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COAL DERIVED FUEL GASES FOR MOLTEN CARBONATE FUEL CELLS

November 1979

Prepared by
TRW
Energy Systems Planning Division

For
UNITED STATES DEPARTMENT OF ENERGY
Morgantown Energy Technology Center
Morgantown, West Virginia

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1.0 EXECUTIVE SUMMARY

This report characterizes product streams from state-of-the-art and future coal gasification systems to guide fuel cell program planners and researchers in establishing performance goals and developing materials for molten carbonate fuel cells that will be compatible with gasifier product gases. Specifically, this report describes:

- The range of gasifier raw-gas compositions available from the major classes of coal gasifiers
- The degree of gas clean-up achievable with state-of-the-art and future gas clean-up systems
- The energy penalties associated with gas clean-up

The study encompasses fixed-bed, fluid-bed, entrained-bed, and molten salt gasifiers operating with Eastern bituminous and Western subbituminous coals. Gasifiers operating with air and oxygen blowing are evaluated, and the coal gasification product streams are characterized with respect to:

- Major gas stream constituents, e.g., CO, H_2, CO_2, CH_4, N_2, H_2O
- Major gas stream contaminants, e.g., H_2S, COS, particulates, tars, etc.
- Trace element contaminants, e.g., Na, K, V, Cl, Hg, etc.

The results of this study indicate that gasifier product raw-gas compositions are influenced by the gasifier type, operating conditions, and coal type. Fixed-bed gasifiers, that do not subject the coal pyrolysis products to temperatures above approximately 1600°F, contain significant quantities of tars, oils, organic sulfur compounds and organic nitrogen compounds in the product raw gas. Fluid-bed, entrained-bed, and molten salt gasifiers, that operate at higher temperatures, produce less of these materials. Increasing operating temperature also favors the formation of H_2 and CO as compared to CO_2, H_2O and CH_4. Since the presence of H_2 and CO is preferred over CH_4 for a molten carbonate fuel cell feed, high operating temperatures seem to be indicated for gasifiers operating with molten carbonate fuel cells.

Other gasifier operating conditions that influence product gas composition are gasifier pressure and overall H/O atomic feed ratio. High pressure operation suppresses the formation of H_2 and CO in favor of increased concentrations of CH_4, CO_2, and H_2O, and high H/O atomic ratios favor the formation of H_2 and CH_4 in comparison to CO and CO_2.

Low-sulfur, Western subbituminous coals produce lower sulfur contents in the gasifier raw gas in comparison to the high-sulfur-content, Eastern bituminous coals. Also, since the Western coals are generally more reactive, the gasifiers can be operated at lower temperatures and higher overall H/O ratios. These conditions tend to produce higher H_2 and CH_4 concentrations and lower CO and CO_2 concentrations.

Very little data are available concerning the fate of trace elements during coal gasification. However, from the available data, we have identified those trace elements most likely to be present in trace amounts in the gasifier product raw gas. These elements are:

Al As B Be Bi Ca Cd
Ce Cl F Fe Ge Hg K
Mg Mo Na Pb S Sb Se
Si Te V Zn Zr

All of these elements are likely to be present in the cleaned gas from high temperature clean-up systems that don't employ wet scrubbers. Even though many of these elements form only non-volatile compounds and exit the gasifier principally with the bottom ash, some will exit with the fly ash and not be completely captured by the high temperature particle removal systems. However, the wet scrubbers of low temperature gas clean-up systems will capture these particles, so only the elements that form volatile, water insoluble compounds, i.e., As, B, Ge, Se, and Te, should be present in the product gas from the low temperature clean-up systems.

Three cases have been analyzed to determine the effect of gas clean-up on product gas composition and the associated energy penalties:

Case 1

- Product raw gas from a fixed-bed gasifier containing tars, oils, and organic sulfur and nitrogen compounds
- Low temperature clean-up system employing state-of-the-art processing units

Case 2

- Product gas from a fluid-bed gasifier containing no tars or oils
- Low temperature clean-up system employing state-of-the-art processing units

Case 3

- Product gas from a fluid-bed gasifier containing no tars or oils
- High temperature clean-up system employing developmental-stage processing units

For Cases 1 and 2, the clean-up systems produce a gas that is essentially free of all particulates, tars, oils, CO_2 and nitrogen compounds while the total sulfur content is less than 1 ppm. For Case 3, the product gas is also free of particulates, tars and oils, with a total sulfur content of less than 1 ppm, but this gas still contains CO_2 and NH_3.

