

Environmental Aspects of the HYGAS Process

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As part of the development of second-generation coal gasification processes, the U. S. Department of Energy has commissioned an environmental assessment of the HYGAS process. The objective of this assessment is to establish systems for sampling, analysis, and data evaluation to determine the fate of potential pollutants generated during operation of the HYGAS pilot plant and to apply these data to demonstration and commercial plant designs.

HYGAS operates at high temperatures to obtain high reaction rates and at high pressure to increase the equilibrium methane yield. The most reactive coal fraction is hydrogasified to form methane while the less reactive fraction remains in the coal char and is used to generate hydrogen and heat. Of the total methane formed in the process, about 64% to 70% is formed in the gasifier.

Figure 1 shows the current processing steps in the HYGAS pilot plant. Lignite and subbituminous coals do not require pretreatment. However, with a caking coal such as Illinois No. 6 bituminous, a pretreatment step is used to destroy any agglomerating tendencies. The pretreatment is a mild surface oxidation carried out in a fluidized bed at 700° to 800°F and slightly above atmospheric pressure. For introduction into the high-pressure gasifier, up to 45 wt % coal is mixed in a light oil slurry which is pressurized with reciprocating piston pumps. Entrained solids in the crude gas which leave the gasifier are removed with a cyclone. Then the gas is quenched to condense steam and light oil. Next, water and oil are separated, recovered, and recycled. Acid gases (H_2S and CO_2) are removed from the product gas with a diglycolamine-water solution which is regenerated and recycled. The product gas is further cleaned to reduce sulfur levels to <0.1 ppm. Then methanation is carried out in a packed-bed of nickel catalyst pellets sensitive to sulfur poisoning. The methanation step upgrades the product gas to essentially pure methane (SNG).

PILOT PLANT HYDROGASIFIER REACTOR

The hydrogasifier reactor vessel is shown schematically in Figure 2. The reactor vessel has four internally connected fluidized-bed contact stages which operate at 1000 psig, with different temperatures in the various fluidized beds. The reactor is designed to accept 3 ton/hr coal feed and to produce 1.5×10^6 SCP/day of pipeline-quality gas.

The feed slurry is introduced into the upper fluidized bed (the slurry-drying bed) which operates at 600°F. The dried coal flows by gravity into a vertical lift line where the first stage of hydrogasification occurs. Here, coal particles are heated by hot gases from the lower stage, and hydrogen contained in the gases reacts with about 20% of the coal to produce methane.

The partially reacted coal (now called a char) then flows to the second-stage gasifier and is further gasified by the steam and hydrogen-rich gas rising from the steam-oxygen gasification stage below. About 25% of the original coal is converted in this reaction stage, making the total conversion about 45% in the first and second stages of hydrogasification. The char then flows to the final reactor stage where steam and oxygen are introduced to convert the char to

hydrogen and carbon oxides and to provide the necessary heat for operation of the gasifier during self-sustained steady plant operation.

SAMPLE COLLECTION

Sampling of pilot plant streams specifically for environmental assessment began with Test 55 with Montana subbituminous coal. Process water streams were sampled every 8 hours and three of these samples were composited to represent 24 hours of plant operation. Water samples were analyzed for total dissolved solids (TDS), total suspended solids (TSS), total organic carbon (TOC), total phenols, total sulfur, ammonia, cyanide, thiocyanate, sulfide, chloride, and oil. Solids samples were collected once per day and analyzed for sulfur species and trace elements. The solids streams sampled included the coal feed, the first and second stages of gasification, and the spent char. Samples of oils in the coal feed slurry were also taken once per day to determine organic compositions using a gas chromatograph mass spectrometer.

HYGAS WATER COMPONENTS

Before the environmental assessment program began with subbituminous coal, HYGAS tests were carried out with both Montana lignite and Illinois No. 6 bituminous coals. In these tests, a single water sample was taken once every 24 hours. Process engineering data from these tests have been examined to determine the water compositions corresponding to periods of self-sustained, steady operation and to normalize pollutant generation to a uniform basis for the three types of coal.

