percent
Ultimate		
Carbon	78.5	84.0
Hydrogen	5.4	5.7
Nitrogen	1.6	1.7
Sulfur	1.4	1.5
Oxygen ^{1/}	7.2	7.1
Ash	5.9	-
Moisture	0.7	-
Proximate		
Moisture	0.7	-
Volatile matter	38.2	40.9
Fixed carbon	55.2	59.1
Ash	5.9	-

^{1/} By difference.

of feed was based on the premise that procedures for overcoming agglomeration would apply to any other coal, whereas the reverse might not be true. The feed was sized 50 x 100 mesh sieve fraction, U.S. Standard.

The feed gas was a mixture of methane and hydrogen having a composition simulating that which could be obtained by the partial conversion of char with hydrogen to produce methane; various gas compositions were used. The feed rate closely approximated 175 scfh. The additional methane produced by hydrogenating coal in dilute-phase using a methane-rich mixture could conceivably raise the heating value of the gas leaving the reaction zone to better than 900 Btu per scf on a clean, dry basis. While the coal was being partially devolatilized, it was also being transformed into dry, free-flowing char which could be hydrogenated in a moving bed without agglomerating.

Equipment and Procedure

The basic elements of the dilute-phase system are shown schematically in figure 1. Feed gas of a given composition was made by blending metered quantities of methane and hydrogen in a gasholder which supplied the gas mixture to a compressor. The compressed gas was heated during flow through coiled tubing immersed in a lead bath to 700° C and entered the top of a reaction vessel heated by external furnaces where it contacted the incoming stream of coal. The coal entered the reactor through a nozzle having a diameter as large as one-half inch and in concurrent flow with the hot gas, passed through the reaction space which was 8 feet in length by 3 inches in diameter. The reactor was heated to a nominal temperature of 725° C which means that its temperature was brought to a maximum of 725° C and constant temperatures were attained over the system before starting the coal feed. Of course, some variations in temperatures occurred especially after coal feed was started. Pressure equalization throughout the coal feeding system was obtained by providing a parallel flow path between the feeder, the nozzle, and the reaction space. Product gas passed through a water-cooled vessel in which water and a small quantity of oil vapors were condensed and collected, and the gases were then reduced in pressure, metered, and collected in a gasholder. A small flow of gas was withdrawn and passed through an analyzer which continuously recorded the specific gravity of the gas, thereby showing when steady conditions had been attained; about 15 minutes were required to reach steady conditions. Samples of the product gas were withdrawn at intervals and analyzed.

Results and Discussion

In dilute-phase hydrogasification, the composition of the effluent gas is determined by the feed gas rate and composition and the gas yield. The feed gas rate and composition can be selected with some degree of freedom, but the gas yield is dependent upon many variables some of which interact. Most prominent of the variables are: coal rate, maximum temperature attained by the solids and the vapors, residence times of the solids and the vapors, total pressure, hydrogen partial pressure, particle size and density, gas viscosity, heat capacity of the feed gas, and thermal conductivity of the gases. Obviously, in an investigation which is primarily concerned with development of a process, a study of the variables is impractical. However, some experimental data have been obtained showing the gross effect of several important variables. The results are given in table 2 for experiments at 1,500 psig and in table 3 for 3,000 psig.

The effect of coal rate on the conversion of coal to gaseous and liquid products was investigated at both pressures using hot feed gas at a rate of 175 scfh and an approximate composition of 50 percent hydrogen, 48 percent methane, and 2 percent nitrogen. Over the relatively narrow range of 5 to 7 pounds per hour, the quantity of coal converted to gases plus a small amount of oil and water was approximately 35 percent to 33 percent based on maf coal. Coal conversion decreased with increasing coal rates, being approximately 27 percent at a rate of 9 pounds per hour because of the greater heat load imposed by the increased coal rate while the heat input was held constant. Carbon conversions were about 28 percent to 27 percent of maf coal at 6 to 7 pounds per hour and decreased to about 22 or 23 percent at 9 pounds per hour.

The effect of coal rate on the yield of hydrocarbon gases (methane and ethane) is shown in figure 2. Approximately 24 percent of the maf coal was converted to methane plus a little ethane at 6 to 7 pounds per hour coal rate and 3,000 psig while the corresponding yield at 1,500 psig was approximately 20 percent. The greater yields were obtained at 3,000 psig because both the hydrogen partial pressure and the retention time of the coal volatiles were twice as great as that obtained at 1,500 psig, which accelerated the thermal decomposition and hydrogenation of the high-molecular weight vapors. Hydrocarbon gas yields showed the same decreasing trend with increased coal rate as was observed for conversion, resulting from the increased heat load causing coal temperatures to decrease.

TABLE 2

DILUTE-PHASE HYDROGASIFICATION AT 1,500 PSIG AND A NOMINAL 725° C REACTOR TEMPERATURE

Coal feed rate, lb/hr	5.9	6.0	6.3	6.4	6.5	6.7	7.5	7.6	9.1
Gas feed rate, scfh	173	173	175	179	177	175	174	176	177
Composition, percent methane ^{2/} ..	42	3	44	47	61	43	43	44	42
Gross heating value, Btu/scf	617	346	627	648	747	621	623	632	617
Conversion, wt pct									
Coal, maf	35	37	1/	32	32	34	1/	32	28
Carbon	28	30	1/	26	26	27	1/	25	22
Product gas, nitrogen-oxygen free									
Hydrogen, vol pct	41.6	76.7	40.4	38.2	25.3	40.9	38.5	35.7	34.7
Methane, do.	56.4	20.3	57.2	58.5	73.2	56.7	58.5	61.2	62.2
Ethane, do.	1.4	2.1	1.7	2.5	1.5	1.7	2.0	2.4	2.1
Carbon monoxide, vol pct	0.6	0.9	0.7	0.8	0.5	0.7	1.0	0.7	1.0
Gross heating value, Btu/scf	734	495	744	764	853	741	757	780	784
Gain in heating value, Btu/scf .	117	149	117	116	106	120	134	148	167
Percent based on feed gas	19	43	19	18	14	19	21	23	27
Yields, wt pct, maf coal									
Methane	18.4	22.0	15.9	14.6	13.3	16.4	15.3	17.2	17.1
Ethane	3.0	4.9	3.9	5.7	3.4	3.5	3.5	4.3	3.1
Carbon monoxide	1.4	2.0	1.5	1.8	0.9	1.4	1.8	1.3	1.5
Recoveries, wt pct									
Overall	97	96	92	97	95	96	92	96	101
Carbon	96	97	94	97	95	95	90	98	99
Hydrogen	100	102	99	100	97	99	97	100	102
Ash	115	101	103	98	102	105	100.	88	110

1/ Conversion values not meaningful.

2/ Balance is hydrogen and 2 percent nitrogen.

TABLE 3

DILUTE PHASE HYDROGASIFICATION AT 3,000 PSIG AND A NOMINAL 725° C REACTOR TEMPERATURE

Coal feed rate, lb/hr	5.3	6.0	6.2	6.3	6.5	6.6	6.8	7.2	7.8	8.3
Gas feed rate, scfh	174	182	174	174	174	177	176	176	175	174
Composition, percent methane ¹ /	50	2	68	47	48	49	48	71	45	48
Gross heating value, Btu/scf	669	337	807	647	653	660	658	814	633	667
Conversion, wt pct										
Coal, maf	33	42	32	33	35	33	34	31	29	31
Carbon	26	35	24	26	28	26	27	23	23	23
Product gas, nitrogen-oxygen free										
Hydrogen, vol pct	34.0	70.1	17.1	34.9	31.3	32.9	30.9	16.9	31.8	28.6
Methane, do.	64.0	28.6	81.0	63.6	66.3	65.5	66.9	81.0	65.0	67.8
Ethane, do.	1.5	0.8	1.7	1.5	1.8	1.6	1.7	1.6	2.6	2.6
Carbon monoxide, vol pct	0.5	.6	0.1	0.0	0.5	0.0	0.4	0.3	0.6	1.0
Gross heating value, Btu/scf	792	533	910	786	808	798	811	905	810	829
Percent based on feed gas	18	58	13	21	24	21	23	11	28	20
Yields, wt pct, maf coal										
Methane	21.0	35.8	13.7	20.3	21.5	19.3	20.8	11.1	19.0	16.5
Ethane	3.9	1.9	3.5	3.5	3.7	3.6	3.7	3.3	4.5	4.2
Carbon monoxide	1.5	1.3	0.2	trace	1.0	0.0	0.8	0.6	1.0	1.6
Recoveries, wt pct										
Overall	98	97	95	97	96	102	96	91	98	97
Carbon	99	100	96	98	97	97	98	95	99	98
Hydrogen	101	97	98	100	100	101	100	98	102	99
Ash	100	102	101	98	100	103	101	105	90	100

¹/ Balance is hydrogen and 2 percent nitrogen.

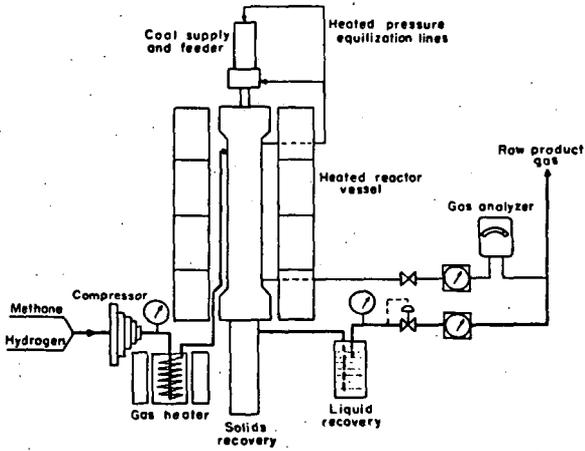


Figure 1.—Schematic diagram of dilute-phase hydrogasification apparatus.

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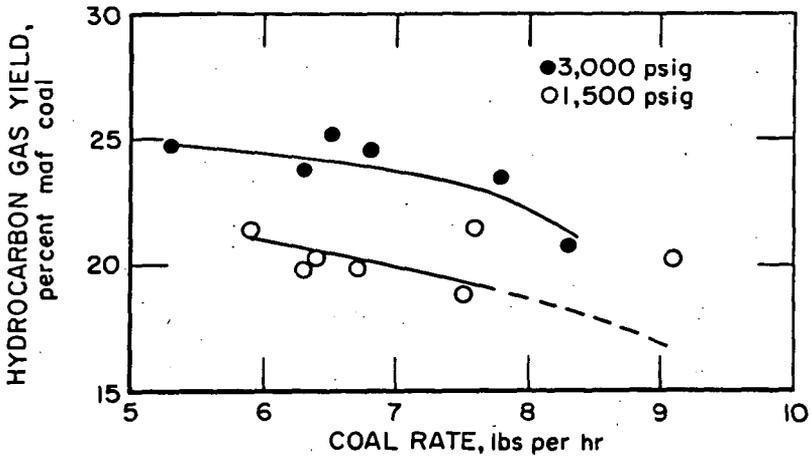


Figure 2.—Effect of coal rate on hydrocarbon gas yield at approximately constant gas feed rate and composition

The effect of pressure upon coal conversion appeared to be less than the accuracy of the conversion data--about 3 percent. Of course, when the total pressure was changed other dependent variables also changed and thereby effected conversion. A coal rate of 9 pounds per hour appeared to be close to the limit of operability because coal temperatures were low and the coal was not being devolatilized sufficiently to produce dry char.

In another series of experiments, the coal and gas rates were approximately constant at 6 to 7 pounds per hour and 175 scfh while the quantity of hydrogen supplied with the feed gas was varied over a fairly wide range between 50 and 175 scfh. Coal and carbon conversions and yields of hydrocarbon gases decreased with decreasing hydrogen concentration in the feed gas; however, some of this change can be attributed to lower reaction temperatures which resulted from the change in feed gas composition. The change in carbon conversion over the range of hydrogen-to-coal ratios between 10 and 30 is shown in figure 3. At 3,000 psig, reducing the hydrogen-to-coal ratio from 30 to 10 scf per pound of coal reduced the carbon conversion from 35 percent to 24 percent based on maf coal.

The hydrogen-to-coal ratio has an important bearing on the quality of the gas leaving the dilute-phase zone. If high-Btu gas is to be produced, the feed gas must have a composition that provides adequate hydrogen for conversion of the coal carbon to hydrocarbon gases in sufficient yield that the effluent gas exceeds 900 Btu per scf in gross heating value. This can be seen in figure 4 which shows how the heating value of the effluent gas changed with the hydrogen-to-coal ratio at total pressures of 1,500 and 3,000 psig. Conditions were the same as those relating to figure 3. The increase in heating value was least at the lowest hydrogen-to-coal ratio, an increase of about 100 Btu per scf with feed gas containing 75 scf per pound of coal at a total pressure of 3,000 psig; however, this was the feed ratio needed to produce an effluent gas having 910 Btu heating value. An increase of 200 Btu in the heating value was obtained at the opposite extreme where the hydrogen-to-coal ratio was 30 scf per pound. The reduction in the differential heating value reflects both decreasing hydrogen partial pressure and the resulting loss of heat of reaction. Of course, these data represent one of many possible feed gas-to-coal ratios, a number of which certainly would give a high-Btu effluent gas. Many experiments would be required before an optimum feed ratio could be selected.

HYDROGENATION OF CHAR

Char from the hydrogenation of coal in dilute-phase was hydrogenated continuously in a moving bed at 3,000 and 1,500 psig. The objective was to determine the hydrogen-to-feed ratio that would produce an effluent gas of a certain selected composition for a particular conversion.

Equipment and Procedure

A schematic diagram of the system is shown in figure 5. The reaction vessel filled completely with dilute-phase char consisted of a 5-foot length of 1-inch pipe connected to a 6-foot length of 1/2-inch pipe. The length of the heated zone was adjusted between limits of 6 and 24 inches according to the char conversion requirements of a particular experiment. A variable speed screw continuously discharged reacted char from the bottom of the vessel. A flow of compressed hydrogen was introduced into the screw housing, and heating occurred during upward flow in contact with the descending stream of hot char. The gases and vapors were withdrawn at the top of the heated zone and flowed through a cold vessel where the vapors condensed and were collected. The uncondensed gases were reduced in pressure, metered, and either collected in a holder from which samples were withdrawn or were discharged to the atmosphere. A small sidestream was passed continuously through a meter that measured its specific gravity. Gas composition could be controlled by varying the hydrogen-to-char ratio, and char conversion could be controlled by varying the retention time of the char in the reaction zone.

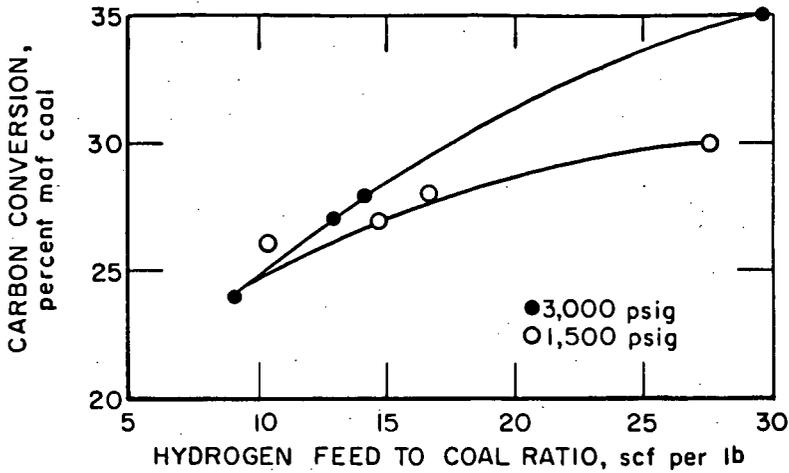


Figure 3.—Effect of hydrogen concentration in feed gas on carbon conversion at approximately constant gas and coal rates.

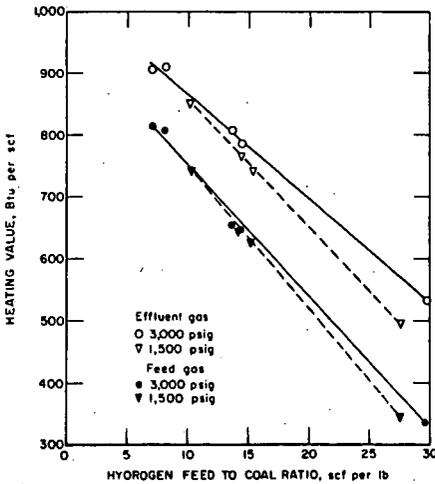


Figure 4.—Effect of hydrogen feed to coal ratio on increasing the heating value of gas by dilute-phase hydrogenation.