Energy penalties have been computed for each of the gas clean-up cases described above. These penalties were taken to be the system work defects, i.e., the decrease in the amount of work that could be derived from the streams leaving the system in comparison to the streams entering the system. These energy penalties are tabulated below:

Case	Energy Penalty (Percent)
1	25.0
2	13.2
3	1.3

2.0 INTRODUCTION

.1 BACKGROUND

One of the promising new concepts for generating electricity from coal involves the mating of a coal gasification system to a molten carbonate fuel cell. A schematic diagram of this concept is shown in Figure 2-1. The gasifier may be operated on coal or coal char, may utilize air or oxygen, and will require removal of hydrogen sulfide from the off-gas. The molten carbonate fuel cell operates with a mixed electrolyte of Li_2CO_3 and K_2CO_3 at temperatures ranging from about 1100°F to 1300°F. The hydrogen and carbon monoxide in the gasification off-gases are oxidized at the nickel anode to H_2O and CO_2 according to the following reactions:

$$H_2 + CO_3^{=} \longrightarrow CO_2 + H_2O + 2e^-$$

$$CO + CO_3^{=} \longrightarrow 2CO_2 + 2e^-$$

At the nickel oxide cathode, oxygen is reduced by carbon dioxide:

$$\tfrac{1}{2}O_2 + CO_2 + 2e^- \longrightarrow CO_3^{=}$$

The carbon dioxide transfer device (CDTD) uses air or O_2 to oxidize unburned fuel before feeding it to the cathode. A large excess of cathode feed is also supplied for cooling purposes.

Because of the early stage of development of molten carbonate fuel cell technology, little is known concerning the exact requirements for a suitable gasifier off-gas. Recent studies at IGT (2.1) have indicated substantial performance penalties with H_2S concentrations in the anode feed of 10 ppm. Problems result from anode sulfidation to produce liquid NiS_x, but an additional fundamental problem is sulfur scavenging from the cathode flow by the electrolyte, followed by transport of sulfate to the anode.

It is anticipated that a nominal fuel sulfur limit of <1 ppm will be required for commercial molten carbonate fuel cells, but acceptable levels for other possible contaminants have not yet been established. Particulates and tars, however, are expected to pose problems, either in the fuel cell itself, where they might plug electrode pores and reduce activity, or in gas turbines used for bottoming cycles.

A variety of gasifier types appears to be available for use. Preliminary analyses indicate that fluidized-bed, entrained-bed, and molten-salt gasifiers are the most likely candidates because of simplicity and low hydrocarbon and tar output. Hydrocarbons,