Compositions of the gasifier feed coals used to calculate pollutant generation in HYGAS Test 37 with Montana lignite, Tests 46 and 54 with Illinois No. 6 bituminous, and Test 55 and 58 with Montana subbituminous are given in Table 1. These compositions were derived from the routine ultimate and proximate analyses made during operation of the HYGAS plant and correspond to the coal feeds when the water samples were taken. Carbon conversions in these HYGAS tests ranged from 44% to 88%. Complete carbon conversion was not one of the objectives in these HYGAS tests; consequently, interpretation of this pollutant data is subject to the constraint that more complete carbon conversion will be obtained in future pilot plant tests.

Effluent production in the quench condensate slurry (from the water quenching of the gasifier crude product gas) is reported in Table 2 as a function of coal type and carbon in the feed on a moisture and ash-free basis (MAF). This stream is a major source of pollutants and has a relatively high water inventory (~2600 gallons) which generally contributes to more precise analytical results. Each of the pollutants was correlated with the carbon in the feed by a linear regression analysis, and the linear correlation coefficients are also given in Table 2. The correlation coefficients were then tested for significance from zero using Fisher's Z test with a two-sided probability at 95% confidence and (n-2) degrees of freedom. According to this test, the strongest significance from zero (77%) is the effect of carbon in the feed on thiocyanate, while the weakest significance (50%) is the effect of carbon on ammonia. What is perhaps most interesting is the negative slopes (meaning pollutant production is inversely proportional to carbon content in the feed) for all pollutants except sulfide and ammonia. This result occurs primarily because of the influence of pretreatment on the bituminous coals, which lowers the levels of total dissolved solids, phenol, total organic carbon, thiocyanate, and total sulfur in the gasifier quench condensate. Significant quantities of these pollutants were found in the pretreater quench waters. The sulfides and ammonia however, appear to be generated primarily in the gasifier.

Table 3 presents the results of linear regression analyses for feed constituents other than carbon and their effect upon selected pollutants in the crude gas quench. These analyses include oxygen on phenol, sulfur on sulfide and thiocyanate, nitrogen on ammonia and thiocyanate, and hydrogen on phenol and ammonia. The regression analysis for hydrogen in the coal feed on phenol production in the gasifier gave the strongest indication of a linear correlation. The correlation coefficient for this regression was 0.921 with a significance from zero of 85%. About 40% of the total phenol from bituminous coal was produced during pretreatment, which appeared to significantly reduce phenol production in the gasifier. Total phenols produced with bituminous coals were 2.9 lb/ton feed (MAF) in Test 46 and 5.6 lb/ton feed (MAF) in Test 54. This total was much less than the phenol production of 11.2 lb/ton feed (MAF) with lignite coal (Test 37) and approximately 16 lb/ton feed (MAF) with subbituminous coal (Tests 55 and 58).

HYGAS OIL COMPONENTS

A net make of light oil (benzene, toluene, and xylene) is produced in the HYGAS process and toluene is used in the pilot plant to represent this product. Coal feed is slurried with the oil for introduction into the high-pressure gasifier. Essentially all the oil is recycled by recovery from the product gas quench condensate and the product gas cyclone slurry. Toluene is added only for losses which are specific to the pilot plant, i.e., pump seals, storage tanks, vent gases, and vapor in product gas. The oil used in the coal feed slurry represents a concentrated source of polynuclear aromatics, potential carcinogens, and potentially toxic organic compounds. Consequently, it is necessary to screen the chemical composition of this oil for possible health and safety hazards. As each HYGAS test progresses, this oil changes in composition as a function of operating time and gasification conditions. Presumably, equilibrium compositions will be reached under extended steady-state conditions.

Compositions for oil samples taken during HYGAS Test 37 using lignite coal and Test 58 using subbituminous coal are shown in Table 4. The differences in compositions for the heavier three-, four-, and five-ring compounds may be due to the type of coal, to plant operation, and possibly other factors. The presence of many compounds in the initial samples occurs because the plant oil inventory of ~6000 gal remaining after one test is reused for coal slurry in the subsequent test.