Results and Discussion

Table 4 shows the results obtained when dilute-phase char was hydrogenated. At

TABLE 4

HYDROGENATION OF DILUTE-PHASE CHAR

Pressure, psig	1,500	1,500	3,000
Temperature, ° C	900	900	700
Residence time, minutes	3.5	7.5	3.5
Hydrogen/char ratio, scf per pound	11	32	25
Conversion, wt pct of maf char	34	52	26
Effluent gas composition, percent			
Hydrogen	31	35	62
Methane	67	63	36
Ethane	1	1	1
Carbon monoxide	1	1	1
Volatile content of residue, wt pct maf basis ^{1/}			
	2.6	2.4	2.6

^{1/} Volatile content of feed char-12.8 percent.

1,500 psig, 900° C, and a residence time of about 3-1/2 minutes the conversion of dilute-phase char was 34 percent, based on maf feed. At the hydrogen-to-char feed (maf) ratio of 11 scf per pound, the effluent gas contained 67 percent methane, 31 percent hydrogen, and 1 percent each of ethane and carbon monoxide. When the residence time was increased to 7-1/2 minutes, the conversion of char increased to 52 percent. The composition of the effluent gas was 63 percent methane, 35 percent hydrogen, and 1 percent each of ethane and carbon monoxide. The hydrogen-to-maf-char needed to produce gas of this composition was 32 scf per pound. An experiment at 700° C and 3,000 psig produced a char conversion of 26 percent with a residence time of 3-1/2 minutes. Because hydrogen-to-char ratio of 25 scf per pound was used in this experiment, the concentration of methane was only 36 percent; the other concentrations were 62 percent hydrogen with 1 percent each of ethane and carbon monoxide.

These data emphasize the considerable range of char conversion and effluent gas compositions that could be obtained simultaneously by varying hydrogen-to-char ratios and retention times. Only a few minutes retention time was required to convert one-quarter to one-third of the char to methane under the conditions used. For equal retention times, more char was converted at 1,500 psig and 900° C than was converted at 3,000 psig and 700° C; hence, temperature had a greater influence than pressure on char conversion.

CONCEPTIONAL PROCESS

Two reaction stages are required in this conceptual process for the direct conversion of coal to high-Btu gas: (1) a dilute-phase stage in which coal is partially devolatilized in a stream of hot gas containing a fairly high concentration of methane; decomposition and hydrogenation of the coal volatiles increases the methane concentration of the gas leaving this stage to the extent that removal of impurities will give a product exceeding 900 Btu per scf heating value, and (2) a dense-phase stage in which the char from the first

stage is hydrogenated in a moving bed thus producing the hot methane-hydrogen mixture that is fed into the first stage. Overall coal conversion can be varied over a wide range through choice of residence time, pressure, and temperature; however, residence time of char in the reaction zone has the greatest influence on overall conversion. Coal conversion is held at a level that will supply sufficient char for the production of the required amount of hydrogen. Conversion of coal would be approximately 54 percent, based on maf coal, and about 45 percent of the coal carbon would appear as hydrocarbon gases in the product.

Figure 6 is a simplified flow diagram of the conceptual process. Coal that has been crushed, dried, and sized to minus 100 mesh sieve size is fed through lock-hoppers into the top of a reaction vessel where it becomes dispersed into a dilute-phase during free-fall through hot gas entering in concurrent flow. The residence time of the coal in the dilute-phase stage is about 6 to 8 seconds and is assumed to result in the conversion of approximately 25 percent of the coal while the coal volatiles, having a residence time of about 30 seconds, are hydrocracked to gas. The partially devolatilized coal or char is held for 3 to 5 minutes in the bottom section of the reactor where the hydrogen feed enters. Approximately 35 percent (ash-free basis) of the char is converted to methane. The gas leaving the top of the char bed mixes with a portion of the gas from the dilute-phase stage and the combined stream is returned to the top of the dilute-phase stage. This very hot gas supplies the heat needed to bring the coal feed to reaction temperature. The hot, outgoing char residue exchanges heat with the cold incoming hydrogen feed before being discharged into lock-hoppers and conveyed to an entrained gasification plant where the hydrogen is produced. The raw product gas is withdrawn from the lower portion of the dilute-phase stage and contains mostly methane with some hydrogen and water vapor and small quantities of carbon oxides, ammonia, and hydrogen sulfide. This gas, being at 200 atm and about 800° C, has considerable potential for producing useful work. We propose to recover electrical power by first removing the entrained solids (dust) and then expanding the gas through a turbine to an exit pressure of 40 atm and temperature of 520° C (970° F). The gas, following cooling and cleaning at pressure to remove contaminants, could go directly into the transmission system, or it could be processed further to obtain some additional methane from the small quantity of residual carbon monoxide and hydrogen.

The hydrogenation reaction, being strongly exothermic, requires the removal of heat to control the temperature. This could be done by pumping water at 3,000 psig through thin-walled tubing distributed throughout the char hydrogenation stage. The superheated steam generated in the tubing is collected and expanded through a turbine to generate additional power, and the condensate is returned to the pump.

CONCLUSIONS

Exploratory experiments have shown that strongly caking coal can be partially devolatilized by dispersing it in a dilute-phase in a methane-hydrogen mixture which becomes enriched with hydrocarbon gases from the coal volatiles and thereby increased in gross heating value to 900 Btu per scf or more. The coal residue was a dry, free-flowing char which is very reactive and easily hydrogenated to produce a methane-rich gas. The composition of this gas was determined by the hydrocarbon gas yields and the hydrogen-to-char feed ratios, while the char conversion was fixed by the residence time and reaction temperature. The two operations were combined to form a conceptual process for producing high-Btu gas on a commercial scale.

Development of dilute-phase hydrogasification is continuing with the objective of determining the effect of higher coal temperatures on yields and gas composition. Coals other than Pittsburgh seam also will be tested.

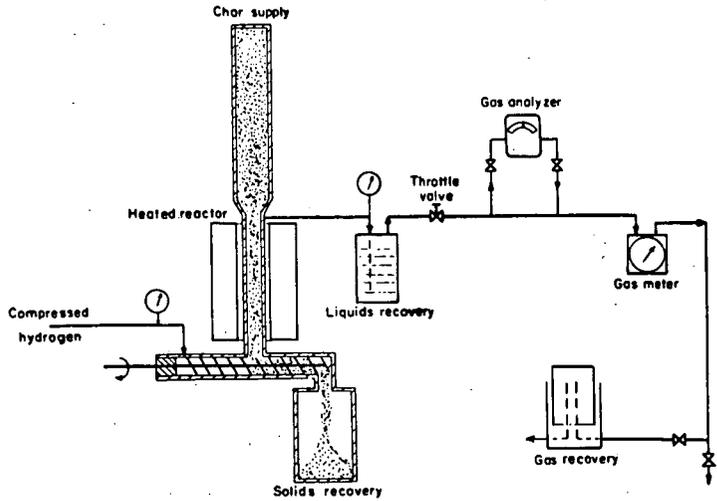


Figure 5.—Schematic diagram of char hydrogasification apparatus.

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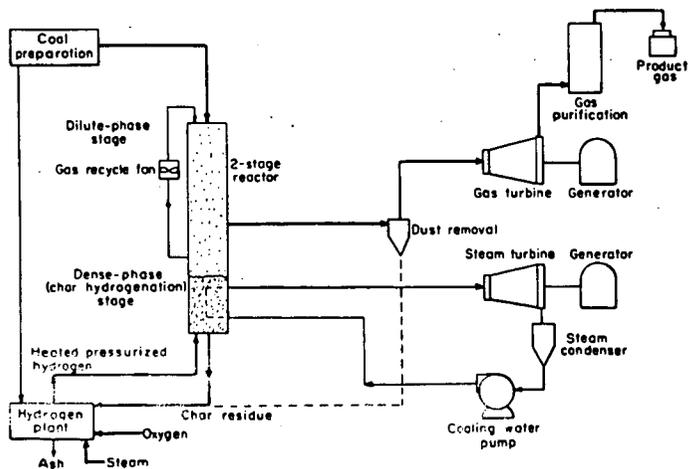


Figure 6.—Simplified flow diagram of the conceptual process.

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2. What are the kinetics of gasification and combustion?
3. What are the effects on gasification of -- feed stock, product gases, bed height, steam preheat, superficial steam velocity, ash content in melt and others?
4. Can coal ash be removed from the melt and the sodium recovered economically?

Some of the answers on gasification and the problems of getting the answers are presented in this report. Other topics will be discussed in subsequent reports.

II. EXPERIMENTAL

A. Apparatus

Most of the experimental work has been concerned with rates of gasification. The equipment for this centers about the reactor, which based upon earlier molten salt research, was made out of 2-inch I.D. Inconel 600 pipe, schedule 40, 26 inches long. A thermowell made out of $\frac{1}{4}$ -inch Inconel tubing entered at the bottom of the reactor. A $\frac{1}{4}$ -inch Inconel tube for steam and nitrogen entered from the top and extended to within $\frac{1}{2}$ inch of the bottom of the reactor. Also affixed to the top of the reactor was a $\frac{1}{2}$ -inch pipe with two quick opening ball type valves which served as a lock hopper for introduction of the carbonaceous solid as 12/20 mesh material. Gases exited near the top of the reactor into $\frac{1}{4}$ -inch pipe which connected to a 4-way tee through which a horizontal and a vertical drill sealed by Conax fittings could be employed to keep the exit line open. A water condenser was followed by a separator, a back pressure regulator, sample taps for gas chromatography, and a wet test meter.

Water was pumped using a Ruska positive displacement pump or Lapp diaphragm LS-10 and 20 pumps. This water with a nitrogen sweep went into a 40-inch long steam generator made out of 1-inch pipe and appropriately wound with heating wire. A superheater, made out of 20 feet of $\frac{1}{4}$ -inch tubing in a coil 10 inches long, employed a 12-inch long furnace. The outlet was connected to the $\frac{1}{4}$ -inch tubing that went internally to the bottom of the reactor. All exposed piping from the generator to the reactor and the hopper to the reactor was wound with covered resistance wire. Nitrogen and other gases were delivered with conventional equipment through calibrated rotameters. The 90% steam-10% nitrogen stream was normally fed at 0.5 ft/sec superficial gas velocity in the reactor.

A 24-inch long Kanthal furnace of 2.75-inch diameter served to heat the reactor. All thermocouples were chromel-alumel. Multiple point recorders were used. Gases were analyzed using a partitioner

to obtain N_2 , CO_2 , CO and hydrogen by difference. Mass spectrometry and other gas chromatography equipment were utilized when necessary.

B. Procedure

Operation consisted in introduction normally of 414 grams of pure, dense sodium carbonate which was melted and brought to the appropriate temperature with a flow of nitrogen through the steam inlet. This amount of molten salt measured four inches in depth under quiescent conditions. Steam rate was then set and the carbonaceous solid introduced. Sufficient solid was charged, based upon its total carbon content, to give 4% by weight of carbon in the melt initially. Collection of an aliquot of the gas stream was made to get the average composition for the first five minutes. Product gas was analyzed at intervals of five and ten minutes until the run was terminated. Total carbon gasified per five minute or other interval was calculated and the percent carbon remaining at each time reading was used to plot first-order kinetics.

First-order kinetics was found to satisfy the data at least to 50% carbon consumption and in many of the runs to 90%. Although some deviations have occurred, it has been found that this serves as an excellent method for interpretation of the data. From the half life, the specific reaction rate constant is obtained. In order to give this more illustrative significance, it has been converted into pounds of carbon gasified per hour per cubic foot of molten salt charged when 4% carbon is present in the melt.

High volatile bituminous coal from Island Creek No. 27 mine, Holden, West Virginia, was used. The proximate analysis was: 1.31% water, 37.3% volatile matter, 57.6% fixed carbon and 3.8% ash. The ultimate analysis, on a dry basis, was 83.6% carbon, 5.14% hydrogen, 1.48% nitrogen, 0.66% sulfur, 5.27% oxygen and 3.85% ash.

III. RESULTS

This report presents the initial studies considered of major importance to the overall process. It is planned that more intensive correlations of the data will be made at a later date.

A. Gasification Studies -- Effect of Variables

1. Temperature

The gasification rate at atmospheric pressure at 0.5 ft/sec superficial gas velocity was determined for bituminous coal at three temperature levels. The results are shown in the following tabulation.

<u>Temperature - °F</u>	<u>lb C Gasified/hr/CF</u>
1740	6.5
1840	15.2
1940	33

The jumps in gasification rate with increasing temperature are high and give an apparent activation energy of 50 kilocalories.

2. Pressure

The effect of steam pressure was determined with 30% steam in nitrogen at 1 atmosphere and with 90% steam in nitrogen at 1, 2, 3, 4 and 10 atmospheres. The data have been obtained from runs using bituminous coal, cokes derived from this coal by coking to 1110°F (Coke II) and to 1740°F (Cokes III and IV). Initial runs were made at 1840°F but the high gasification rates decreased the accuracy as shown by scatter in the points for the top curve in Figure 1. Dropping the melt temperature to 1740°F gave an excellent series of points as depicted in the bottom curve of Figure 1. All these runs were made at 0.5 ft/sec superficial gas velocity with a 4-inch bed of molten sodium carbonate and at an initial concentration of 4% carbon in the bed.

There appears to be a linear relationship between the logarithm of the rate and of the steam pressure above one atmosphere which allows a reasonable extrapolation to the desired commercial pressure of 400 psi. For the conditions given, rates of 35 and 66 pounds of carbon gasified per hour per cubic foot of melt at 1740°F and 1840°F, respectively, appear possible at 400 psia. Runs at higher pressures will be made in a pilot plant unit now being designed.

3. Bed Height

The effect of the height of the molten salt bed on the kinetics is of importance for commercial design which at the present calls for bed heights of 10 to 20 feet. Ideally for ease of design, one would like to have no effect of bed height on the kinetics of gasification. Physical limitations of the test equipment have allowed only a limited amount of evidence to be obtained in this area.

The effect of bed height was studied from 3 to 8 inches in the 2-inch diameter reactor. The results at 3, 4 and 6 inches are shown in Figure 2. Conditions for these runs are given in the figure. Adjustment of the position of the reactor in the furnace allowed identical temperature profiles to be obtained for 3 to 6-inch beds but not with the 8-inch high bed.