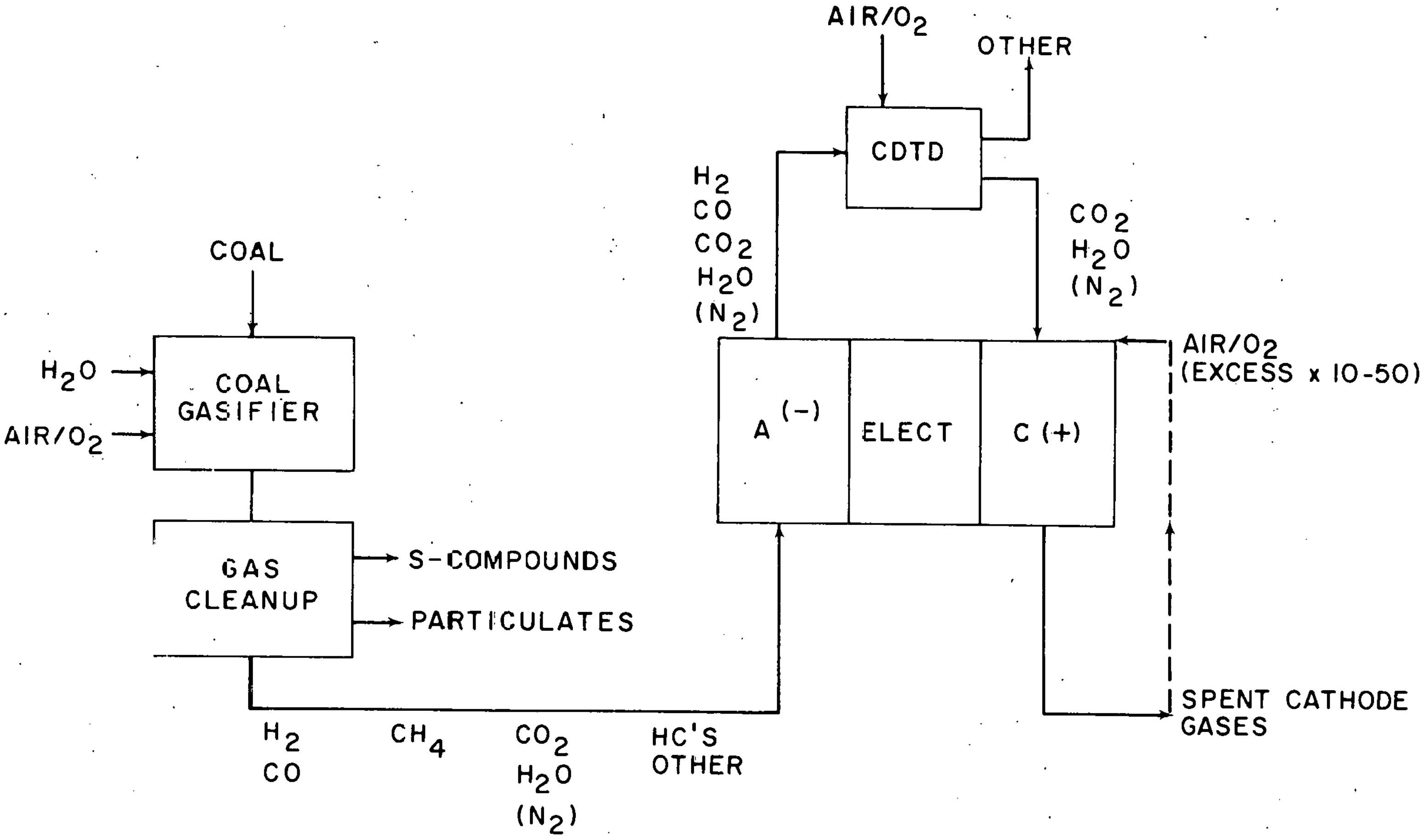


Figure 2-1. Schematic Diagram of Gasifier/Fuel Cell

including methane, are undesirable gasification products in this application, because they are not oxidized at the fuel cell anode. Molten-salt gasifiers produce the lowest raw-gas sulfur contents, but these gasifiers might be severely penalized by complexity, and they might not be developed in time for inclusion in early demonstrations. Entrained-bed gasifiers are in an advanced state of development, but it is not clear whether the high sensible heat content of the exit stream is compatible with highest system efficiency.

2.2 TASK OBJECTIVE

The objective of this task was to characterize product streams from state-of-the-art and future gasification systems in order to guide fuel cell program planners and researchers in establishing performance goals and developing fuel cell materials that will be compatible with these product streams. Specific subtasks were to:

- Present the range of gasifier raw-gas compositions available from the major classes of coal gasifiers
- Illustrate the degree of gas clean-up achievable with state-of-the-art and future gas clean-up systems
- Compute the energy penalty associated with different degrees of gas clean-up

The study encompasses fixed-bed, fluid-bed, entrained-bed, and molten-salt gasifiers operating with Eastern bituminous and Western subbituminous coals. Gasifiers operating with air, oxygen, and oxygen-enriched air were to be evaluated, but no data were available for gasifiers operating with oxygen-enriched air. However, the performance of such gasifiers is bracketed by their oxygen and air blown counterparts.

Coal gasification product streams were characterized with respect to:

- Major gas stream constituents, e.g., CO, H_2, CO_2, CH_4, N_2, H_2O
- Major gas stream contaminants, e.g., H_2S, COS, particulates, tars, etc.
- Trace element contaminants, e.g., Na, K, V, Cl, Hg, etc.

It was recognized at the outset that there would be significant gaps or inconsistencies in the available data and that reasonable approximations based on sound engineering judgment would be needed to present a coherent and comprehensive characterization.

2.3 REPORT OVERVIEW

Section 3.0 of this report presents the available information concerning coal gasifier raw-gas compositions. First, available information concerning major gas stream constituents and contaminants is presented, and raw-gas compositions representative of the different classes of gasifiers, coal feeds, and air or oxygen blowing are presented.