Phenol composition is important because of the effects various water-soluble phenols may have on biosystems designed for wastewater cleanup. Phenols in the feed coal-oil slurry with lignite coal are characterized as major fractions, 40% each, C₁- and C₂-phenols (where C represents the methyl or alkyl groups, i.e., isomers were not separated) and 10% each for phenol and C₃-phenols. With the subbituminous coal, the major phenolic fractions consisted of C₁-, C₂-, and C₃-phenols (approximately 30% each) with minor fractions of phenol and C₄-phenols (about 10% each) and about 1% C₅-phenols.

HYGAS SOLIDS COMPOSITION

During gasification, transformation and elimination of sulfur from one class of compounds to another occurs as the coal chars move through the various gasification stages. For the subbituminous coal used in Test 58, about 91% of the total sulfur entered the gasifier as organic and pyritic sulfur in the coal feed. In the gasifier, sulfide sulfur increased significantly in the presence of hydrogen (from 1.2% in feed coal to 25% of total sulfur in first-stage char) while the remaining sulfur species all decreased. Table 5 lists the quantities

of each sulfur class during gasification. The normalized data, based upon 100 lbs of coal feed, show that the bulk of the sulfur (approximately 70%) is reacted during the first stage of gasification and that lesser amounts of 12% each are reacted in the second-stage and in the steam-oxygen bed. Overall, about 70% of the sulfide and sulfate species were gasified along with 95% of the organic and pyritic sulfurs for an overall sulfur removal of 92% from the coal feed to the spent char.

The trace elements in solids obtained from gasification of subbituminous coal during Test 55, can be split into several categories according to the quantities found in the feed coal as compared to those found in the spent char.

- Group 1: 90% to 100% recovery in the ash –
Be, V, Mn, Zn, Li, Cr, Pb
- Group 2: 50% to 90% recovery in the ash –
Fe, Ba, As, B, F, Tl, Ni, Cu, Mo
- Group 3: Less than 50% recovery in the ash –
Cl, Se, Cd, Hg.
- Elements primarily released from char in the steam-oxygen zone –
Fe, As, Se, Tl, Ni, Cu, Cd, Mo
- Elements primarily released from char in first and second stages of gasification – Ba, B, Cl, F, Hg
- Elements in chars from first and second stages of gasification with higher concentrations than in the feed coal – Fe, Tl, Ni, Cu, Cd, Pb, Mo, Cr.

For the latter group of elements, material balances indicated that >130% existed in gasifier chars compared with the feed coals. Two of these elements, Pb and Cr, showed essentially no net disappearance from coal feed to char ash. For three elements, Pb, Mo, and Cd, 208%, 247%, and 262%, respectively, of coal feed input was found in the upper stages of gasification. With the exception of As and Se, all of the elements released primarily in the steam-oxygen zone showed an increased concentration in chars from the upper stages of gasification. The trace element distribution reported here may have resulted from the large temperature differences used in the various zones of the reactor and in this respect, the HYGAS reactor is not unique but is comparable to other industrial processes (power plants, steel plants, and other coal gasification reactors) where large temperature gradients exist. Moreover, these trace element data represent a single test of the gasifier and additional testing is required to determine "average" distributions and also the ultimate fate of the trace elements.

Table 2. EFFECT OF CARBON IN COAL FEED ON POLLUTANTS IN PRODUCT GAS QUENCH CONDENSATE STREAM FOR HYGAS REACTOR

Test 37: Montana Lignite
 Tests 46, 54: Pretreated Illinois No. 6 Bituminous
 Tests 55, 58: Montana Subbituminous (Rosebud)