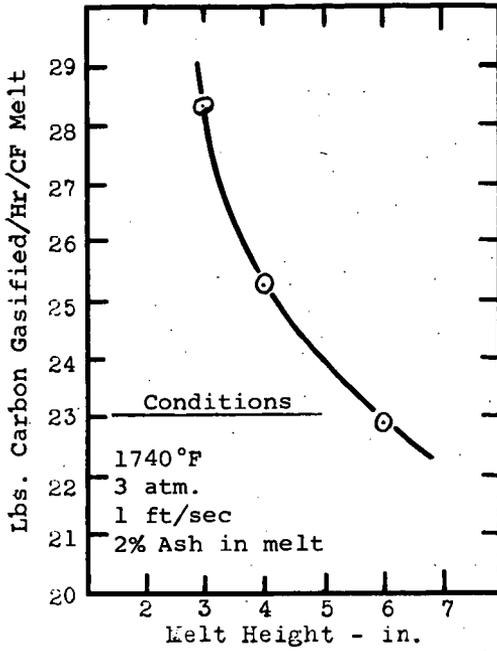


Fig. 2 - Melt Height vs. Rate

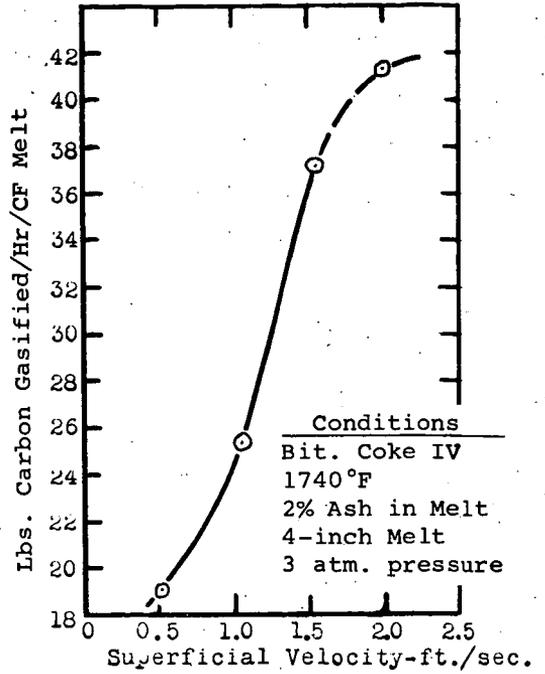


Fig. 3 - Velocity vs. Rate

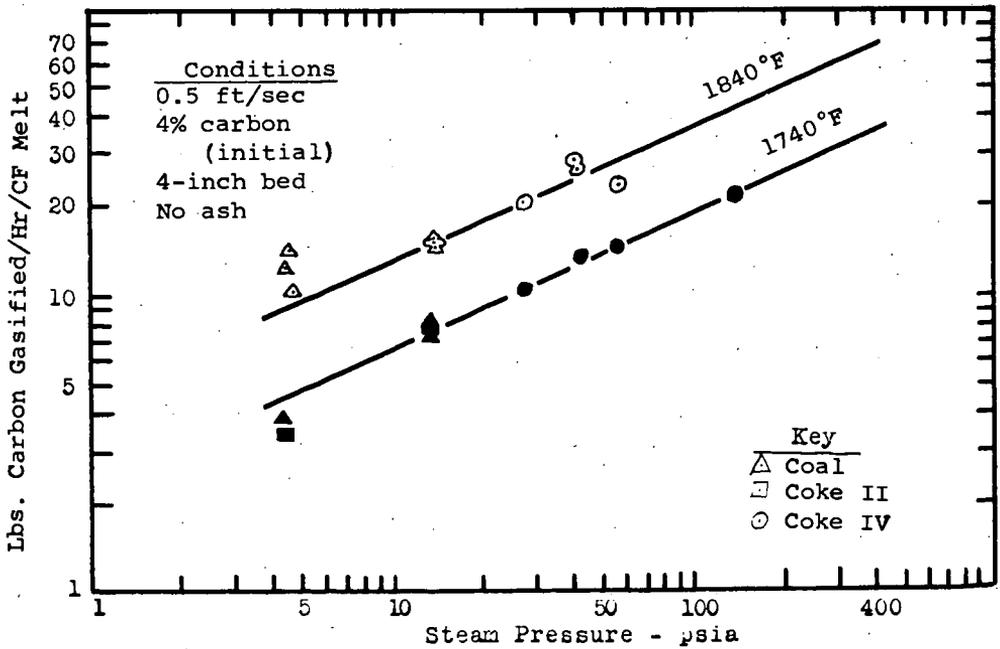


Fig. 1 - Effect of Steam Pressure on Gasification Rate.

A significant effect of bed height on gasification rate was obtained in the two-inch diameter reactor. It was concluded that this height effect must be due to poorer contact of carbon and steam with increasing height. Size of steam bubbles and distribution of carbon are the principal variables. The latter appears most suspect at this time. It is believed that larger diameter reactors will allow better mixing to be achieved and thus lessen the effect observed here. Further evaluation must await construction of pilot plant equipment.

4. Superficial Steam Velocity

Original adoption of 0.5 ft/sec superficial steam and nitrogen velocity was based upon simulated visual experiments with aqueous zinc chloride system of 2 gr/cc density and charcoal which showed excellent mixing at 0.25 ft/sec and higher velocities. The results of a separate study under gasification conditions are shown in Figure 3. The run at 2 ft/sec taxed the steam generating and condensing system as well as the heat supply from the Kanthal furnace. Temperature dropped from 1740° to 1710°F in the initial part of the run and required a correction back to 1740°F. Thus the dashed part of the curve in Figure 3 is an adjusted value. It does appear that the rate levels off around 2 ft/sec.

The velocity effect very definitely indicates that this system is sensitive to mixing. It appears to confirm the conclusions reached above in the study of bed height.

5. Ash Content in Melt

Normally, operation has been with non-ash containing melts of sodium carbonate because of greater ease of removal by washing and less corrosion on the Inconel reactors. In commercial operation, a steady state content of ash will exist in the melt, the concentration of which will depend on viscosity, degree of sodium recovery, etc. The presence of ash increases the tendency of the melt to froth which increases the interfacial area. Comparison of runs containing 10% bituminous coal ash in the melt with non-ash melts at two temperatures, 0.5 ft/sec velocity and 4-inch bed heights are shown in the following tabulation.

<u>Temperature, °F</u>	<u>Gasification Rate - lbs C/hr/CF</u>	
	<u>Non-Ash</u>	<u>10% Ash</u>
1740	7.5	13.6
1840	14.7	31.9

Approximately a twofold enhancement of rate appears due to the presence of ash. The rates of some runs at 1 ft/sec superficial velocity without ash are about equivalent to rates for runs with ash at 0.5 ft/sec. Some

runs at 1 ft/sec with ash present showed even slightly higher rates over similar runs without ash. Melts with ash have been maintained under carbon dioxide until near the start of the run to decrease the solubilization of ash components.

6. Miscellaneous

Some initial work on particle size of coal indicated the rate was unchanged in using 40/60 mesh rather than the usual 12/20 mesh coal particles. A poor test with -200 mesh material qualitatively indicated an enhanced rate. More work is planned for this area.

Only very little has been done on variation in feed stock. Bituminous coal and coke derived from this coal appear to react at about the same rate while Renner's Cove lignite showed double the rate. Rates are tabulated below for runs at atmospheric pressure, 0.5 ft/sec velocity and 4-inch melt height.

	Gasification Rate - lbs C/hr/CF	
	<u>1740°F</u>	<u>1840°F</u>
Bituminous Coal	6.5	15.2
Bituminous Coke IV	-	14.8
Renner's Cove Lignite	16.5	27.1

Some concern that gas temperature may have been below melt temperature was caused by the product gas composition indicating equilibrium for the water gas reaction was 200° to 300°F below the melt temperature. Several runs with superheated steam entering the reactor at 1500° to 1600°F had no effect on the rate of gasification. Equilibrium for the water gas reaction is not dictated by the melt temperature alone but by some temperature at the wall before cooling and fixing of the gas composition.

In a preliminary study of the effect of product gases upon rate, 30% steam in hydrogen was found to give about the same rate as 30% steam in nitrogen. Hence, hydrogen had no effect upon the kinetics at atmospheric pressure and 1840°F. Although 30% steam in carbon dioxide led to about a 25% decrease in rate, this is viewed with caution since the difference between two large numbers, 10.60 and 9.53 moles, represents the carbon gasified. Carbon monoxide added to steam (30%) reacted with the steam first.

It is planned that at some future date, studies of combustion, viscosity, sodium recovery and solid carryover will be presented to complete this initial picture.

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HYDROGASIFICATION OF PRETREATED COAL
FOR PIPELINE GAS PRODUCTIONB. S. LEE
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INTRODUCTION

There has been a long-standing need for an economic process to produce synthetic pipeline gas either as a supplement to or a substitute for natural gas. Development of a process for direct hydrogenation of coal to form an essentially methane gas has been in progress at IGT since 1955. Various facets of this hydrogasification process have been reported.^{3, 5, 6, 8, 9, 11, 12, 13} Process concepts were revised as experimental results became available.

In the current concept hydrogasification is carried out in two stages, with the gas flow countercurrent to the solids flow. The first stage, at temperatures of 1200°-1400°F, rapidly gasifies the most reactive fractions of the incoming coal, forming methane almost exclusively. The second stage, at 1700°-2000°F, gasifies the less reactive remainder from the first stage with hydrogen and steam to yield methane along with carbon oxides. The carbon residue from the second stage is used to generate the required hydrogen.

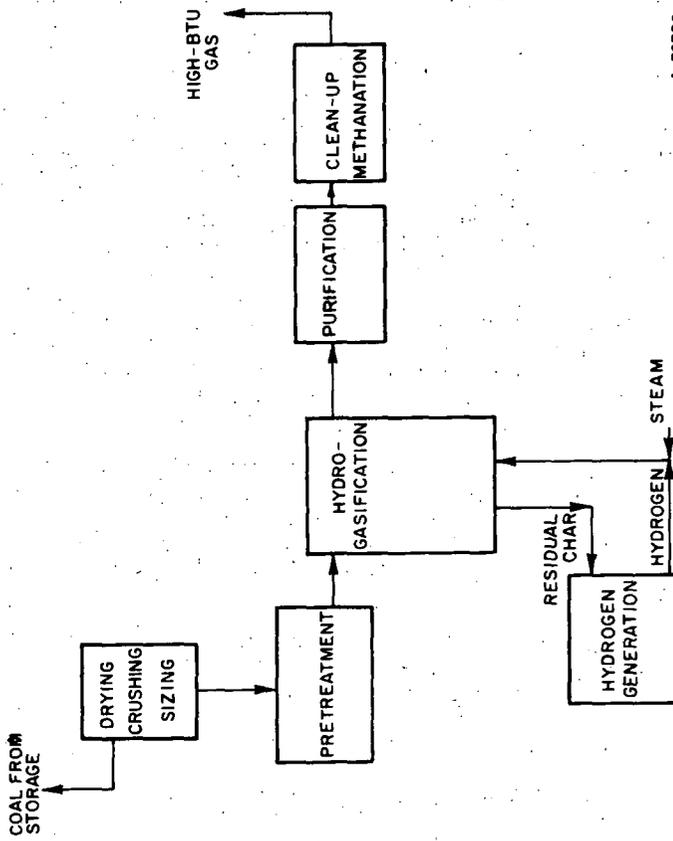
The low-temperature first stage permits high equilibrium methane concentration in the gas. The high-temperature second stage, on the other hand, favors the steam-carbon reaction for in situ hydrogen production.

The overall process is shown schematically in Figure 1. Raw coal is first rendered nonagglomerating in the pretreater, then is fed to the hydrogasifier. The residue is used to generate external hydrogen. The hydrogasifier effluent gas is first purified, then cleaned up in a methanator to reduce its carbon monoxide content and to upgrade the heating value. The entire system, except the pretreater, operates at 1000 psig or higher.

Although in our present program, coals ranging in rank from lignite to anthracite will be studied, we are focusing attention on high-volatile-content bituminous coals because the volatile matter in coal gasifies easily and produces a rich yield of methane. However, the high volatile content tends to make the coals strongly agglomerating when exposed to the hydrogasification conditions. As an operating necessity, the coals are pretreated by mild oxidation to destroy the agglomerating tendency. Such treatment is held to a minimum to preserve a maximum amount of the volatile matter for reaction.

The program objectives are:

1. To establish through operating experience the minimum pretreatment for coal.



A-76706

Figure 1. Block-Flow Diagram of IGT Coal Hydrogasification Process

2. To simulate in sequence the operation of the two-stage hydrogasification.
3. To study different modes of gas-solid contact, aiming at maximum throughput and controllable reaction rates.
4. To determine the extent of reaction equilibrium and kinetics limitations that relate to scale-up beyond this pilot unit.
5. To test and observe the mechanical operation of this high-pressure, high-temperature reactor system, in terms of materials of construction, instrumentation and control, special equipment, and safety.

EQUIPMENT AND PROCEDURE

The pilot reactor system has been described in detail.⁴ Briefly, referring to the schematic flowsheet in Figure 2, the balanced-pressure reactor is a 4-inch Schedule 40 pipe, made of Type 446 alloy steel, 21 feet in length of which 18 feet is electrically heated. The reactor is designed to withstand 2000 psig and 2200°F. Coal is stored in the hopper and fed to the reactor through a screw feeder. A screw at the bottom of the reactor discharges the residue to the receiver. Inlet gases are preheated in furnaces and enter the reactor at the bottom. Effluent gases leave at the top and are condensed, filtered, metered, sampled, then flared. Reactor operation is continuous within the limits of the 400-pound feed hopper capacity for pretreated coal. The entire system is tested at the pressure of the run before coal feed is charged to the hopper.

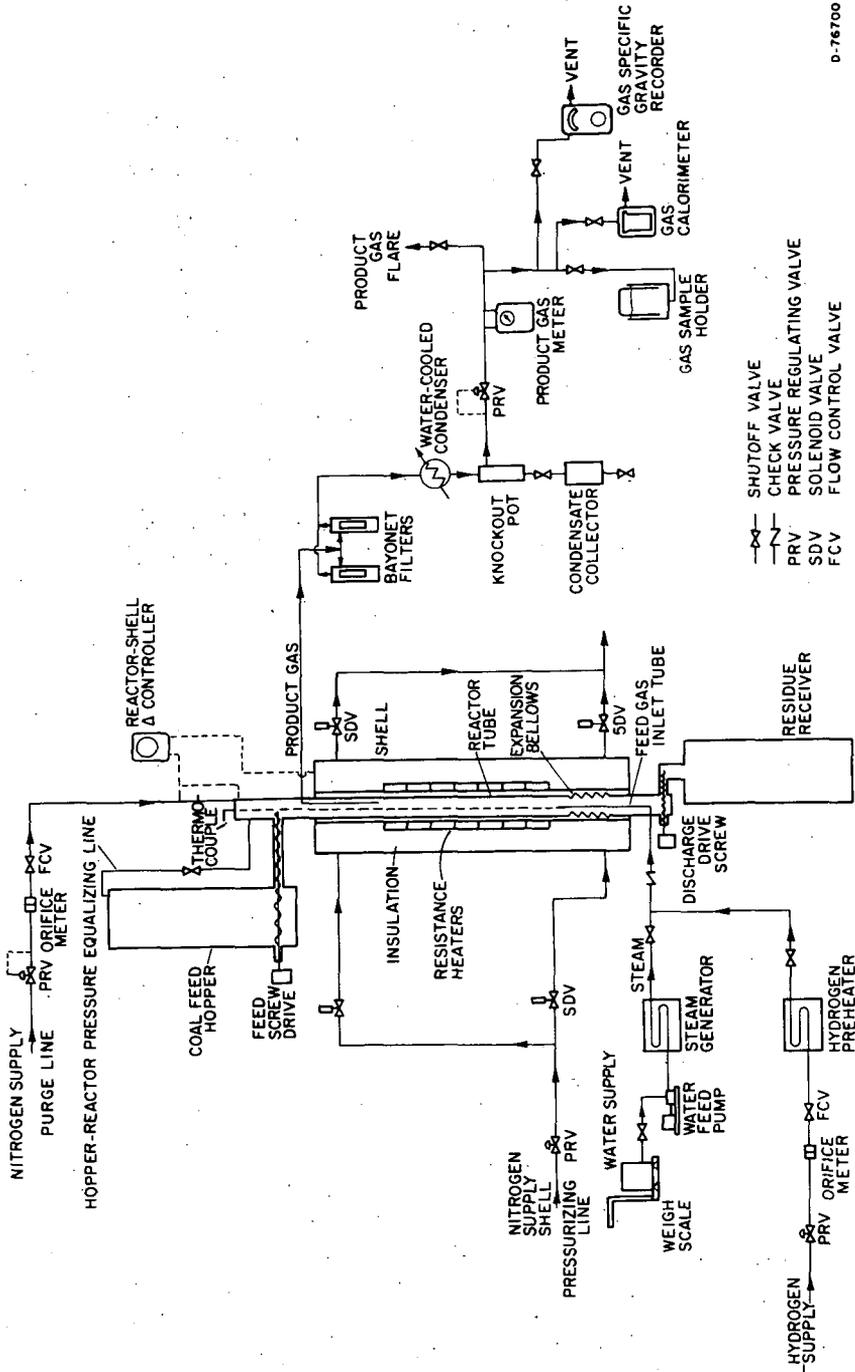
In simulating the two stages sequentially, pretreated coal is contacted in the low-temperature stage with a hydrogen-steam-natural gas mixture which approximates - except for the absence of carbon oxides - the gas leaving the high-temperature stage. The partially gasified coal is collected and fed against a hydrogen-steam mixture in the high-temperature stage.

By adjusting the feed and discharge rates of the coal, the reaction can be made to take place either in free fall, or in a combination of free-fall and moving-bed conditions. The moving bed was operated at a height of either 7 or 3.5 feet. Gas sample probes in the bed indicated reaction profile.