Once the major gas stream constituents and contaminants are addressed, a survey of the available information concerning trace elements in gasifier product streams is presented. Those trace elements consistently appearing in the gasifier product streams are identified along with estimates of the range of concentrations that might be experienced. Finally, the stable molecular forms of the trace elements in the gasifier product streams are identified.

Section 4.0 of this report discusses the clean-up of gasifier raw gases to produce fuels suitable for operation with molten carbonate fuel cells. First, a brief survey of gas clean-up technology is presented, followed by a description of the rationale adopted for synthesizing appropriate gas clean-up trains for analysis in this study. These representative gas clean-up trains are then described together with their impact on major gas stream constituents, contaminants and trace element compounds. Finally, the energy penalties associated with different degrees of gas clean-up are discussed.

3.0 GASIFIER RAW-GAS COMPOSITION

.1 MAJOR CONSTITUENTS AND CONTAMINANTS

3.1.1 Availability of Data

The availability of gasifier raw-gas composition data as a function of gasifier type, coal type and oxygen or air blowing is summarized in Figure 3-1. As indicated, data are available for all combinations of gasifier type, coal type, and air or oxygen blowing except that data are not available for a molten-salt gasifier operating with subbituminous coal or for an air blown entrained-bed gasifier operating with subbituminous coal.

Representative raw-gas composition data for each of the gasifiers designated in Figure 3-1 are given in Tables 3-1 to 3-4. Also contained in these tables are the operating conditions for each gasification run upon which the composition data are based. Much of the data presented were taken from summaries presented in references 3.1 and 3.2. These data were complemented with additional composition data contained in references 3.3 to 3.19. In many cases, only data for major gas stream constituents are available in the literature, but in other cases, concentrations of major contaminants, such as H_2S, COS, tars, particulates etc., are presented. The presence of trace elements in the gasifier raw gases is discussed in Section 3.2 below.

3.1.2 Representative Raw-Gas Compositions

From the data base presented above in Tables 3-1 to 3-4, representative cases were selected for each gasifier type operating with bituminous and subbituminous coal and air and oxygen blowing. The data for these representative cases are summarized in Table 3-5. As indicated above, no data are available for a molten-salt gasifier operating with subbituminous coal or for an air blown entrained-bed gasifier operating with subbituminous coal.

In selecting the representative cases given in Table 3-5, major consideration was given to the completeness of the data; cases for which complete contaminant data are available were selected over cases for which contaminant data are sketchy or not present at all. Secondary consideration was given to the consistency of the data with the general trends observed for the influence of gasifier operating conditions on product gas compositions. These trends are discussed below.

Figure 3-1

AVAILABILITY OF EXPERIMENTAL DATA

		GASIFIER TYPE			
Oxidant	Coal	Fixed Bed	Fluid Bed	Entrained	Molten Salt
Air	Bituminous	METC, Lurgi Wellman-Galusha Woodall-Duckham Riley-Morgan	BCR Westinghouse Synthane, U-Gas	Foster-Wheeler Combustion Eng. Bi-Gas	Atomics, Int.
	Subbituminous	METC, Lurgi	Winkler		
Oxidant	Coal	Fixed Bed	Fluid Bed	Entrained	Molten Salt
Oxygen	Bituminous	Lurgi, BGC Slagging Woodall-Duckham	Hygas Synthane	Babcock-Wilcox Bi-Gas Koppers-Totzek Texaco	Atomics, Int.
	Subbituminous	Lurgi	Hygas Synthane Winkler	Bi-Gas	

