MAJOR, MINOR AND TRACE ELEMENT BALANCES FOR THE SYNTHANE PDU GASIFIER - ILLINOIS NO. 6 COAL

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Summary

Two typical coal gasification tests were performed in the SYNTHANE process development unit (PDU) primarily to determine the distribution and quantity of trace elements in all process streams. For these tests, an Illinois No. 6 coal was gasified in a fluidized-bed with steam and oxygen at 40 atmospheres and a nominal 940° C. Sixty-five trace elements were identified by spark source mass spectrometry (SSMS) and quantified by computer assisted photoplate analysis. The distribution and quantities of only some potentially hazardous elements such as arsenic (As), beryllium (Be), cadmium (Cd), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se) and vanadium (V) are discussed. Mercury (Hg) was determined by flameless atomic adsorption spectrometry (AAS) using double gold amalgamation. Within the precision of both these analytical techniques it was found that most of the trace elements in the feed coal were recovered in the char. The trace elements in the feed coal ranged from a low of 0.1 ppm of Hg to a high of 19 ppm of Ni. The major elements, carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S) were determined by standard ASTM procedures while the minor elements, iron (Fe), aluminum (Al), silicon (Si), sodium (Na), calcium (Ca), potassium (K), magnesium (Mg) and chlorine (Cl) were determined by gravimetric or atomic adsorption techniques. Average overall recoveries of over 95 percent were obtained for the major elements, which were found primarily in the product gas. Recoveries of better than 87 percent were attained for the minor elements, found principally in the char except for Cl which was found principally in the condensate water.

Introduction

Conversion of coal to a high-energy gaseous fuel in an environmentally acceptable manner is an important part of the U. S. energy program. The Pittsburgh Energy Research Center's SYNTHANE process is one of these coal conversion processes. While this coal-to-gas conversion process was being developed in the Process Development Unit (PDU) the environmental aspects of the process were being studied. Forney et.al.(1) and Schmidt et.al. (2) first reported on the analysis of the various effluent streams discharging from this PDU. Later, Forney et.al (3) attempted to make a mass balance of the trace and major elements around the SYNTHANE PDU gasifier. While the balance of major elements was satisfactory, the recovery and balance of the trace elements was less so. This paper describes two coal gasification tests, performed in the same PDU gasifier, in which a several fold improvement in recovery and balance of a selected group of trace elements was made. Means were taken to obtain representative samples of the various solid, gas and liquid streams, followed by meticulous care in preparing the samples to prevent contamination.

The SYNTHANE PDU System

The system consists primarily of a fluid-bed gasifier, a free-fall carbonizer, and a fluid-bed pretreater, figure 1.

The gasifier is a 6-ft. long, 4-in. diameter, Schedule 40 pipe of 310 stainless steel. It is surrounded by three individually controlled, insulated, electric heaters that supply heat for startup and counter radiation loss during operation.