Coal feed rates ranged from 8 to 23 lb/hr. Gas rates corresponded to less than 0.1 ft/sec linear superficial velocity in order to stay below the threshold of fluidization and thus maintain true countercurrent gas-solid contact along the entire reactor length.

RESULTS AND DISCUSSIONS

Typical results of the hydrogasification tests are shown in Tables 1, 2, and 3. Reported coal residence times are based on measured bulk densities of the reactor residues and the coal bed volume. Time in free fall was negligible compared to that in the bed. Feed gas residence times are based on the flow rate at average bed conditions and coal bed volume. Time in the free-fall section is not included.



D-76700

Figure 2. SCHEMATIC FLOWSHEET FOR PILOT PLANT HYDROGASIFICATION SYSTEM

TABLE 2. SOLID PRODUCTS FROM HYDROGASIFIER

Coal Feed	Pre-treated Pittsburgh Coal				Partially Hydrogasified Pittsburgh Coal				Pre-treated Pittsburgh Coal				Partially Hydrogasified Pittsburgh Coal			
	HR-60	HR-61c	HR-65	HR-66	HR-66	HR-71	HR-76	HR-80	HR-87	HR-83	HR-84	HR-85	HR-89	HR-86	HR-87	
Run	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue		
Proximate Analysis, wt %																
Moisture	0.5	1.1	0.6	0.5	0.6	2.1	1.1	1.3	0.9							
Volatiles	26.5	23.0	25.0	25.0	25.0	61.6	72.5	62.4	61.3							
Fixed Carbon	61.4	68.6	63.5	63.5	63.5	77.6	61.6	72.5	72.5							
Ash	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0							
Ultimate Analysis (dry), wt %																
Carbon	70.5	68.5	71.7	71.7	71.7	76.9	73.0	71.8	71.8							
Hydrogen	3.77	2.42	3.73	3.73	3.73	4.04	3.37	3.83	3.83							
Nitrogen	0.36	0.27	0.28	0.28	0.28	0.37	0.31	0.31	0.31							
Oxygen	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0							
Sulfur	3.53	2.53	3.07	3.07	3.07	3.26	3.17	2.99	2.99							
Ash	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0							
Screen Analysis, USS, wt %																
+20	19.1	18.7	18.5	18.5	18.5	26.1	24.5	23.9	23.2							
+40	38.8	38.0	36.9	36.9	36.9	21.1	22.4	20.9	18.8							
+60	23.9	23.5	23.3	23.3	23.3	24.5	20.9	24.6	24.6							
+80	1.6	1.9	2.0	2.0	2.0	3.4	3.0	2.7	2.7							
+100	0.8	0.8	0.6	0.6	0.6	1.1	1.1	1.1	1.1							
+325	0.6	0.7	0.8	0.8	0.8	2.6	2.9	2.4	2.4							
+355	0.6	0.8	0.7	0.7	0.7	1.0	0.2	0.5	0.6							
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0							
Proximate Analysis, wt %																
Moisture	1.9	3.0	3.9	3.9	3.9	5.7	21.0	21.0	21.0							
Volatiles	23.3	24.9	25.5	25.5	25.5	31.3	24.5	24.5	24.5							
Fixed Carbon	62.4	74.9	65.5	65.5	65.5	77.4	68.5	77.4	77.4							
Ash	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0							
Ultimate Analysis (dry), wt %																
Carbon	70.6	72.8	79.9	73.2	73.2	78.2	81.8	76.4	76.4							
Hydrogen	3.68	1.37	3.68	3.68	3.68	3.86	3.87	1.21	1.21							
Nitrogen	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.76							
Oxygen	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85	8.85							
Sulfur	3.65	3.31	3.31	3.31	3.31	3.23	3.23	1.61	1.61							
Ash	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0							
Screen Analysis, USS, wt %																
+20	10.1	6.1	12.0	12.0	12.0	12.3	12.3	8.4	10.1							
+40	26.1	26.7	28.2	28.2	28.2	30.3	28.4	28.2	28.2							
+60	22.4	27.9	23.8	23.8	23.8	23.5	23.4	23.4	23.4							
+80	10.6	10.3	9.8	9.8	9.8	11.1	16.5	4.1	3.9							
+100	9.4	5.7	5.9	5.9	5.9	7.1	5.6	7.1	5.3							
+325	3.4	0.6	1.0	1.0	1.0	0.8	0.8	1.1	0.8							
+355	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6							
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0							
Proximate Analysis, wt %																
Moisture	1.1	0.7	0.9	0.9	0.9	1.1	1.2	2.0	2.0							
Volatiles	78.9	67.6	75.9	74.1	74.1	60.8	64.5	64.0	64.5							
Fixed Carbon	16.3	30.4	21.5	21.5	21.5	36.2	18.7	31.4	31.4							
Ash	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0							
Ultimate Analysis (dry), wt %																
Carbon	80.2	68.1	76.1	76.9	76.9	62.3	76.0	65.6	73.7							
Hydrogen	1.36	0.98	1.24	1.23	1.23	1.65	1.69	0.43	1.59							
Nitrogen	0.76	0.69	0.67	0.67	0.67	0.69	0.69	0.69	0.69							
Oxygen	2.03	2.57	1.84	1.84	1.84	2.22	2.06	1.10	1.57							
Sulfur	16.4	16.4	16.4	16.4	16.4	16.4	16.4	16.4	16.4							
Ash	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0							
Screen Analysis, USS, wt %																
+20	1.4	4.0	15.7	11.2	11.9	4.4	7.7	6.5	12.3							
+40	24.5	21.2	20.5	20.6	20.6	22.2	27.0	27.0	27.0							
+60	11.5	11.1	4.4	6.1	10.3	12.7	12.9	11.6	10.7							
+80	10.5	6.4	1.7	2.1	4.9	4.7	2.6	4.7	4.9							
+100	10.5	6.4	1.7	2.1	4.9	4.7	2.6	4.7	4.9							
+325	4.6	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0							
+355	4.6	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0							
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0							

Table 3. LIQUID PRODUCTS FROM HYDROGASIFIER

Coal Feed	Pretreated Pittsburgh Coal											
	HT-50	HT-51e	HT-52	HT-53	HT-71	HT-78	HT-81	HT-84	HT-85	HT-86	HT-87	HT-88
Run	0.126	0.734	0.652	0.668	0.554	0.598	0.330	0.235	0.379	0.1127	0.379	0.1127
Weight, lb/lb coal												
Composition, wt %												
Oil	64.92	92.98	90.13	94.58	94.79	92.02	95.26	92.90	95.28	89.84	95.28	89.84
Composition of Oil Fraction, wt %	35.08	7.02	9.57	5.42	5.21	7.98	3.74	7.70	4.72	10.16	4.72	10.16
Carbon	87.4	92.0	88.2	87.8	85.5	85.2	84.8	87.4	82.1	86.4	82.1	86.4
Hydrogen	7.18	6.50	7.02	6.21	6.25	6.19	6.57	6.18	6.15	6.93	6.15	6.93
Total	94.58	98.50	95.25	94.11	91.75	91.69	91.37	93.58	88.25	93.35	88.25	93.35
Carbon in Oil Fraction, wt % of carbon in coal	6.05	6.56	7.68	4.67	2.56	5.12	1.48	2.17	2.00	1.36	2.00	1.36

Coal Feed	Partially Hydrogenated Pittsburgh Coal						Partially Hydrogenated Ohio Coal		
	HT-59	HT-60	HT-67	HT-66	HT-61	HT-72	HT-77	HT-81	HT-82
Run	0.747	0.194	0.1081	0.1764	1.198	0.119	0.0774	0.582	0.155
Weight, lb/lb coal									
Composition, wt %									
Oil	100.0	100.0	100.0	100.0	97.0	100.0	100.0	91.94	100.0
Composition of Oil Fraction, wt %								8.46	
Carbon	--	--	--	--	3.0	--	--	86.4	--
Hydrogen	--	--	--	--	6.5	--	--	6.51	--
Total	--	--	--	--	91.5	--	--	92.91	--
Carbon in Oil Fraction, wt % of carbon in coal	--	--	--	--	4.01	--	--	5.77	--

Minimum Coal Pretreatment

Two high-volatile-content bituminous coals were tested, one from the Pittsburgh No. 8 seam (Ireland mine) and the other from the Ohio No. 6 seam (Broken Arrow mine). Most of the work to date has been with the former. The proximate and ultimate analyses of these two coals are shown in Table 4. These coals were pretreated to various extents and then hydrogasified. Using volatile matter content as an index of severity of pretreatment, we found that pretreated coal with 24-26% volatile matter can be processed without agglomeration. Raw coal was tested but it swelled badly during the reaction and stuck to the reactor to cause bridging. It is entirely possible that in larger size reactors in which the coal feed would not contact reactor walls immediately, coals with less pretreatment - or even raw coal - could be fed successfully. However, we consider our ability to feed pretreated coal with as much as 24-26% volatile matter a significant achievement. Adjustment of feed tube size, length, and location; the amount of nitrogen purge gas through the tube; and the start-up sequence are factors that were learned through experience.

Two-Stage Simulation

The stage-by-stage simulation procedure used is realistic except for the fact that the partially gasified coal is fed to the second stage at ambient temperature instead of between 1200° and 1400°F. Since hydrogen represents the largest share of the total pipeline gas cost, practically all the runs were conducted at the minimum hydrogen/coal ratio that would produce a total carbon gasification of about 50%. At this degree of gasification, sufficient residual carbon would be available for generating the necessary hydrogen. These figures resulted from an overall system analysis based on existing data on equilibrium, kinetics, and heat and material balances.

Key results obtained in two-stage simulations are summarized in Figure 3a with pretreated Pittsburgh seam coal, and in Figure 3b with pretreated Ohio seam coal. Product gas analyses were adjusted to a nitrogen-free basis because of the high nitrogen purge rates actually used in the tests. The purge gas was needed to prevent hot reactor gases from entering the coal feed tube.

High concentrations of unreacted hydrogen in the product gas from the low-temperature stages limited the heating value to about 700 Btu/SCF. To obtain a high-Btu gas (900 Btu/SCF) requires catalytic methanation of the carbon oxides. Note the absence of carbon oxides in the feed gas to the first stage. Because of the low temperature in the first stage, no steam-carbon reaction is expected. Thus, CO is considered an inert insofar as methane formation is concerned. Therefore, to simplify preparation of the simulation gas mixture, CO was not included in this feed. This assumption appears valid, judging from the low carbon oxide concentration in the first-stage effluent. The amount measured came from the organic oxygen in the coal rather than from the steam-carbon reaction.

Steam, however, appears to play an active role in the low-temperature gasification. Two runs were made, one with a steam-natural gas-hydrogen mixture and the other with a nitrogen-natural gas-hydrogen mixture. Significantly greater amounts of carbon oxides were formed and significantly less water was released from the coal when steam was used. Steam, then, seems to suppress the release of organic

Table 4. ANALYSES OF HIGH-VOLATILE-CONTENT
BITUMINOUS COALS

Seam Mine	Pittsburgh No. 8 Ireland	Ohio No. 6 Broken Arrow
Proximate Analysis, wt %		
Moisture	1.0	1.0
Volatile Matter	35.9	39.6
Fixed Carbon	51.8	53.6
Ash	<u>11.3</u>	<u>5.8</u>
Total	100.0	100.0
Ultimate Analysis (dry), wt %		
Carbon	71.1	74.1
Hydrogen	4.95	5.41
Nitrogen	1.18	1.39
Oxygen	7.35	9.42
Sulfur	4.03	3.87
Ash	<u>11.39</u>	<u>5.81</u>
Total	100.00	100.00
Particle Size, USS		
(As prepared for pretreatment)	-16+80	-16+80

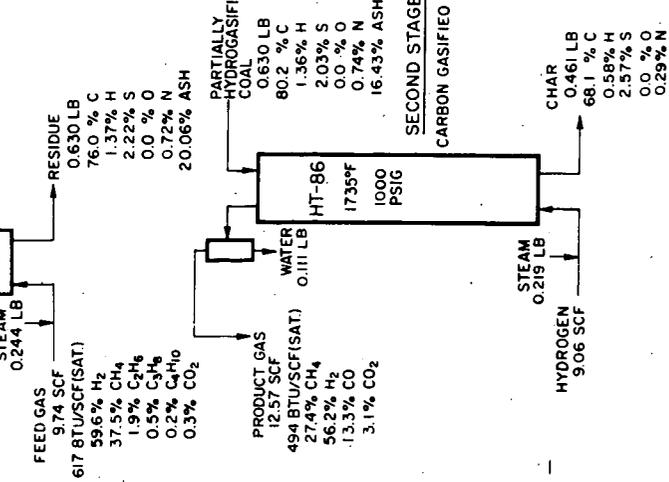
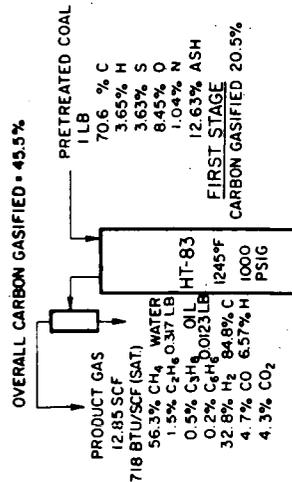
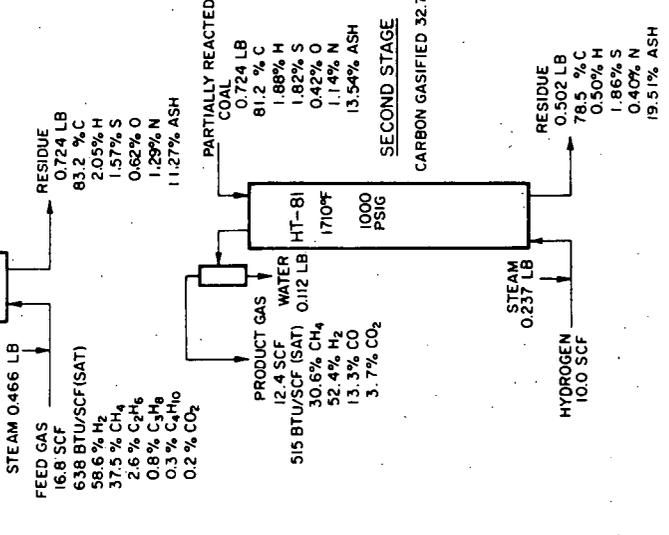
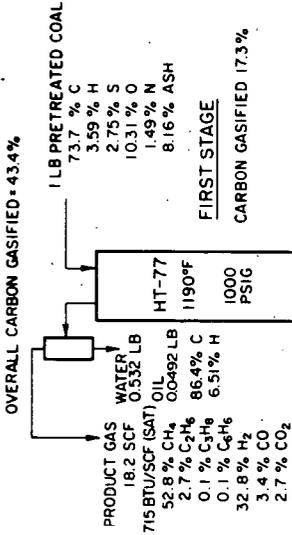


Figure 3a. STAGE-BY-STAGE SIMULATION IN
Figure 3b. STAGE-BY-STAGE SIMULATION IN

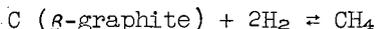
oxygen from coal as water, but forces the oxygen to leave as carbon oxides. This phenomenon seems plausible from the mass action standpoint. From a process standpoint, the release of organic oxygen in coal as carbon oxides is more desirable than as water. In the latter case, hydrogen (either from coal or from external sources) is lost by being combined with the oxygen to form water. In contrast, when the oxygen is released as carbon oxides, these can be converted to more hydrocarbon by subsequent catalytic methanation.

Methane Formation

Equilibrium

It has been well established that the hydrogenation of the volatile matter in coal proceeds very rapidly,¹² and yields methane concentrations higher than the equilibrium value in a β -graphite-hydrogen system. This excess is conveniently attributed to a greater-than-unity coal activity in reference to β -graphite activity. In fact, of course, the hydrogenation of the reactive carbon groups proceeds by splitting off the carbon chains and functional groups rather than by reacting with graphitic carbon. Such reactions lead to methane formation because methane is the predominant stable hydrocarbon at the temperature and pressure in question. The first-stage hydrogasification demonstrates this type of reaction as shown, for example, by the predominance of methane versus other hydrocarbons or carbon oxides in the effluent gas (Figure 3a).