Table 3-1. Product Gas Compositions for Fixed-Bed Gasifier Runs

NAME	Wellman-Galusha	Woodall-Duckham	Riley Morgan	Wellman-Galusha	Riley Morgan	METC	METC	METC	Wellman-Galusha	Lurgi	METC	BGC Slagging	BGC Slagging	BGC Slagging	Lurgi	Lurgi	Lurgi
TYPE	Fixed Bed	Fixed Bed	Fixed Bed	Fixed Bed	Fixed Bed	Fixed Bed	Fixed Bed	Fixed Bed	Fixed Bed	Fixed Bed	Fixed Bed	Fixed Bed Slagging	Fixed Bed Slagging	Fixed Bed Slagging	Fixed Bed	Fixed Bed	Fixed Bed
PRESSURE, psia	14.7	14.7	14.7	165	14.7	120	222	125	220	300	148	300	300	300	375	385	435
PRODUCT TEMP., °F	1088 (norm)	250 1200 (norm)	1090 (norm)	1030	1090 (norm)	1000	1000	1000	1200 (norm)	---	820	---	---	---	1126	718	700-1100
MAX. TEMP., °F	2400 (norm)	2200 (norm)	1800-2000 (norm)	2400-2500 (norm)	1800-2000 (norm)	2500	2500	---	2400-2500 (norm)	1500-2500 (norm)	---	>2300 (norm)	>2300 (norm)	>2300 (norm)	1800-2500 (norm)	1900-2500	1100-1400
COAL																	
Type	Bituminous	High Volatile C Bituminous	High Volatile A Bituminous	Pittsburgh High Volatile A Bit.	Medium Volatile Bituminous	W.V. Upper Freeport	Kentucky #9	Illinois #6	New Mexico Sub-Bituminous A	New Mexico Sub-Bituminous C	Mont. Rosebud	Donisthorpe Weakly Caking Bituminous	Donisthorpe Weakly Caking Bituminous	Newstead Bituminous	Illinois #6 HVC Bit.	Montana Sub-Bituminous A	Navajo Sub-Bituminous
Size, in.	1.25-2.0	0.25-1.5	0.25-1.25	0.75-1.25	0.25-1.25	---	---	---	1.5	0.08-1.75	---	1.0-1.5	1.0-1.5	1.0-1.5	.25-1.25	.25-1.25	1.75
Volatiles, %	---	---	30.8	35.1	21.4	26.9	34.0	---	31.2	31.0	---	---	---	---	34.7	29.2	---
Moisture, %	---	---	5.5	1.1	7.1	1.2	5.0	0.41	8.8	16.4	3.77	12.7	13.8	12.6	10.2	24.7	16.5
Ash, %	---	---	7.1	8.7	5.0	14.8	15.4	11.17	24.2	17.8	10.26	7.4	5.6	7.6	9.1	9.7	17.3
Sulfur, % (dry basis)	---	---	0.8	2.7	0.7	2.1	4.1	---	1.1	0.63	---	1.45	1.3	0.7	3.13	1.45	.95
HHV, Btu/lb	14,000 (DRY)	12,900	13,405 (as received)	13,750	13,830 (as received)	12,840 (as received)	11,450 (as received)	11,860 (as received)	8900	8838	10,306	---	---	---	12,770	11,436	7500-10,250
Rate, lb/ft^2/hr	---	74 (norm)	35-150 (norm)	186	35-150 (norm)	---	---	---	155	248	---	980	1436	928	96	103	---
FEEDS																	
Steam/Coal, lb/lb	~0.4	.25 (norm)	0.56	0.4	---	.43	.50	.44	0.68	0.965	.82	0.29 (DAF)	0.29 (DAF)	0.31 (DAF)	1.9 (DAF)	1.9 (DAF)	1.5 (DAF)