Test	Carbon in Feed, wt % ^a	Total Dissolved Solids		Phenol		Total Organic Carbon		Thiocyanate		Sulfide		Ammonia		Total Sulfur	
		\bar{x}	s_x^b	\bar{x}	s_x^b	\bar{x}	s_x^b	\bar{x}	s_x^b	\bar{x}	s_x^b	\bar{x}	s_x^b	\bar{x}	s_x^b
		lb/ton feed (MAF)													
37	69.5	4.31	0.24	5.22	0.30	9.97	0.53	0.88	0.11	0.28	0.013	9.28	0.52	--	--
46	82.8	0.98	0.12	0.26	0.10	0.35	0.06	0.032	0.01	0.52	0.19	13.0	2.64	0.62	0.16
54	82.6	1.94	0.13	2.28	0.10	1.78	0.38	0.17	0.01	1.30	0.10	12.0	1.35	1.01	0.20
55	74.2	6.54	1.05	11.5	0.44	22.0	0.82	1.15	0.07	0.32	0.04	12.5	0.97	5.11	2.27
58	74.6	4.50	1.30	10.0	0.92	7.60	0.82	0.48	0.04	0.43	0.06	13.8	1.20	2.91	0.35
Linear Correlation Coefficient, r		-0.782		-0.653		-0.659		-0.836		0.722		0.517		-0.912	
Significance ^d From Zero, %		72.4		61.6		62.1		77.0		67.4		49.6		63.3	

^a Moisture- and ash-free (MAF) basis.

^b $s_x = s/\sqrt{n}$ where s = standard deviation = $[\sum(x - \bar{x})^2 / (n - 1)]^{1/2}$.

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^c Perfect linear correlation is indicated at $r = \pm 1$; linear independence is indicated at $r = 0$.

^d Using Fisher's Z test, two-sided $T[0.95, (n - 2)DF]$.

Table 3. EFFECT OF COMPONENTS IN COAL FEED ON POLLUTANTS FOUND IN PRODUCT GAS QUENCH CONDENSATES FOR HYGAS TESTS 37, 46, 54, 55, AND 58

Regression ^a	Linear Correlation Coefficient, r ^b	Significance ^c From Zero, %
Oxygen on Phenol	0.676	-- ^d
Sulfur on Sulfide	0.640	60.4
Sulfur on Thiocyanate	-0.855	78.7
Nitrogen on Ammonia	0.151	15.0
Nitrogen on Thiocyanate	-0.856	78.7
Hydrogen on Phenol	0.921	84.8
Hydrogen on Ammonia	-0.156	15.6

^a Elements in coal feed (MAF) on pollutant levels (reported in Tables 1 and 2).

^b $r = 1$ for perfect linear correlation, and $r = 0$ for linear independence.

^c Using Fisher's Z test, two-sided $T[0.95, (n - 2)DF]$.

^d Oxygen in coal determined by difference; therefore, only 2 degrees of freedom and a very low significance.

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Table 4. COMPOSITION OF LIGHT OIL IN COAL FEED SLURRY TO HYGAS REACTOR
HYGAS TEST 37 USING MONTANA LIGNITE FEED
HYGAS TEST 58 USING MONTANA SUBBITUMINOUS FEED

Test No. Sample Age (Days of Plant Operation)	37		58	
	<u>1</u>	<u>12</u>	<u>2</u>	<u>12</u>
	wt %			
Aliphatics	0.49	1.08	6.85	7.27
Benzene	1.37	6.94	5.13	7.10
Toluene	94.9	85.2	71.3	69.8
C ₇ -C ₉ Benzenes	0.98	1.90	3.98	3.98
Indenes	0.041	1.41	0.25	0.27
Indanes	--	--	1.27	1.02
Phenols	0.20	1.14	3.80	2.44
Napthalenes	0.62	1.65	4.47	5.00
Biphenyls	0.077	0.086	0.30	0.28
Acenaphthenes	0.020	0.11	0.11	0.11
Acenaphthalenes	--	--	0.10	0.092
Fluorenes	0.06	0.11	0.49	0.35
Phenanthrenes/Anthracenes	--	--	0.44	0.44
Pyrene	0.013	0.027	0.059	0.029
Flouranthenes	--	--	0.12	0.089
Benzofluorenes	--	--	0.006	0.003
Benzoflouroanthene	--	--	0.005	0.016
Benzo-Pyrene	--	--	0.005	0.002
Furans	--	--	0.62	0.67
Miscellaneous & Unknowns	1.22	0.34	0.67	0.90
Totals	99.99	100.0	99.98	99.86