Figure 4 presents the calculated "equilibrium ratio" obtained from the pilot plant tests as a function of the maximum bed temperatures. The curve represents true equilibrium ratio for the reaction:



We note the many runs yielding equilibrium ratios higher than the curve. The group of points below the curve between 1450° and 1550°F came from runs in which a high hydrogen/coal ratio was used, resulting in low methane concentration.

We found the initial gasification so rapid that 20% of the carbon was gasified in merely free-falling through a distance of 18 feet. There appears to be little equilibrium hindrance in view of the mechanism of methane formation discussed above. However, once the reactive carbon is gone, the remaining fixed carbon reacts much more slowly in the second stage. Here we check the approach to β -graphite equilibrium to see if the coal, after the first stage, still has sufficient reactive carbon left to show activity greater than unity. Since methane formation is exothermic, from the process standpoint, the more methane that is formed in the second stage, the more heat there would be available to furnish the endothermic heat for the steam-carbon reaction, which, in turn, would produce hydrogen *in situ* and reduce the external hydrogen requirement. With partially gasified Pittsburgh No. 8 seam coal, we have so far observed a carbon activity between 1 and 2 at 1700°-1950°F.

Reaction Rate

We compared the integral methane formation rates from our pilot plant tests with those reported by others.^{1, 2, 6, 14} To do so

on the same basis, we took the reaction rate to be pseudo-first order with respect to the hydrogen partial pressure. The calculated reaction rate constant for each run is plotted against carbon gasification in Figure 5. Several observations can be made:

1. The rate of methane formation for pretreated Pittsburgh coal is not slowed by the presence of methane in the feed gas. This is in agreement with Zielke and Gorin¹⁴ in their study of hydrogasification of Disco char.
2. The pretreated coal is quite reactive. For example, at 25-30% carbon gasification with steam-hydrogen mixtures, the rate constant is more than twice that reported by Feldkirchner and Linden⁶ in reacting low-temperature bituminous char with hydrogen. The greater reactivity is most likely attributable to the higher volatile content of our pretreated coal (24-26%) than that of their char (17%).
3. Partially hydrogasified coal, upon further reaction in the high-temperature second stage, gave rate constants quite similar to those obtained with Disco char¹⁴ and residual Australian brown coal,¹ both containing very little volatile matter.

Steam-Carbon Reaction

The reaction $C + H_2O = CO + H_2$ was significant only at temperatures above 1700°F, and was found to increase with temperature. For example, at 1695°F (Run HT-80), 50% of the feed steam decomposed, but at 1825°F (Run HT-72), 70% was decomposed. Carbon oxides formation was related directly to the steam fed and to the steam decomposition. As much as 5.5 SCF of carbon oxides per pound of coal were produced at the maximum 70% steam decomposition. With little or no feed steam decomposition, carbon oxides formation was about 1 SCF or less per pound of coal. In the low-temperature first stage, the presence of steam in the feed gas is responsible, through the laws of mass action, for converting a major fraction of the oxygen in coal to carbon oxides. This oxygen is converted to water when steam is omitted from the feed, e.g., when only hydrogen is fed.

The rate at which the steam-carbon reaction proceeds is highly temperature-dependent,⁹ requiring heat above 2000°F to approach equilibrium.¹¹ Since hydrogasification tests are conducted at less than 2000°F in order to preserve the methane formed, the carbon-steam reaction is expected to be substantially removed from equilibrium. This fact is shown by Figure 6 where calculated "equilibrium ratios" are plotted against maximum bed temperature. The curve represents true equilibrium for comparison.

The carbon-steam reaction is important from the process standpoint not only as a source of generating in situ hydrogen, but also as a temperature controller. When pure hydrogen is the gasifying medium, the strong heat release by the methane-forming reaction causes runaway temperatures. In a hydrogen-steam mixture, this released heat is absorbed by the carbon-steam reaction, thereby stabilizing temperature.

Reaction Profile

To gain some insight into the path of reaction in free-fall or moving-bed zones, gas sample probes were located at several levels

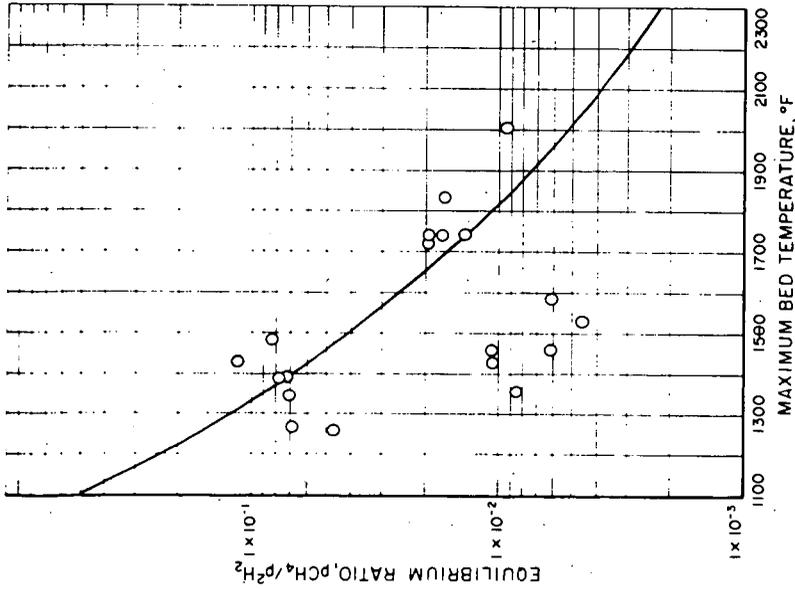


Figure 4. APPROACH TO CARBON-HYDROGEN REACTION EQUILIBRIUM FOR PRETREATED PITTSBURGH SEAM BITUMINOUS COAL

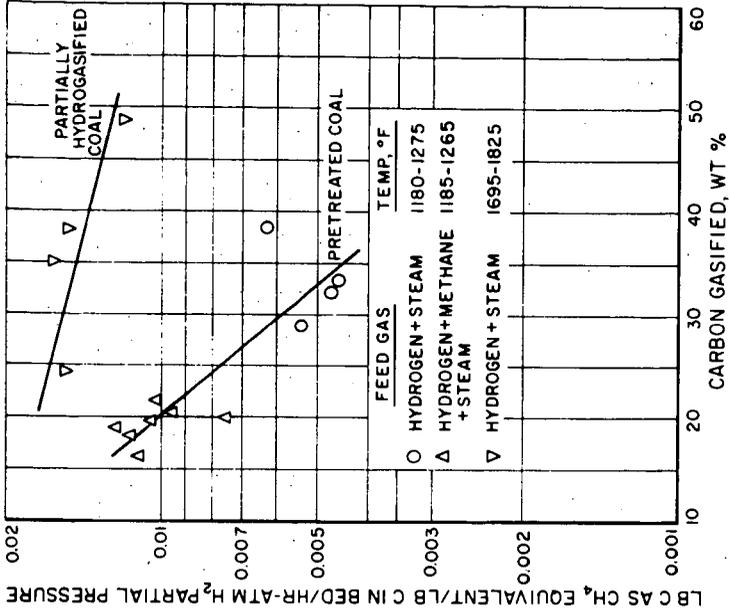


Figure 5. INTEGRAL METHANE FORMATION RATE FOR PRETREATED PITTSBURGH SEAM BITUMINOUS COAL

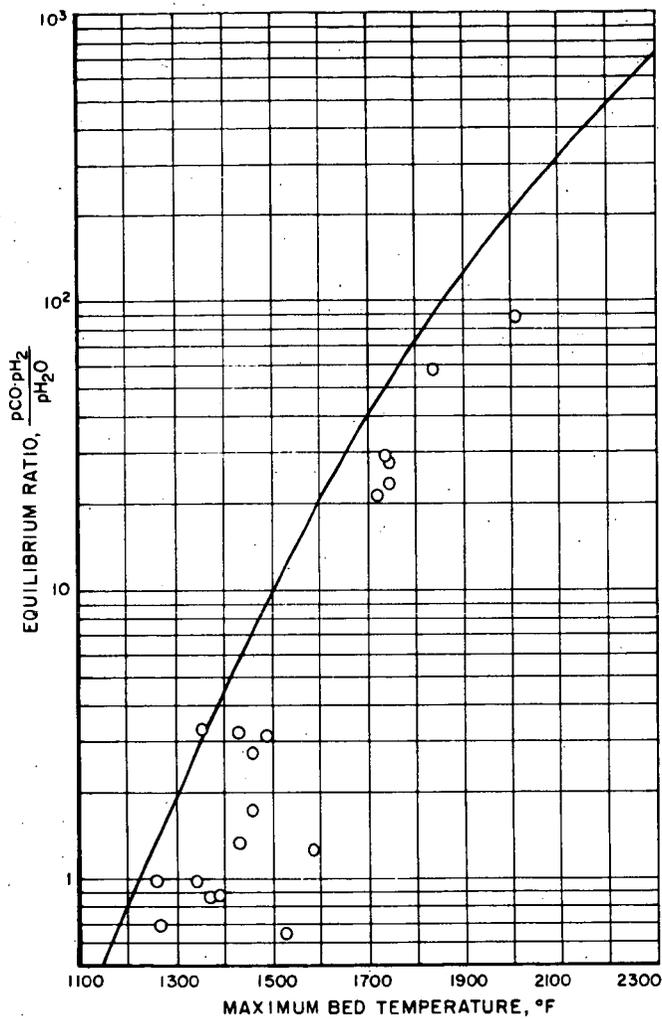


Figure 6. APPROACH TO STEAM-CARBON REACTION
EQUILIBRIUM FOR PRETREATED
PITTSBURGH SEAM BITUMINOUS COAL

in the bed. Compare (Table 5) the probe gas analyses from a low-temperature run, HT-67, and a high-temperature run, HT-72. Both runs were made with a 7-foot-deep moving bed. Note that in the high-temperature test, the reaction was practically complete in the lower half of the bed, with very little reaction in the upper half of the bed and in the free-fall zone above the bed. On the other hand, in the low-temperature test, the reverse was true: The bulk of the reaction took place in the free-fall zone and at the top of the bed, with very little reaction in the rest of the bed. It follows then that at both temperatures the bed height could be reduced to 3.5 feet without any loss of gasification. This is in fact the case as shown in Table 5 by the probe samples from HT-86, a high-temperature run using a 3.5-foot-deep bed.

The high-temperature reaction is apparently equilibrium-limited; it attains its limit in a relatively short contact time, in a short bed. The low-temperature reaction is extremely rapid, requiring only a matter of seconds to complete. The reactive portion of coal, discussed by Wen and Huebler,¹² is quickly gasified, after which the remainder of the carbon is not reactive at the low temperature. In view of these facts, a likely hydrogasifier configuration would incorporate a low-temperature free-fall zone followed by a shallow high-temperature stage.

ACKNOWLEDGMENT

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Fluid-Bed Gasification of Pretreated Pittsburgh-Seam Coals

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INTRODUCTION

An efficient coal gasification process operating at 800°-1,000° C and at pressures of 20-30 atmospheres is desirable for producing a synthesis gas which can be used to make a high-Btu gas. At these temperatures considerable methane is produced and less oxygen is consumed than at the higher temperatures of 1,100°-1,200° C used generally in entrained gasification systems. A fluidized bed can be operated at the lower temperature with sufficient residence time to obtain high conversion of the coal. Because most of the coals found in the East and Midwest are caking, they must be treated to destroy their caking properties before they can be used in a fluidized bed. The purpose of these tests was to investigate an integrated pretreatment and gasification system whereby the pretreated coal would be processed in a fluid-bed gasifier at conditions to produce a synthesis gas with high methane content.

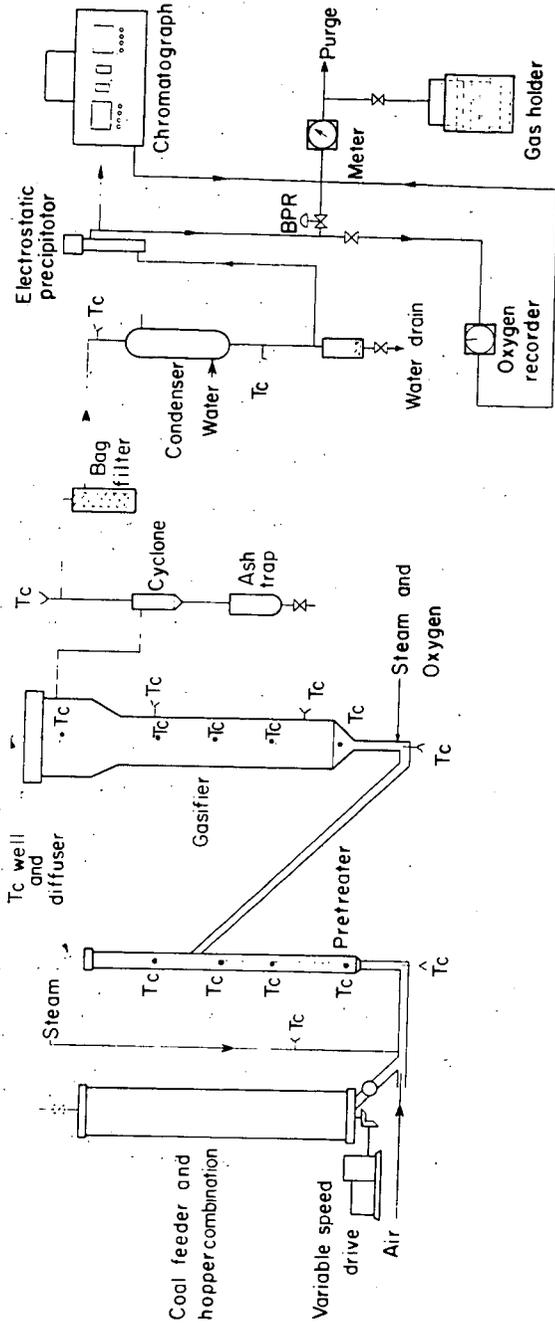
Two methods of pretreating caking coal in a fluid bed to produce a free-flowing char have been developed--one at high temperature and one at low temperature. In the high temperature treatment, ²/₃ coal is fluidized in steam plus air or oxygen at 430° C for 5-10 minutes. The oxygen-to-coal ratio is about 0.4 SCF per pound. In the low temperature treatment, ¹/₁ coal is fluidized in air at 240° C for 30-40 minutes. The oxygen-to-coal ratio is about 2.4 SCF per pound.

EXPERIMENTAL PROCEDURE AND RESULTS

Equipment and Method of Operation

Briefly, the technique used in the experiments was to test the treated coals in the gasifier to find if the coals were sufficiently noncaking to use in the gasifier. If the gasification were operable, then the pretreater and gasifier would be operated in series starting with a raw coal feed. When the coal was pretreated using steam plus oxygen, the gas from the pretreater, as well as the pretreated coal, would be sent to the gasifier.

The equipment used is shown in figure 1. In the usual method of operation, raw Pittsburgh-seam coal from the Bruceton mine (70 percent through 200 mesh with coarser than 35 mesh removed) is fed into a fluid-bed pretreater, 1 inch diameter by 30 inches long, operated at



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Figure 1. Fluid-Bed Pretreater and Gasifier System.

either 450° or 260° C. The fluidizing gas is steam plus air (or oxygen). The products, gas, tars, and treated coal, pass from the top of the pretreater and flow with additional steam (or steam plus oxygen) into the fluid-bed gasifier (3 inches diameter by 30 inches long, topped by an expanded section 6 inches in diameter by 12 inches long). The product gas and coal fines pass to a cyclone and bag filter to remove the dust, then through a condenser and electrostatic precipitator to remove water plus tar, and finally to a gas meter. An inline chromatograph analyzes the gas for six components every 20 minutes. An oxygen analyzer continuously monitors the product gas. The range of process variables, such as gas fluidizing velocity and coal-feed rate, is limited. An increase in the coal feed rate decreases the residence time of the coal in both the pretreater and gasifier. The superficial gas velocity for most tests was about 0.25 foot per second.