O_2/Coal, lb/lb	---	---	---	---	---	---	---	---	---	---	---	0.48 (DAF)	0.48 (DAF)	0.53 (DAF)	0.4 (DAF)	.4	.41 (DAF)
Air/Coal, lb/lb	~3.5	2.3	2.74	3.02	---	2.69	2.87	2.7	2.31	1.99	3.0	---	---	---	---	---	---
PRODUCT STREAM VOLUME % (DRY)																	
CO	28.6	28.3	21.0	21.6	23.5	20.8	18.5	20.3	16.0	17.4	15.3	61.3	60.85	60.55	17.3	15.1	19.5
H_2	15.0	17.0	17.92	18.7	16.4	17.0	13.6	16.4	19.0	23.3	16.7	28.05	28.1	28.65	39.1	41.1	38.7
CH_4	2.7	2.7	2.0	2.9	1.7	2.5	2.0	2.8	3.5	5.1	1.7	} 7.65	} 7.7	} 7.25	9.4	11.2	11.0
C_2H_4	---	0.3	} 0.45	} 0.2	} 0.35	---	---	---	} 0.3	} 0.63	---				} 0.7	} 0.5	.4
C_2H_6	---	---				0.1	0.2	---			---	0.45	0.55	1.05			.6
CO_2	3.4	18.0	8.85	7.3	7.3	8.3	10.8	9.4	12.6	14.8	12.9	2.55	2.7	2.35	31.2	30.4	28.8
N_2+Ar	50.3	47.2	49.62	48.9	50.62	51.0	54.5	50.1	48.4	38.5	50.3	---	---	---	1.2	1.2	---
H_2S	---	---	0.16	0.4	0.12	0.3	0.5	---	0.2	0.23	---	1.2×10^{-2} (DAF)	---	7.4×10^{-3} (DAF)	1.1	0.5	.3
COS+CS_2	---	---	---	---	---	---	---	---	---	---	---	9.8×10^{-4} (DAF)	---	---	5.4×10^{-4} (lb/lbCoal)	9.2×10^{-4} (lb/lb Coal)	.004
SO_2	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
H_2O, lb/lb Coal	---	---	0.322	2.32	---	.21	.19	---	0.64	---	---	---	---	---	---	---	1.13
Naphthas, lb/lb Coal	---	---	---	---	---	---	---	---	---	1.6×10^{-2}	---	---	---	---	1.0×10^{-2}	8.6×10^{-3}	1.6×10^{-2}
Tar, lb/lb Coal	0.06	} 0.079	0.037	0.026	---	.02	.01	---	0.034	---	---	7.3×10^{-2} (DAF)	---	6.9×10^{-2} (DAF)	3.8×10^{-2}	3.0×10^{-2}	2.3×10^{-2}
Tar Oil, lb/lb Coal	---		0.040	---	---	---	---	---	---	---	---	---	---	---	3.5×10^{-3}	3.2×10^{-2}	3.2×10^{-2}
Crude phenols, lb/lb Coal	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	$.4 \times 10^{-2}$
NH_3, lb/lb Coal	---	---	---	---	---	---	---	---	---	---	---	---	---	---	4.0×10^{-6}	2.0×10^{-6}	$.96 \times 10^{-2}$
HcN, lb/lb Coal	---	---	---	---	---	---	---	---	---	---	---	---	---	---	6.2×10^{-5}	6.0×10^{-6}	---
Particulates, lb/lb Coal	---	---	0.027	3.5×10^{-3}	---	.02	.01	---	0.017	---	---	1.1×10^{-2} (DAF)	2.3×10^{-2} (DAF)	9.6×10^{-3} (DAF)	5.6×10^{-3}	3.7×10^{-2}	---
GAS RATE, SCF/LB COAL	---	---	58.9 (norm)	64.4	58.9 (norm)	---	---	---	46.9	52.4	---	34.4	33.2	36.2	36.8	35.3	---
HHV, BTU/SCF (DRY BASIS)	168	175	156	164	153	150	128	151	150	195	132	374	375	379	298	307	---
REFERENCE	3-1	3-1	3-1	3-4	3-1	3-4	3-4	3-8	3-1	3-1	3-8	3-1	3-1	3-1	3-1	3-1	3-13