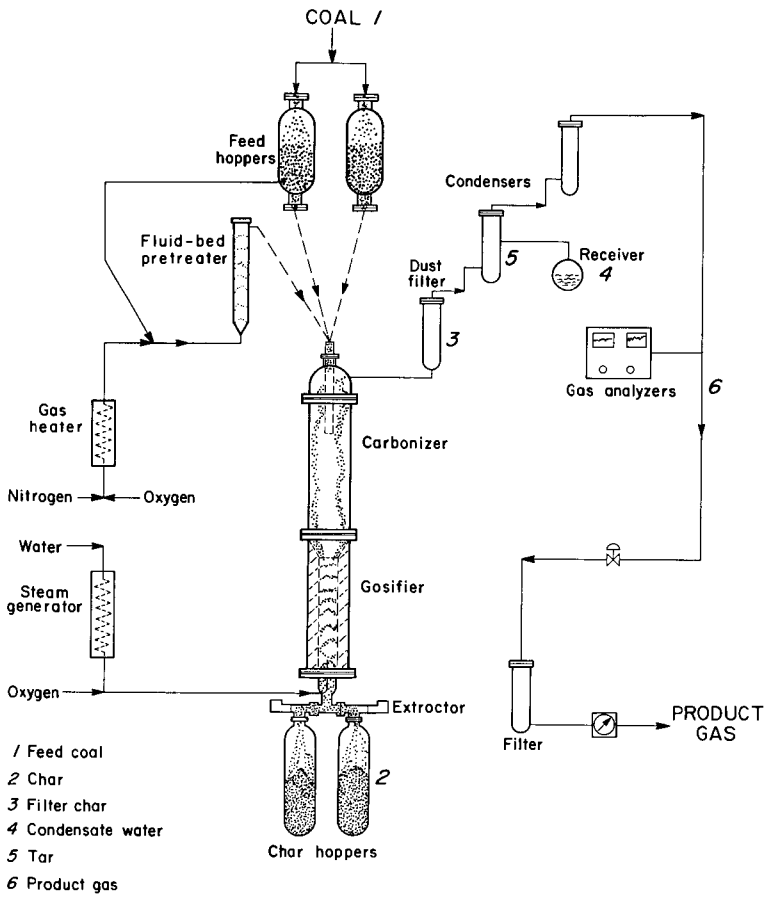

Figure 1.-Schematic flowsheet of the SYNTHANE PDU gasifier and sample points.

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The carbonizer is a 6-ft. long, 10-in. diameter Schedule 40 pipe of 304 stainless steel. Electric heaters surrounding the carbonizer maintain it at a nominal 560° C during gasification.

The pretreater is a 7.5-ft. long, 1-1/2-in. diameter Schedule 80 pipe of 304 stainless steel. Four individually controlled heaters enclose the pretreater and normally maintain heat for adiabatic conditions at 430° C.

Operations

When gasifying the caking Illinois No. 6 coal, the pulverized (20 x 0 mesh) coal is conveyed to the base of the pretreater and through the pretreater with nitrogen containing 10-15 vol.% oxygen at a fluidizing gas velocity of 0.3-0.5 ft/sec. Pretreating or decaking occurs at a nominal oxygen-to-coal ratio of 1.0 cu.ft. per lb., a temperature of 430° C and a coal-to-gas contact time of 8 mins. The decaked coal empties from the top of the pretreater and falls by gravity through the carbonizer countercurrent to the product gas exiting from the top of the fluidized-bed in the gasifier. A mixture of steam and oxygen enters the base of the gasifier and maintains the coal in a fluidized state at a nominal gas velocity of 0.3 ft/sec. A fluidized-bed height of 68 ins. is maintained by a combination of coal feed, gasification and extraction rates.

Sampling

Samples of the feed coal, char, tar, condensate water and gas were collected from the sampling points shown in figure 1. All samples for SSMS analysis were collected in polyethylene containers, those containers for condensate and tar were acid-cleaned. All coal and char samples were collected and prepared according to ASTM (D-2234-72 and D-2013-72) methods. To improve homogeneity the coal and char samples were further crushed to a fine powder using a boron carbide mortar and pestle. Due to the high hydrocarbon and low ash content of the tars they were examined as low temperature ash. Condensate samples were prepared by evaporation onto ultra-pure graphite. Product gas was passed through graphite-packed filters. Analysis of the filters by SSMS indicated low concentration of sulfur and no other elements above the instrument background levels.

Analysis

Spark source mass spectra were recorded as a series of graded exposures on ion-sensitive photoplates. Resolution was maintained near 1 part in 10,000 on ashed samples. A wider beam-defining slit giving resolution near 1 part in 4,000 was used on a few longer exposures for the ultra-trace elements in order to improve ion transmission and shorten the length of time required for ion collection. The lower resolution slit was also used on the condensate samples to avoid blockage by organic material. After developing, the photoplates were placed on a densitometer and the densitometer output transferred to a strip chart recording. Elemental concentrations were determined from the percent transmission of analytical mass lines by standard procedures, assuming validity of the Hull (4) equation. All calculations were done at PERC on a PDP-11/70 computer.

Elemental sensitivities for the SSMS analysis were determined, where possible, from runs of NBS SRM 1632 (fly ash). Sensitivities of a few minor elements were determined from USGS standard BCR-1 (basalt). A few sensitivities for elements such as Cd and Se were determined from prepared solutions evaporated onto graphite.