Tests with Pretreated Coals

The first tests in the gasifier were made with coals which were pretreated in a separate unit so the free-swelling indices (FSI) and other coal properties could be determined. Pittsburgh-seam coal was used in all tests. The tests were made with high temperature treated coals (HT) having indices of 2, 1, and noncaking, respectively, and low temperature treated coals (LT) with indices of 1-1/2 and noncaking, respectively. The gasifier was operated at 2-1/2 atmospheres and 871° C with a coal feed rate of 0.4 pound per hour. Table 1 shows the analysis of the coals and the method of pretreatment.

The main difference between the LT and HT coals is that the loss of volatile matter is greater in the HT coals (35.6 percent in the raw coal and 26.0 percent in HT-440), and the oxygen content is greater in the LT (8.1 percent in the raw coal and 11.8 percent in LT-56). HT coals with an FSI of 2 and the LT coals with an FSI of 1-1/2 were caked in the reactor, while the coals with FSI of 1 or less were operable.

The main difference in gasifying LT and HT coals is that the HT coals yield more gas and are less likely to agglomerate in the gasifier. Test 61 made with HT-2 coal had a yield of 22 SCF (CO₂- and N₂-free) per pound compared to 17 in tests 58 with LT-56 coal. The temperature was held constant in both tests, but 1/2 SCFH of oxygen had to be fed to the gasifier in test 58 to prevent caking. In tests 62 and 59, oxygen was fed to the gasifier. The HT-2 coal yielded 23 SCF per pound compared to 22 for LT-56, even though the LT coal had greater carbon conversion. The quality of the product gas was about the same in all the above tests. (See Table 2.)

TABLE 1.- Analyses of pretreated coals used in the gasifier

	Raw	Raw					
	Coal ^{1/}	Coal ^{1/}	HT-400 ^{2/}	HT-440 ^{3/}	HT-1 ^{4/}	LT-55 ^{5/}	LT-56 ^{6/}
	D-2	D-1					
Moisture	1.5	1.5	0.5	0.8	0.8	0.9	0.9
Volatile matter	36.6	35.6	30.4	26.0	22.7	34.0	31.2
Fixed carbon	53.2	56.5	62.2	67.1	69.3	56.2	57.5
Ash	8.7	6.4	6.9	6.1	7.2	8.9	10.4
Hydrogen	5.1	5.2	4.8	4.5	4.1	4.7	4.2
Carbon	75.2	77.4	77.8	78.8	78.2	73.6	70.9
Nitrogen	1.5	1.5	1.4	1.5	1.7	1.5	1.4
Oxygen	8.1	8.4	8.0	8.1	7.8	9.8	11.8
Sulfur	1.4	1.1	1.1	1.0	1.0	1.5	1.3
FSI	8	8	2	1	NC ^{7/}	1½	NC ^{7/}

- ^{1/} Bruceton coal; 70 percent through 200 mesh with coarser than 35-mesh removed.
- ^{2/} Pretreated at 400° C; O₂/coal ratio = 0.4 SCF/lb. Residence time is 10 minutes.
- ^{3/} Pretreated at 440° C; O₂/coal ratio = 0.4 SCF/lb. Residence time is 30 minutes.
- ^{4/} Pretreated at 440° C; O₂/coal ratio = 1.1 SCF/lb. Residence time is 30 minutes.
- ^{5/} Pretreated at 240° C with air; O₂/coal ratio = 2.4 SCF/lb. Residence time is 30 minutes.
- ^{6/} Pretreated at 250° C with air; O₂/coal ratio = 2.4 SCF/lb. Residence time is 30 minutes.
- ^{7/} Noncaking.

Pretreater and Gasifier in Series

In these tests the pretreater and gasifier were operated in series; the products from the raw coal pretreatment--the char, tars, and gases--were sent directly to the gasifier. The gasifier operated satisfactorily with no agglomeration of the coals. Table 2 shows a comparison of the gasification of the two types of treated coal. The coals pretreated at 450° C yielded more product gas than those treated at 260° C. When no oxygen was fed to the gasifier, the HT coal (test 36) yielded 22 SCF of H₂+CO+CH₄, compared to 18 SCF per pound coal from the LT coal (test 60). When oxygen was fed to the gasifier the results were similar; 21 SCF per pound in test 33 compared to 19 for test 63.

TABLE 2.- Conditions of operation and results of tests using pretreated coals in the fluid-bed gasifier; pressure is 2½ atmospheres

Test No.	61	58	62	59	36	60	33	63
Coal	HT-2	LT-56	HT-2	LT-56	Raw coal D-1	Raw coal D-2	Raw coal D-1	Raw coal D-2
Input								
Steam, SCFH	14	15	15	15	15	13	14	17
Oxygen, SCFH, pretreater	0	0	0	0	1.0	1.6	1.0	1.6
Oxygen, SCFH, gasifier	0	0.5	2.5	2.5	0	0	1.4	1.1
Nitrogen, SCFH	9	10	10	10	10	10	10	10
Coal, lb/hr	0.38	0.40	0.38	0.36	0.37	0.36	0.36	0.36
Temperature, °C								
Pretreater	-	-	-	-	450	261	450	258
Gasifier, avg	868	871	872	873	860	869	857	863
Gasifier, max	875	874	877	878	874	877	873	866
Oxygen/coal, SCF/lb	0	1.3	6.6	6.3	2.7	4.5	6.7	7.5
Steam/coal, SCF/lb	37	38	41	42	41	36	39	47
Carbon conversion, pct	51	43	77	83	51	54	68	73
Steam conversion, pct	-	-	-	-	20	-	17	-
Product gas, ^{1/} SCF/lb coal	22	17	23	22	22	18	21	19
Product gas ^{2/} pct								
H ₂	59	55	45	44	55	48	45	42
CH ₄	3	3	2	2	4	3	3	2
CO	20	22	25	26	22	24	29	24
CO ₂	18	20	28	28	19	25	23	32

^{1/} Nitrogen- and CO₂-free.

^{2/} Nitrogen-free.

These tests show that pretreatment at 450°-460° C with less oxygen is superior to pretreatment at 250° C, not only in increased gas production, but also because there is less likelihood of the coal caking in the gasifier. There is more CO₂ made from the coals with the 250°-260° C treatment because of oxygen added to the coal during pretreatment as shown in table 1. This evolution of CO₂ from the LT coal was also noted in earlier tests.^{1/} These present tests also show more gas is produced in the 2-stage process with raw coal feed than in the gasification of a coal pretreated separately considering the 15-20 percent loss of coal in pretreatment.

Table 3 shows some results in tests where oxygen, coal, and steam rates were varied to give a range of operability. At a constant coal feed rate, an increase in the oxygen rate from 2.4 to 9.1 SCF per pound coal increased the conversion from 46 to 80 percent and also the product gas (H_2+CH_4+CO) yield from 19 to 23 SCF per pound coal. The hydrogen and methane yields decreased. Increasing the steam from 26 to 56 SCF per pound (tests 31 and 35) resulted in only minor changes in carbon conversion and gas yield. The hydrogen content of the product gas increased from 42 to 48 percent. An increase in the coal rate from 0.36 to 0.91 pound per hour decreased the carbon conversion from 68 to 50 percent and the gas yield from 21 to 16 SCF per pound coal.

TABLE 3.- The effect of variables on the gasification of Bruceton coal using the pretreater and gasifier in series; pressure is 2-1/2 atmospheres

Test No.	39	37	31	35	33	30
Input						
Steam, SCFH	11	15	10	22	14	35
Oxygen, SCFH, pretreater	1.0	1.0	1.5	1.0	1.0	1.5
Oxygen, SCFH, gasifier	0	2.2	0.9	1.4	1.4	4.5
Nitrogen, SCFH	8	10	12	10	10	12
Coal, lb/hr	0.33	0.35	0.39	0.39	0.36	0.91
Temperature, °C						
Pretreater	450	450	450	450	450	450
Gasifier, avg	860	865	867	858	857	858
Gasifier, max	874	876	875	875	873	871
Oxygen/coal, SCF/lb	2.4	9.1	6.2	6.1	6.7	6.6
Steam/coal, SCF/lb	32	43	26	56	39	38
Carbon conversion, pct	46	80	61	64	68	50
Steam conversion, pct	20	13	11	11	17	10
Product gas, ^{1/} SCF/lb coal	19	23	19	21	21	16
Product gas, ^{2/} pct						
H ₂	56	42	42	48	45	47
CH ₄	4	2	2	3	3	3
CO	21	29	30	24	29	30
CO ₂	19	27	26	25	23	20

^{1/} N₂-, H₂O, and CO₂-free.

^{2/} N₂- and H₂O-free.

The Effect of Pressure

The effect of pressure on the methane yield and on the caking property of the coal treated at high temperature was studied at 2-1/2, 5, and 8 atmospheres (table 4). With an increase in pressure, however, the gas flow of steam plus oxygen must be increased to maintain the same linear velocity in the fluid-bed. To maintain the desired ratios of oxygen/coal and steam/coal the coal feed must be increased, but with a fixed-bed height the residence time of the coal in the pretreater and gasifier will decrease. At 8 atmospheres pressure operation of the gasifier was difficult because of coal agglomeration due to the decreased residence time in the pretreater. At 0.4 pound per hour the residence time of the coal in the pretreater was about 40 minutes, and at 1.25 pounds per hour about 13 minutes, apparently too short a time for pretreatment at these operating conditions. When the coal rate was decreased to about 1 pound per hour the unit operated satisfactorily, with no coal agglomeration, but the carbon conversion was low, indicating insufficient residence time of the coal in the gasifier.

TABLE 4.- Effect of pressure on gasification of Bruceton coal using pretreater and gasifier in series

Test No.	39	41	45	44	46	55	54
Pressure, atm	2.5	2.5	5	5	8	8	8
Input							
Steam, SCFH	11	14	36	34	65	50	42
Oxygen, SCFH, pretreater	1.0	2.0	1.6	1.6	2.2	2.0	1.2
Oxygen, SCFH, gasifier	0	1.0	0	4.0	0.6	0	5.2
Nitrogen, SCFH	8	8	11	11	8	22	27
Coal, lb/hr	0.33	0.37	0.75	0.73	1.25	0.91	0.97
Temperature, °C							
Pretreater	451	451	455	456	456	453	452
Gasifier, avg	860	855	862	831	842	823	864
Gasifier, max	874	867	873	874	869	869	866
Oxygen/coal, SCF/lb	2.4	8.1	2.1	7.6	2.2	2.2	7.0
Steam/coal, SCF/lb	32	38	48	46	52	55	43
Carbon conversion, pct	46	66	52	66	43	41	53
Steam conversion, pct	20	18	16	13	-	14	8
Product gas, ^{1/} SCF/lb coal	19	18	20	20	16	17	15
Product gas, ^{2/} pct							
H ₂	56	46	54	46	52	58	45
CH ₄	4	3	5	3	8	6	5
CO	21	22	20	23	18	13	20
CO ₂	19	29	21	28	22	23	30

^{1/} N₂-, H₂O-, and CO₂-free.

^{2/} N₂- and H₂O-free.

The methane content of the product gas increased from 4 percent at 2-1/2 atmospheres (test 39) to 8 percent at 8 atmospheres (test 46) when there was no oxygen fed to the gasifier. Less amounts of methane and hydrogen were formed when oxygen was used in the gasifier.

There was also less methane formed at 8 atmospheres when the coal-feed rate was decreased from 1.25 to 1.0 pound per hour. At this lower rate the nitrogen rate had to be raised to maintain fluidization since the steam and oxygen rates are fixed by the coal feed. This increase in nitrogen decreased the partial pressure of the reacting gases. To operate at the desired 20 atmospheres to produce the maximum yield of methane the gasifier height must be increased to increase the residence time, or possibly the product gas could be recycled so that the coal rate could be decreased. A recycle probably would not be effective if oxygen were being fed to the gasifier since present tests showed that oxygen would react with gas in preference to the coal.

Methane yields in these tests may be compared with yields from the Lurgi gasifier⁴ where 11 percent of methane is produced at a pressure of 8 atmospheres; however, the carbon conversion of the brown coal used in the Lurgi is much higher than in our tests.

The best coal-feed rate for this size gasifier at 2-1/2 atmospheres is about 0.4 pound per hour. The minimum oxygen rate to the pretreater is 1.2 SCF per pound of coal feed when oxygen is fed to the gasifier also but 2.0 SCF per pound with no oxygen to the gasifier. These figures compare with only 0.4 SCF oxygen per pound needed in the earlier tests³ to pretreat the same coal.

Advantages of the 2-Stage Process

The advantages of the present process using two fluidized beds in series are:

1. Raw caking coal can be fed to this system without difficulty. Coal which had been drastically pretreated did not agglomerate in the gasifier.
2. Mixing the treated coal from the pretreater with ash in the gasifier reduced the possibility of the coal caking in the gasifier.
3. Feeding treated coal into the bottom of the gasifier with oxygen and steam also reduced the possibility of the coal caking in the gasifier. This is shown in the tests where oxygen fed into the gasifier prevented agglomeration of the coal treated at 250° C in the pretreater.

Disadvantages of the 2-Stage Process

The disadvantages of the 2-stage system are:

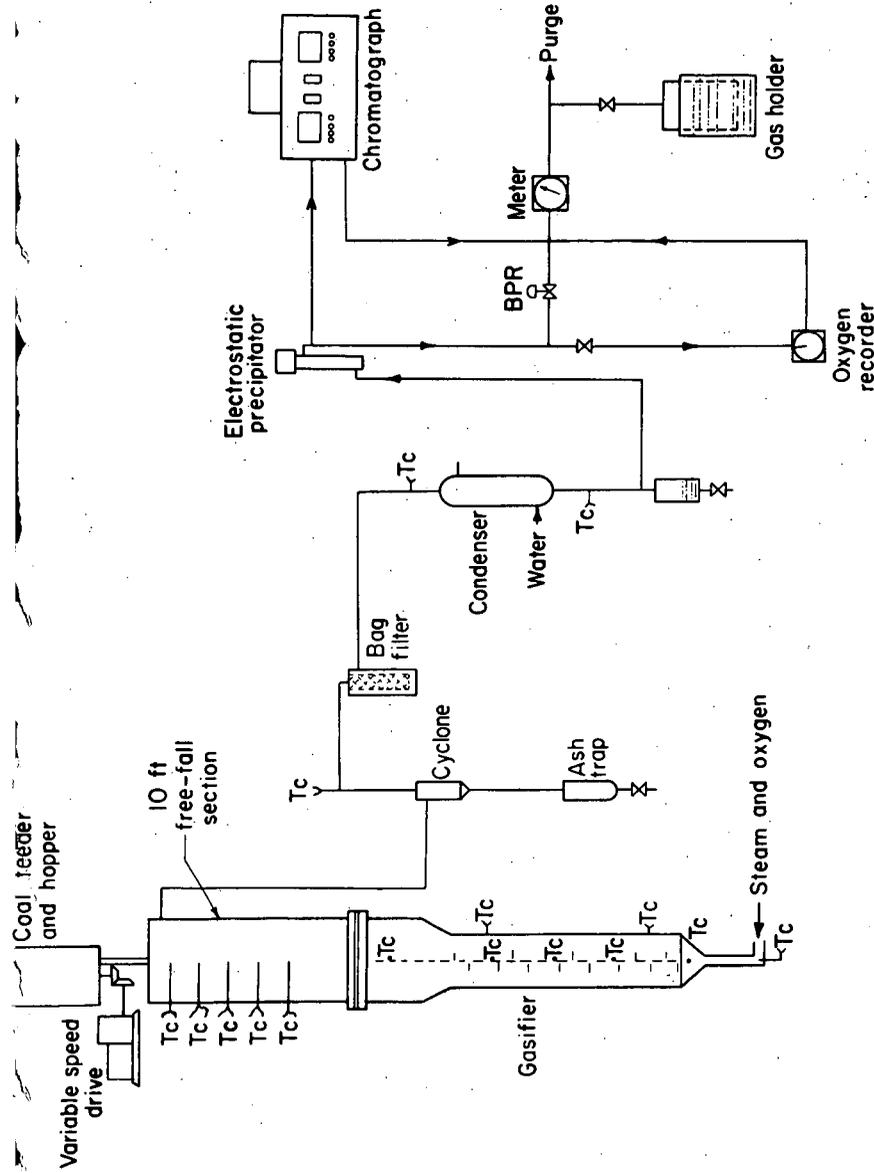
1. Two fluid beds in series are difficult to operate. Any surge in the pretreater throws untreated coal into the gasifier.
2. The coal, gases, tars, and oxygen entering at the bottom of the gasifier, make temperature control difficult.
3. At least 1.2 SCF oxygen per pound coal is needed for pretreatment. This is almost one-third the requirement for gasification in the Lurgi^{5/} which requires 4 SCF per pound.
4. Production of methane is lower than the Lurgi because in this system the gas-solids flow is not countercurrent.