Table 3-2. Product Gas Compositions for Fluid-Bed Gasifier Runs

NAME	BCR	Synthane	U-Gas	Westinghouse	U-Gas	Winkler	HYGAS	Synthane	HYGAS	Winkler
TYPE	Fluid. Bed	Fluid. Bed	Fluid. Bed	Fluid. Bed	Fluid. Bed	Fluid. Bed	Fluid. Bed	Fluid. Bed	Fluid. Bed	Fluid. Bed
PRESSURE, psia	up to 250	1015	65-365	145-215	315	14.7	1180	1015	1180	14.7
PRODUCT TEMP., ^{o}F	---	1400	1550-1990	1600-1800	1550-1900	1300 (norm)	---	---	---	1300 (norm)
MAX. TEMP., ^{o}F	600-2100 (norm)	1800	1900	2100	1900	1800 (norm)	1720	1800	1720	1800 (norm)
COAL										
Type	Eastern Coal	Illinois #6	Bituminous	Eastern Coal	Pittsburgh Seam	Subbituminous A	Pittsburgh #8	Illinois #6	Montana Sub-Bituminous	Subbutiminous
Size, in.	.002-.003	.03	0.25	0.125-0.25	0.25	<0.38	.006-.07	.03	.006-.07	<.31
Volatiles, %	---	---	---	---	---	---	---	---	---	39
Moisture, %	---	---	---	---	6.0	16	---	---	---	3
Ash, %	---	---	---	---	12.49	19	---	---	---	24
Sulfur, % (dry basis)	---	---	---	---	4.4	---	---	---	---	---
HHV, Btu/lb	14,090	11,695	12,235	13,600	13,178	10,600	13,200	11,695	11,290	---
Rate, lb/ft^2/hr	---	---	---	---	---	---	---	340	---	---
FEEDS										
Steam/Coal, lb/lb	0.7	---	0.4-0.6	0.5	.61	∿0.2	1.00	1.25	.96	.2-.3
O_2/Coal, lb/lb	---	---	---	---	---	---	0.21	.35	0.23	∿.5
Air/Coal, lb/lb	3.25	---	2.8-3.3	2.8	3.02	∿2.5	---	---	---	---
PRODUCT STREAM VOLUME % (DRY)										
CO	25.7	10.1	19.6	19.2	19.3	22.0	23.8	13.2	26.1	37.0
H_2	23.4	21.5	17.5	14.4	13.2	14.0	30.2	32.3	30.7	37.0
CH_4	---	5.6	3.4	2.7	4.7	1.0	18.6	15.0	16.6	3.0
C_2H_4	---	---	---	---	---	---	---	---	---	---
C_2H_6	---	0.7	---	---	---	---	0.7	1.6	1.3	---
CO_2	5.2	17.9	9.9	9.3	10.0	7.0	24.5	36.2	24.1	20.0
N_2+Ar.	45.5	43.5	48.9	54.3	52.1	56.0	0.1	Negl.	.2	3.0
H_2S	0.2	0.7	0.7	0.1	.68	---	1.2	1.6	0.2	---
COS+CS_2					.02	---				---
SO_2	---	---	---	---	---	---	---	---	---	---
H_2O, lb/lb Coal	---	---	---	---	0.38	---	---	---	---	---
Naphthas, lb/lb Coal	---	---	---	---	---	---	---	---	---	---
Tar, lb/lb Coal	---	---	---	---	---	---	---	$4.7x10^{-2}$	---	---
Tar Oil, lb/lb Coal	---	---	---	---	---	---	0.4 (%, BTX)	$0.5x10^{-2}$ (BTX)	0.4 (%, BTX)	---
Crude phenols, lb/lb Coal	---	---	---	---	---	---	---	---	---	---
NH_3, lb/lb Coal	---	---	---	---	---	---	0.5 (%)	$0.8x10^{-2}$	0.4 (%)	---
HCN, lb/lb Coal	---	---	---	---	---	---	---	---	---	---
Particulates, lb/lb Coal	---	---	---	---	---	---	---	---	---	---
GAS RATE, SCF/LB COAL	---	13.9	63.3	85.1	64.6	---	---	13.9	---	---
HHV, BTU/SCF (DRY BASIS)	160	165	154	135	158	125	370	355	375	270
REFERENCE	3-2	3-2	3-2	3-2	3-9	3-1	3-2	3-2	3-2	3-1