Table 5. GASIFICATION OF SULFUR BY SPECIES DURING HYGAS TEST 58
USING ROSEBUD SUBBITUMINOUS COAL

From HYGAS Routine Ultimate Analyses*	Coal Feed	First-Stage Gasification	Second-Stage Gasification	Spent Char	
No. of Samples:	63	22	20	85	
Ash	9.48 ± 0.055	18.19 ± 0.71	23.61 ± 1.41	28.45 ± 0.68	
Sulfur	0.91 ± 0.012	0.48 ± 0.07	0.40 ± 0.08	0.16 ± 0.003 [†]	
	wt %				
Sulfur Species	lb S/100 lb Coal Feed				Sulfur Gasified Spent Char/Feed, %
Sulfide	0.01	0.062	0.052	0.003	70.0
Sulfate	0.06	0.031	0.034	0.020	66.7
Organic	0.45	0.125	0.070	0.030	93.3
Pyritic	0.29	0.036	0.006	0.010	96.6
Sum	0.81	0.255	0.162	0.063	
Total Sulfur Gasified, %	0	68.5	80.0	92.2	

* Limits shown are 95% confidence levels determined by $(\bar{x} \pm \frac{1.96\sigma}{\sqrt{n}})$. Data are from normal HYGAS operations.

[†] 70 samples involved in sulfur analysis.

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Phenanthrenes/Anthracenes	--	--	0.44	0.44
Pyrene	0.013	0.027	0.059	0.029
Flouranthenes	--	--	0.12	0.089
Benzofluorenes	--	--	0.006	0.003
Benzofluoranthene	--	--	0.005	0.016
Benzo-Pyrene	--	--	0.005	0.002
Furans	--	--	0.62	0.67
Miscellaneous & Unknowns	1.22	0.34	0.67	0.90
Totals	99.99	100.0	99.98	99.86

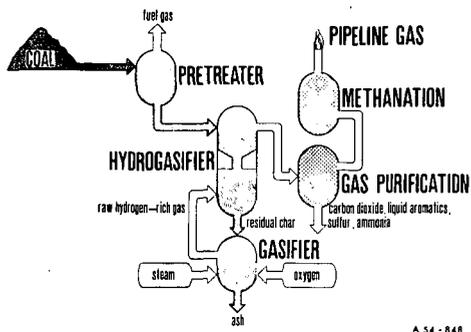
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Sulfur Species	lb S/100 lb Coal Feed				Sulfur Gasified Spent Char/Feed, %
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Sulfate	0.06	0.031	0.034	0.020	66.7
Organic	0.45	0.125	0.070	0.030	93.3
Pyritic	0.29	0.036	0.006	0.010	96.6
Sum	0.81	0.255	0.162	0.063	
Total Sulfur Gasified, %	0	68.5	80.0	92.2	

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Figure 1. THE HYGAS PROCESS USING A STEAM-OXYGEN GASIFIER TO PRODUCE HYDROGEN-RICH GAS

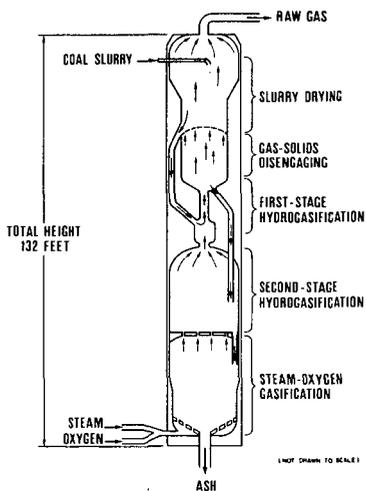


Figure 2. HYGAS PILOT PLANT REACTOR