Results and Discussion

Operating conditions and results for the subject tests are shown in table 1. Major element analyses and amounts of coal and feed streams to the gasifier are shown in table 2. Major element analyses of the exit streams from the gasifier are shown

TABLE 1. - Operating conditions and results from gasification of an Illinois No. 6 coal with steam and oxygen at 40 atmospheres

Test No.	228	235
Time, hrs.	4.5	5.0
Input, kgs		
Coal	40.179	38.136
Steam	73.030	71.732
Oxygen	17.932	15.436
Nitrogen	69.149	80.340
Output, kgs		
Gas	119.297	131.468
Condensate	57.500	64.476
Char	11.613	10.930
Tar	1.599	.812
Temp., max. avg.°C		
Pretreater	428	430
Gasifier	947	933
Results		
Carbon gasified, %	67.9	75.5
Carbon converted, %	72.9	78.3
Steam converted, %	14.7	13.8
Make gas[1] SCM/kg coal	.96	1.0
Tar make, % of coal	3.98	2.13

1/ $H_2+CO+CH_4+C_2H_6$.

TABLE 2. - Major element analysis of feed stream to gasifier

Test No.	228	235
Coal feed, gms	40,179	38,136
Elements, wt.%		
Carbon	64.5	64.2
Hydrogen	5.0	6.0
Oxygen	9.9	12.3
Nitrogen	1.1	1.2
Sulfur	4.0	3.7
Ash	15.5	12.7
Moisture	3.8	4.3
Fixed Carbon	46.6	47.8
Volatile Matter	34.1	35.2
Water,[1] gms	73,030	71,732
Hydrogen, wt.%	11.1	11.1
Oxygen, wt.%	88.9	88.9
Oxygen,[2] gms	17,932	18,436
Nitrogen,[3] gms	69,149	80,340

1/Distilled water, less than 1.0 ppb Hg.
2/Cylinder oxygen, 99.5% O_2, 0.5% N_2+Ar less than .03 ppb Hg.
3/Liquid nitrogen, 99.9985% N_2, typically less than 3 ppm H_2, O_2 with trace of Ar and less than 0.2 ppb Hg.

in table 3 and the mass balances of the major elements around the gasifier are shown in table 4. The tabulated results reveal that, at the particular gasification conditions, the largest portions of the major elements appear in the product gas and condensate. The gas was analyzed by mass spectrometry and gas chromatography and the condensate by gravimetric, colorimetric and titrametric methods.

TABLE 3. - Major element analysis of exit streams from gasifier

	Gas gm	Extractor char, gm	Filter Char, gm	Tar gm	Condensate gm	Total gm
Test No. 228						
Carbon	16,495	6,545	417	1,290	920	25,667
Hydrogen	2,636	131	11	107	6,268	9,153
Oxygen	29,883	165	29	136	50,025	80,238
Nitrogen	69,149	42	4	22	218	69,435
Sulfur	1,134	81	7	43	288	1,553
Test No. 235						
Carbon	16,914	6,140	362	676	1,032	25,124
Hydrogen	2,698	198	13	59	7,028	9,996
Oxygen	30,355	136	14	58	56,094	86,657
Nitrogen	80,340	52	4	9	257	80,685
Sulfur	1,161	73	5	10	129	1,378

TABLE 4. - Mass balance of the major elements

	IN, kg	OUT, kg	% Recovery
Test No. 228			
Elements;			
Carbon	25.92	25.67	99.0
Hydrogen	10.18	9.15	89.9
Oxygen	86.77	80.24	92.5
Nitrogen	69.59	69.44	99.8
Sulfur	1.60	1.55	96.9
	194.06	186.05	95.8
Test No. 235			
Carbon	24.48	25.12	102.6
Hydrogen	10.32	10.00	96.9
Oxygen	83.83	86.66	103.4
Nitrogen	80.80	80.69	99.9
Sulfur	1.41	1.38	97.9
	200.84	203.85	101.5

The mass balance reveals a relatively good recovery, ranging from 90-97% for H to 99.8-99.9% for N. Even the recovery of the comparatively small amount of S was in the range of 96.9 to 97.9%. Most of it was found in the product gas.