New Gasification System

In an attempt to overcome these difficulties, the system has been revised as shown in figure 2. Now the coal is fed into the top of a 10-foot long, 6-inch diameter pipe and falls freely through an upward flow of gas from the 3-inch diameter fluid-bed gasifier. The coal, as it drops, is carbonized and devolatilized so by the time it enters the fluid bed it should be noncaking. Preliminary tests of the revised system indicate that it is operable, but no data are available at this time. The methane yield should be higher due to countercurrent flows.

CONCLUSIONS

Low-temperature (250° C) treated coal and high-temperature (450° C) treated coal can be reacted in a fluid-bed gasifier operated at 870° C without agglomeration of the coal. The Pittsburgh-seam coal passes first to a pretreater and then to a gasifier, the two being in series. The raw coal used in the 2-stage system yielded more product gas than when the coal was pretreated separately. The minimum oxygen needed is 1.2 SCF per pound of coal. At a pressure of 8 atmospheres the methane content of the product gas is 8 percent. An increased methane yield is anticipated by use of countercurrent free-fall system. Further improvement in the gasification can result if means are found of supplying heat indirectly to decrease the oxygen requirement.



Tc=Thermocouple

9-1-65

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Figure 2. Free-Fall Reactor and Fluid-Bed Gasifier System.

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CLEANUP METHANATION FOR HYDROGASIFICATION PROCESS

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INTRODUCTION

Catalytic methanation is the final gas cleanup step in the process for producing a high-Btu pipeline gas from coal being developed at the Institute of Gas Technology. The development project is sponsored jointly by the American Gas Association, Inc., and the U. S. Department of the Interior, Office of Coal Research.

The coal hydrogasification process produces 600-800 Btu/SCF gas consisting primarily of methane, hydrogen, carbon monoxide, and carbon dioxide. Smaller amounts of ethane, hydrogen sulfide, nitrogen, ammonia, and other constituents are also present. Carbon dioxide, sulfur compounds, and nitrogen compounds can be removed rather simply by conventional gas purification methods. However, the final gas should ideally contain less than 0.1 mole percent of carbon monoxide and have a heating value of at least 900 Btu/SCF. Because the raw gas contains rather large amounts of hydrogen, it is not of value to merely shift and scrub to remove carbon monoxide. It seems preferable to first scrub out most of the carbon dioxide and then to methanate the remaining carbon oxides.

Methanation has not been well studied at the pressures (approximately 1000 psig) and feed gas compositions (2 to 10 mole percent CO, 2 mole percent CO₂, and 53 to 87 mole percent CH₄) expected to enter this cleanup step in the IGT process. Based on thermodynamic equilibrium calculations, carbon deposition may be a problem with these feed gases. Moreover, the extent to which CO₂ will be methanated is not definitely known. IGT is therefore obtaining information needed to design large-scale catalytic methanation reactors. Effects of temperature, pressure, and catalyst composition on the process operation are main laboratory study areas.

The first step in the overall methanation study is to find the best commercial catalyst for this cleanup step. The catalyst used must first of all be able to actively catalyze the methanation reaction without catalyzing carbon deposition reactions. It must also be highly active and long-lived at high temperatures. These properties of the catalyst are directly related to chemical events occurring on its surface.

Instead of the commonly used packed-tube reactor, IGT is using a continuous stirred tank catalytic reactor (CSTCR)³ which permits studying these chemical events without any complicating control of the reaction rate by gas-solid mass or heat transfer. This reactor has several other advantages:

1. The CSTCR operates at conditions where "perfect mixing" prevails, and bulk gas temperature and concentration gradients are eliminated.
2. With sufficient gas velocity at the catalyst surface, temperature and concentration gradients between the bulk gas and the catalyst surface can be minimized.
3. All but the fastest and most exothermic reactions can be studied at nearly isothermal conditions and nearly complete conversion.

4. Because all the catalyst surface "sees" gas of the same composition and temperature, the reaction rate can be calculated by a simple algebraic equation:

$$R = \frac{F_i C_i - F_o C_o}{W} \quad (1)$$

This procedure is, in general, simpler and more accurate than rate calculation from data obtained with packed-tube reactors.

5. Finally, studies can be made using catalyst pellets of commercial size and shape.

This type of reactor has been used in the past to study solid-catalyzed gaseous reactions. Tajbl, Simons, and Carberry³ used a CSTCR to study the highly exothermic oxidation of carbon monoxide on a commercial palladium catalyst. Ford and Perlmutter² used a CSTCR with a catalytic wall to study sec-butyl alcohol dehydrogenation. In both studies, the authors found data were obtained more easily and accurately with a CSTCR.

This paper deals with:

1. Defining the operating range for "perfect mixing" in the IGT reactor
2. Determining whether gas-solid heat or mass transfer effects were present at the conditions of operation.
3. Preliminary screening of commercial methanation catalysts.

APPARATUS

Figure 1 is a flow diagram of the catalyst testing unit. The gas inlet system and the components operating at elevated temperatures and pressures are stainless steel. Feed gas, stored in high pressure cylinders, is metered by an orifice. Orifice pressure, pressure drop, and temperature are recorded. The feed gas is preheated before it enters the bottom of the reactor. Both the reactor and the preheater are electrically heated.

Exit gas leaves the top of the reactor and passes through a heated line (to avoid condensation of liquids) to a cooler-condenser. Liquid products are collected in a knockout pot and are drained through a solenoid valve actuated by a sonic liquid level controller. A dome-loaded back-pressure regulator controls the reactor pressure and reduces the pressure of the exit gas. The exit gas rate is measured by a wet-test meter. Carbon monoxide and carbon dioxide concentrations in the feed and exit gases are measured by two continuous infrared analyzers and are recorded. Aliquot samples of feed and exit gases are taken during each test period for analysis of all components by mass spectrometer (Consolidated Engineering Model 21-103).

Figure 2 shows the construction of the reactor, built by Autoclave Engineers, Inc. It was constructed of Type 316 stainless steel so that it could be used in the future to test the effects of elevated temperatures on catalyst stability. A magnetic drive rotates the stirrer shaft. The reactor has an inside diameter of 12 in. and an inside

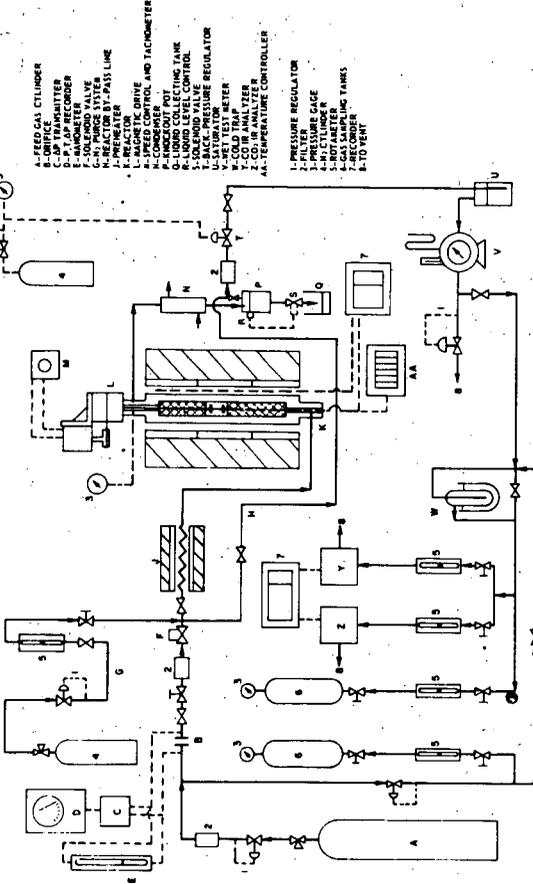


Figure 1. CATALYST TESTING UNIT

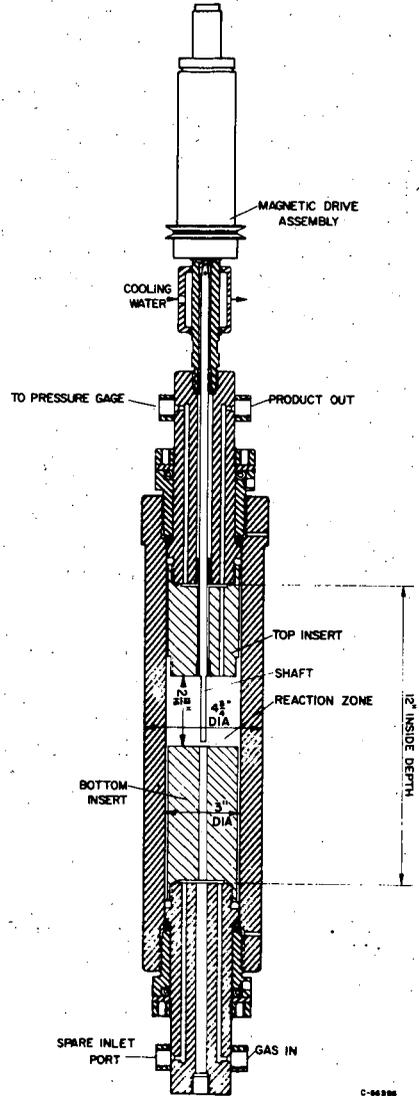


Figure 2. CONTINUOUS STIRRED TANK CATALYTIC REACTOR

C-66286

diameter of 3 in. For CSTCR operation, two inserts are installed which reduce the inside depth to 2-13/16 in.

Two methods of catalyst mounting are employed. Catalyst can be placed in an annular basket or in a paddle-basket arrangement as shown in Figure 3. When the paddle basket is used it replaces the radial impeller which is used only with the annular basket. For either arrangement the propellers remain in place. The cylindrical wall and the top and bottom of the reactor each have four 1/8-in.-wide baffles. The wall baffles extend along the total height of the stirred chamber; the top and bottom baffles extend radially to the cylindrical wall.

Catalyst temperatures are measured easily in the annular basket. Since the catalyst is stationary, a thermocouple is simply inserted in a hole drilled into the center of a catalyst pellet.

For either basket arrangement, the gas temperature is measured with a 0.025-in.-OD magnesium-oxide-insulated thermocouple made of Chromel-Alumel with a swaged stainless steel sheath.

DISCUSSION

Mixing Theory

Several tracer techniques can be used to check for perfect mixing. These consist of measuring the response in the reactor effluent to either:

1. The injection of a very small amount of tracer into the reactor over a very short time (pulse test); or
2. The instantaneous switching from a steady flow of inert gas to a steady flow of tracer (step test) or vice versa (purge test).

After the tracer concentration reaches a maximum value, the response for any of these tests is an exponential decay of tracer concentration with time. For the pulse test the response is:

$$\frac{C}{C_M} = e^{-tF/V} \quad (2)$$

where C_M is the gas concentration in the reactor at the instant the pulse enters, and $-$ in actual tests - the maximum gas concentration measured in the effluent.

For the step test the response is:

$$1 - \frac{C}{C_S} = e^{-tF/V} \quad (3)$$

where C_S is the steady-state tracer concentration. For the purge test the response is the same as Equation 2 except that $C_S = C_M$. A plot of line C/C_M versus tF/V yielding a straight line of slope -1 indicates "perfect mixing."

Mixing Test

All of these techniques were used in our mixing studies. Because of the difficulty of injecting a perfect pulse of tracer, the step or purge tests were easier to carry out. In spite of this, the pulse tests have an advantage because of the small amount of tracer used. In step or purge tests an allowance must be made for transfer of tracer (or purge) contained in the reactor dead volume before switching, i.e., in the lines to the pressure gages, etc. This, in effect, increases the volume to be purged and affects the slope of the line C/C_M versus tF/V plot.

Of the three tracer tests, then, the pulse test is most accurate in systems with extensive dead volumes.

CO or CO₂ was used as tracer with nitrogen as the inert gas in these tests. A switching valve served to inject the pulse of tracer or to change from tracer to inert. Flow rates ranged from 1 to 40 SCF/hr. measured at flowing conditions, this flow range is about that used in the Hajbl-Simons-Carberry reactor. Shaft speed was varied from 0 to 2500 rpm. Tracer response was measured by the in-line infrared analyzers. A typical response to a pulse test is shown in Figure 4.

Typical test results are plotted in Figure 5. The data at 200 rpm indicate imperfect mixing. As the shaft velocity is increased, perfect mixing is realized for high and low flows and at high and low pressures. Above 1500 rpm perfect mixing is ensured for the range of flows studied. Changing temperature or tracer gas had no effect. The purge and step tests also gave linear semilog plots of C/C_S versus tF/V , but the slope was not -1 because of the reactor dead volume previously noted.

Interphase Transport

Transport phenomena between the catalyst surface and the bulk gas may control the reaction rate for very fast - or very exothermic or endothermic - reactions. To study chemical events on the catalyst surface these transport effects must be minimized. It is simple to check for the influence of transport effects in a CSTCR. In the case of catalyst mounted in a stationary basket, the stirrer speed is varied while all other variables are held constant. Changes in conversion with varying stirrer speeds indicate the presence of transport effects. A temperature gradient between the gas and the catalyst will exist if the reaction is heat-transfer limited. Both gas and catalyst temperatures can be easily measured with the stationary catalyst mounting.

Mass transfer was found not to control above about 750 rpm at 115°F with a 10.2% CO-31.2% H₂ feed, and nickel catalyst in the annular basket. Of course, a check should be made for mass transfer at each run temperature. Since the rate constant increases with increased temperature, mass transfer should be more important at higher temperatures.

Commercial Catalyst Comparison

A variety of products can be produced catalytically from hydrogen and carbon oxides. The type of products depend upon the catalyst composition, temperature, pressure, and the hydrogen/carbon oxides ratio. Nickel catalysts produce mainly methane at almost all useful operating conditions. Iron, ruthenium, and cobalt catalyze the Fischer-Tropsch synthesis, producing higher hydrocarbons. Iron and ruthenium catalysts are nevertheless considered since higher hydrocarbon formation would

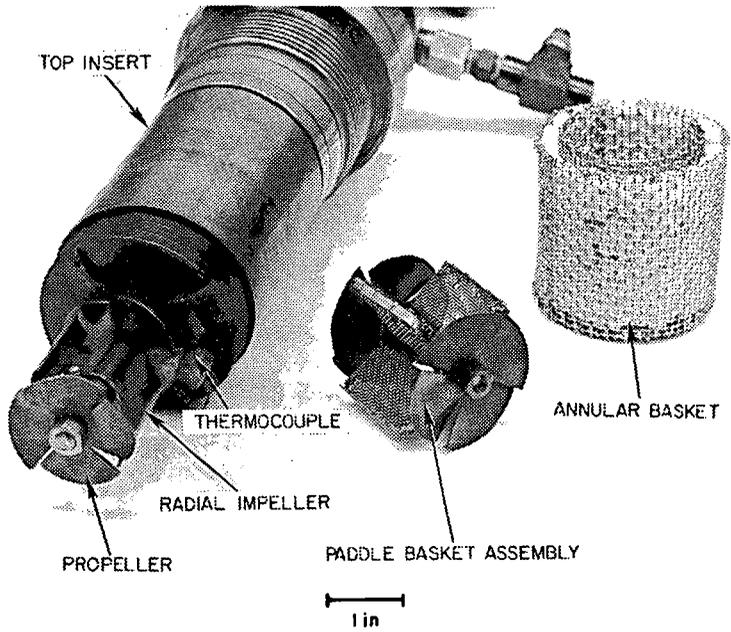


Figure 3. CATALYST BASKETS

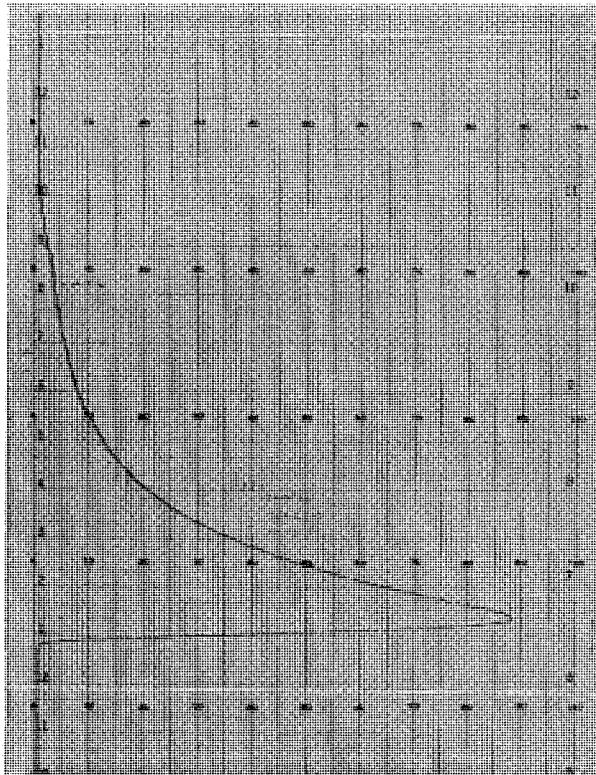


Figure 4. TYPICAL PULST TEST RESPONSES

ve the final gas a higher heating value. Cobalt catalysts were not considered because they operate best at lower pressures (1-10 atm).¹

Catalysts were compared by measuring their rate of carbon monoxide conversion. Test variables were temperature, feed gas composition, and the feed rate/catalyst weight ratio. All tests were made at 1000 psig. Three feed gases, covering a range of compositions typical of projected methanation feeds, were selected.