Minor elements, (Al, Ca, Cl, Fe, Mg, K, Na, Si, and Ti) found in the ash of the coal were recovered in the gasified char except for Cl, which was found primarily in the condensate water, as shown in table 5. Analysis was done by AAS and gravimetric methods. Recovery of the minor elements ranged from a low of 62.5% for the least prevalent element in this group, Cl, to 101.6% for the most prevalent element, Si.

TABLE 5. - Minor element analysis of solids and mass balance

	IN gm	Coal wt.%	OUT gm	Char wt.%	Recovery percent
Test No. 228					
Elements:					
Silicon	1,665	4.14	1,694	14.6	101.6
Aluminum	753	1.87	754	6.5	100.1
Iron	1,173	2.92	1,033	8.9	88.1
Titanium	48	.12	45	.4	93.8
Calcium	418	1.04	409	3.5	97.8
Magnesium	41	.10	45	.4	93.8
Sodium	24	.06	21	.2	87.5
Potassium	112	.28	113	1.0	100.9
Chlorine 1/	16	.04	2	.02	12.5

1/ 8 gms found in condensate water, total recovery 62.5.

As in the case of the minor elements, the trace elements (As, Be, Cd, Ni, Pb, Se, V) from the coal were recovered in the gasified char, except for Hg. Only 12.5 to 20.0% of the Hg was recovered. In test 235, this represented a recovery of 0.6 mg of Hg out of the 3.0 mg present in the 38 KG of gasified coal, table 6. Of this amount 0.44 mg was found in the char and 0.16 mg was found in the tar and condensate. Although the whereabouts of the major portion of the Hg remains unresolved, it seems reasonable to assume that because of the volatility of Hg, it should be found in the product gas. For coal combustion Kalb (5) reports that the major portion of mercury was indeed detected in flue gas.

TABLE 6. - Trace element analysis of solids and liquid streams

	Coal		Extractor	Filter		Tar	Condensate
	ppm	mg	char, mg	ppm	char, mg	mg	mg
Test No. 228							
Arsenic	3.2	130	120	6.2	3.7	1.6	2.6
Beryllium	1.1	44	41	0.2	0.1	-	<0.2
Cadmium	0.5	20	23	3.6	2.2	<0.5	<0.3
Lead	5.1	200	120	14.0	8.4	0.3	<0.3
Mercury	0.10	4	.24	.02	.06	.01	.19
Nickel	16	640	600	11.0	6.6	7.6	0.5
Selenium	2.8	110	94	0.7	0.4	<0.5	<2.1
Vanadium	14	560	680	17.0	10	0.7	0.3
Test No. 235							
Arsenic	2.9	110	100	7.6	3.8	0.7	3.0
Beryllium	1.4	53	39	0.4	0.2	.02	<0.4
Cadmium	0.5	19	17	5.9	3.0	0.1	<1.0
Lead	8.5	320	150	25.0	13.0	1.2	<3.0
Mercury	.08	3	.40	.03	.14	.03	.13
Nickel	19	720	400	17	8.5	6.1	2.0
Selenium	2.6	99	86	1.5	0.8	.09	<20
Vanadium	13	500	380	24.0	12	0.2	0.6

Another unresolved condition was the relatively high ratio of As, Cd and Pb in the filter char as compared to that found in the coal. On a percentage basis, the char contained about twice the As, eight times the Cd and 3-50 times the Pb as was found in the coal. The filter char which has essentially the same ultimate analysis as does the coal, represents, however, only 1.3-1.5 percent of the coal feed. Whether the disparate ratio between the filter char and coal is caused by the volatilized material in the product gas, depositing onto the fine filter char or whether this represents particle size effect, i.e., the finer coal or char contains a greater percentage of these three elements, remains to be resolved.

Total recoveries ranged from a nominal low of 49% for Pb to a nominal high of 124% for Cd and V. The apparent low recovery of Pb may be an artifact arising from an inhomogeneity of Pb in the coal or chars.

Trace elements content of the coal as determined by our SSMS and flameless AAS analysis were reasonably close to those determined by AAS analysis, as reported by Attari (6), for a similar Illinois No. 6 coal.

Conclusions

Results from two typical coal gasification tests, performed in the SYNTHANE PDU, indicated that a mass balance of major and minor elements can be achieved with a relatively high degree of precision by standard analytical methods.

A reasonable degree of precision can be obtained for trace elements, with the exception of mercury.

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