Table 1. COMPOSITIONS OF FEED GASES

Feed Composition, mole %	High CO	Intermediate CO	Low CO
Carbon Monoxide	10.0	7.0	2.4
Carbon Dioxide	2.1	2.1	2.0
Hydrogen	34.5	26.1	13.5
Ethane	53.4	64.8	82.1
Total	100.0	100.0	100.0

Nickel Catalysts

The nickel catalysts studied were:

- Catalyst A: Nickel on kieselguhr
- Catalyst B: Nickel on alumina
- Catalyst C: Nickel on alumina

Catalyst A is more active than catalysts B and C. For comparable feed rate/catalyst weight ratios and the same low-CO feed gas, catalyst A converts more carbon monoxide at 560°F than catalyst B at 700°F (Figure 7). This also holds true for other feed gases. Figure 7 shows typical data for catalyst A in isothermal runs with low-CO feed gas.

Iron Catalyst

An ammonia-synthesis catalyst was studied. Much lower feed rate/catalyst weight ratios must be used with this catalyst to obtain conversions approaching those of catalyst A (Table 2).

Table 2. RESULTS WITH IRON CATALYST

Temp., °F	F _i /W, SCF/hr-g catalyst	Feed Gas	CO Conv., %	Dry Prod Gas Content, mole %	
				CH ₄	C ₂ +
509	0.036	Int. CO	13.0	68.2	0.8
604	0.027	Int. CO	55.7	73.4	1.3
700	0.026	Int. CO	62.2	74.7	1.3
800	0.026	Int. CO	66.3	76.2	1.4

Longer-chained hydrocarbon formation is much lower than expected. This is presumably because of the high hydrogen/carbon monoxide ratio of the feed gas and the high pressure. Bond¹ cites both these conditions as favoring hydrogenolysis.

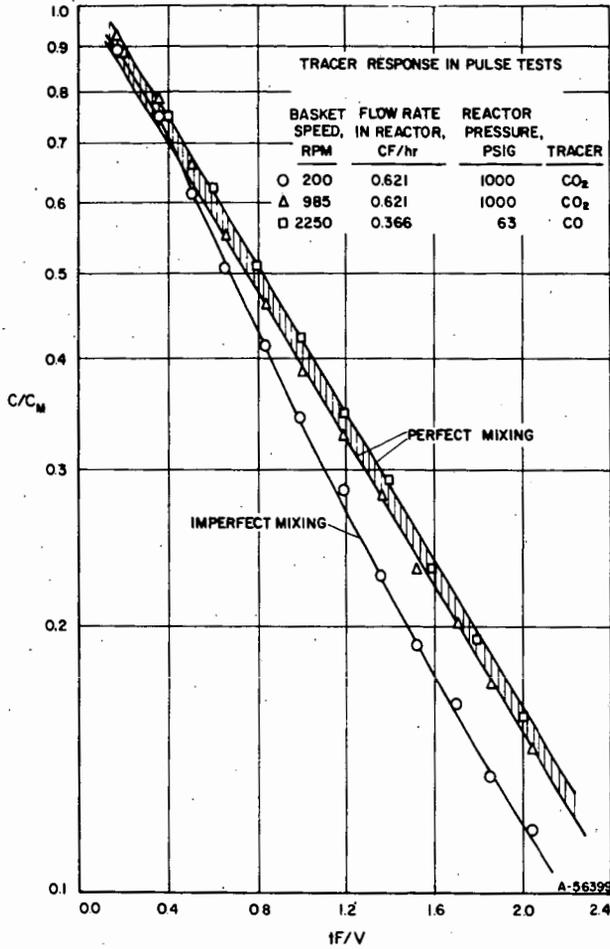


Figure 5. TYPICAL PULSE TEST RESULTS

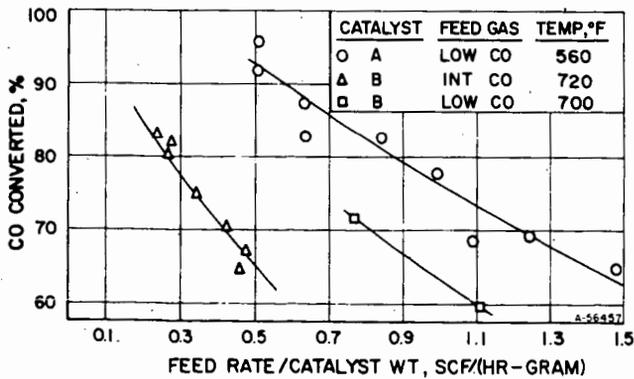


Figure 6. COMPARISON OF ACTIVITY OF NICKEL CATALYSTS A AND B

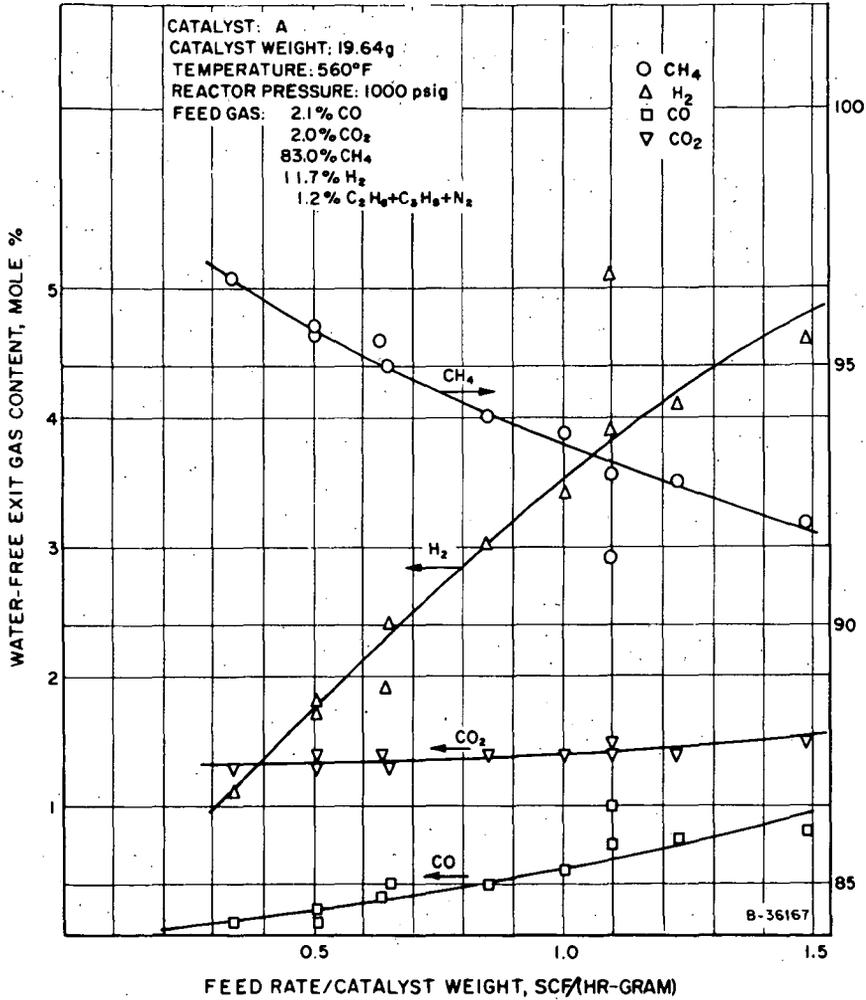


Figure 7. METHANATION PRODUCT GAS COMPOSITIONS AS A FUNCTION OF STIRRED REACTOR SPACE VELOCITIES

Ruthenium Catalyst

The ruthenium catalyst studied was 0.5% ruthenium on alumina. Data in Table 3 show that at low temperatures and low feed rate/catalyst weight ratios, this catalyst is an effective methanation catalyst. Higher hydrocarbon formation is, again, lower than expected, possibly due to hydrogenolysis. Trace yields of oils containing paraffins, olefins, and aromatics were obtained.

Table 3. RESULTS WITH RUTHENIUM CATALYST

Temp, °F	Fi/w SCF/hr-g Catalyst	Feed Gas	CO Conv, %	Dry Prod Gas Content, mole %	
				CH ₄	C ₂₊
210	0.059	Int. CO	5.5	66.6	0.9
290	0.058	Int. CO	6.0	67.7	0.9
347	0.058	Int. CO	20.3	69.5	1.1
405	0.056	Int. CO	27.7	71.1	0.7
470	0.056	Int. CO	86.2	84.1	1.6
547	0.055	High CO	90.0	85.2	1.3
600	0.503	Int. CO	44.0	76.7	0.8
670	0.503	Int. CO	89.3	89.2	0.7

CONCLUSIONS

Conditions for "perfect mixing" were determined in a continuous stirred tank catalytic reactor operated at 1000 psig. "Perfect mixing" was obtained at stirring speeds above 1500 rpm over the flow range used in this study.

Neither gas-solid heat nor mass transfer effects were found in this methanation study of typical feed gases produced from coal hydrogasification.

Evaluation of commercial catalysts showed that nickel-on-kieselguhr catalyst is more active than nickel-on-alumina, iron, and ruthenium catalysts for cleanup of CO in IGT's hydrogasification process. Longer-chained hydrocarbon formation is much less than expected for tests with iron and ruthenium catalysts.

ACKNOWLEDGMENT

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NOMENCLATURE

C = concentration, lb moles/cu ft

C_M = maximum concentration of tracer in pulse test, lb moles/cu ft

C_S = steady-state tracer concentration in purge or step test, lb moles/cu ft

F = flow rate, SCF/hr

R = reaction rate, lb moles/hr-g

t = time, hr

V = reactor volume, cu ft

w = catalyst weight, g

Subscripts

i refers to gas entering reactor

o refers to gas leaving reactor

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The Fuel Chemistry Division of the American Chemical Society is an internationally recognized forum for scientists, engineers and technical economists concerned with the conversion of fuels to energy, chemicals, or other forms of fuel. Its interests center on the chemical problems, but definitely include the engineering and economic aspects as well.

Any chemist, chemical engineer, geologist, technical economist, or other scientists concerned with either the conventional fossil fuels, or the new high-energy fuels--whether he be in government, industry or independent professional organizations--would benefit greatly from participation in the program of the Fuel Chemistry Division.

The Fuel Chemistry Division offers at least two annual programs of symposia and general papers, extending over several days, usually at National Meetings of the American Chemical Society. These include the results of research, development, and analysis in the many fields relating to fuels which are so vital in today's energy-dependent economy. Members of the Division have the opportunity to present papers of their own, or participate in discussions with experts in their field. Most important, the Fuel Chemistry Division provides a permanent record of all of this material in the form of complete preprints.

Starting in September 1959, the biennial Fuel Cell Symposia of the Division have been the most important technical meetings for chemists and chemical engineers active in this field. These symposia have all been published in book form. The recent landmark symposium on Advanced Propellant Chemistry is to be published in book form also. Further, the Division is strengthening its coverage of areas of air and water pollution, gasification, and related areas.

In addition to receiving several volumes of preprints, each year, as well as regular news of Division activities, benefits of membership include: (1) Reduced subscription rates for "Fuel" and "Combustion and Flame," (2) Reduced rates for volumes in the "Advances in Chemistry Series" based on Division symposia, and (3) The receipt card sent in acknowledgment of Division dues is good for \$1.00 toward a complete set of abstracts of all papers presented at each of the National Meetings.

To join the Fuel Chemistry Division as a regular member, one must also be or become a member of the American Chemical Society. Those not eligible for ACS membership because they are not practicing scientists, engineers or technical economists in areas related to chemistry, can become Division Affiliates. They receive all benefits of a regular member except that they cannot vote, hold office or present other than invited papers. Affiliate membership is of particular value to those in the informational and library sciences who must maintain awareness of the fuel area. Non ACS scientists active in the fuel area and living outside of the United States are invited also to become Division Affiliates.

Membership in the Fuel Chemistry Division costs only \$4 per year, or \$11 for three years, in addition to ACS membership. The cost for a Division Affiliate, without joining ACS, is \$10 per year. For further information, write to:

Dr. Frank Rusinko, Jr., Secretary-Treasurer
ACS Division of Fuel Chemistry
c/o Speer Carbon Company
St. Marys, Pennsylvania 15857
Telephone: 814-834-2801

RECENT FUEL DIVISION SYMPOSIA

Volume	Title	Presented At
Vol. 8, No. 1	Symposium on Gas Generation General Papers	Philadelphia, Pa. April, 1964
Vol. 8, No. 2	Symposium on Chemical Phenomena in Plasmas Symposium on Kinetics and Mechanisms of High Temperature Reactions	Philadelphia, Pa. April, 1964
Vol. 8, No. 3	Symposium on Pyrolysis and Carbonization of Coal Symposium on Mineral Matter in Coal	Chicago, Illinois August, 1964
Vol. 9, No. 1	Symposium on Advanced Propellant Chemistry*	Detroit, Michigan April, 1965
Vol. 9, No. 2	Symposium on Fuel and Energy Economics General Papers	Detroit, Michigan April, 1965
Vol. 9, No. 3 Parts 1 & 2	Symposium on Hydrocarbon-Air Fuel Cells**	Atlantic City, N. J. September, 1965
Vol. 9, No. 4	Symposium on Coatings Based on Bituminous Materials General Papers	Atlantic City, N. J. September, 1965
Vol. 10, No. 1	Symposium on Fossil Fuels and Environmental Pollution Joint with the Division of Water, Air, and Waste Chemistry	Pittsburgh, Pa. March, 1966
Vol. 10, No. 2	Symposium on Pyrolysis Reactions of Fossil Fuels Joint with the Division of Petroleum Chemistry	Pittsburgh, Pa. March, 1966

* To be published by Advances in Chemistry.

** Published by Academic Press, Inc.

PROJECTED PROGRAMS

Symposium on Chemical Reactions in Electrical Discharges Joint with Division of Physical Chemistry Bernard D. Blaustein, Chairman	Miami Beach, Fla. April, 1967
Symposium on Electrochemical Reactions in Solution General Papers Joint with Divisions of Physical Chemistry and Analytical Chemistry and in cooperation with Electrochemical Society Ernest Yeager, Chairman	Miami Beach, Fla. April, 1967
Symposium on Detonations and Reactions in Shock Waves Joint with Division of Physical Chemistry R. W. Van Dolah, Chairman	Chicago, Illinois September, 1967
Symposium on Advances in Spectrometry of Fuels and Related Materials Joint with Division of Analytical Chemistry R. A. Friedel, Chairman	Chicago, Illinois September, 1967
Symposium on Fuel Cell Technology B. S. Baker, Chairman	Chicago, Illinois September, 1967
Symposium on Oil Shale James H. Gary, Chairman (Tentative; may be Spring 1968)	Chicago, Illinois September, 1967
General Papers Irving Wender, Program Chairman	Chicago, Illinois September, 1967