Table 3-3. Product Gas Compositions for Entrained-Bed Gasifier Runs

NAME	Bi-Gas	Foster-Wheeler	Comb.-Eng.	Babcock-Wilcox	Koppers-Totzek	Koppers-Totzek	Bi-Gas	Texaco	Bi-Gas
TYPE	Entrained	Entrained	Entrained	Entrained	Entrained	Entrained	Entrained	Entrained	Entrained
PRESSURE, psia	455	365	14.7	315	14.7	14.7	1170	365	765-1435
PRODUCT TEMP., °F	1800	---	1600	1800	2700 (norm)	2700 (norm)	1700	450	1550
MAX. TEMP., °F	2700 (norm)	1800-2800	3000	3400	3500 (norm)	3500 (norm)	2700 (norm)	2300 (norm)	---
COAL									
Type	Illinois #6 Bituminous	Illinois #6 Bituminous	Kentucky Bituminous	Pittsburgh #8	High Volatile B Bituminous	High Volatile C Bituminous	Western Kentucky #11 Bituminous	Illinois #6 High Vol. C Bituminous	Wyoming Elkol, Lincoln Co., Subbituminous
Size, in	70%<0.03	70%<.003	70%<.003	70%<.003	70%<.003	70%<.003	70%<0.03	70%<0.003	70%<.003
Volatiles, %	---	---	---	---	---	---	42.5	38.1	34.3
Moisture, %	4.2	---	---	---	2	2	1.3	3.7	17.9
Ash, %	8.7	---	---	---	10.2	13.7	7.2	13.7	3.5
Sulfur, % (dry basis)	3.9	---	---	---	2.5	1.1	7.9	---	.85
HHV, Btu/lb	12,200	12,800	12,600	13,860	13,000	12,640	13,285	13,000	10,250
Rate, lb/ft²/hr	---	---	157	---	317-540 (norm)	317-540 (norm)	---	---	3,000
FEEDS									
Steam/Coal, lb/lb Coal	0.57	---	---	---	0.412 (DAF)	0.405 (DAF)	0.47	~0.15	1.4-2.3
O_2/Coal, lb/lb Coal	---	---	---	---	0.860 (DAF)	0.349 (DAF)	0.57	~0.75	1.19-1.90
Air/Coal, lb/lb Coal	3.1	---	~3.5	---	---	---	---	---	.6-1.6 (N_2 add.)
PRODUCT STREAM VOLUME % (DRY)									
CO	20.2	29.2	22.1	23.3	53.35	52.51	40.6	37.6	18.5
H_2	14.6	14.5	17.0	8.4	35.66	35.96	22.5	39.0	35.8
CH_4	4.0	3.5	.03	---	---	.11	14.3	0.5	7.5
C_2H_4	---	---	---	---	---	---	---	---	---
C_2H_6	---	---	---	---	---	---	---	---	---
CO_2	9.2	3.3	7.0	4.6	10.0	100	12.9	20.8	22.6
N_2+Ar	51.0	48.7	53.3	63.5	1.12	1.15	0.6	0.6	15.6
H_2S	.6	0.7	0.6	0.2	0.82	0.36	1.3	1.5	---
$COS+CS_2$	.1				0.05	0.02	---	---	---
SO_2	---	---	---	---	---	.003	---	---	---
H_2O, lb/lb Coal	0.4	---	---	---	---	---	7.7	---	---
Naphthas, lb/lb Coal	---	---	---	---	---	---	---	---	---
Tar, lb/lb Coal	---	---	---	---	---	---	---	---	---
Tar Oil, lb/lb Coal	---	---	---	---	---	---	---	---	---
Crude phenols, lb/lb Coal	---	---	---	---	---	---	---	---	---
NH_3, lb/lb Coal	.4 (%)	---	---	---	<0.2	<0.2	---	---	---
HCN, lb/lb Coal	---	---	---	---	---	0.04	---	---	---
Particulates, lb/lb Coal	---	---	---	---	0.06 (DAF)	0.08 (DAF)	---	---	---
GAS RATE, SCF/LB COAL	77.3	---	67	---	34.3 (DAF)	33.5 (DAF)	39.5	---	55.5
HHV, BTU/SCF (DRY BASIS)	142	177	127	102	290	290	350	253	350
REFERENCE	3-1	3-2	3-2	3-2	3-1	3-1 & 3-15	3-1	3-1	3-16

Table 3-4. Product Gas Compositions for Molten Salt Gasifier Runs

NAME	Atom. Int.	Atom. Int.	Atom. Int.	Atom. Int.	Atom. Int.	Atom, Int.	Atom. Int.
TYPE	Molten Salt	Molten Salt	Molten Salt	Molten Salt	Molten Salt	Molten Salt	Molten Salt
PRESSURE, psia	---	15-300	14.7	14.7	14.7	14.7	14.7
PRODUCT TEMP., °F	---	~1700	---	---	---	---	---
MAX. TEMP., °F	---	~1800	1700-1800	1700-1800	1700-1800	1700-1800	1700-1800
COAL							
Type	Kentucky Coal	Kentucky #9	Kentucky #9	Kentucky #9	Kentucky #9	Kentucky #9	Kentucky #9
Size, in.	---	---	---	---	---	---	---
Volatiles, %	---	---	---	---	---	---	---
Moisture, %	---	---	---	---	---	---	---
Ash, %	---	---	15	15	15	15	15
Sulfur, % (dry basis)	---	---	---	---	---	---	---
HHV, Btu/lb	---	12,000	11,408	11,408	11,408	11,408	11,408
Rate, lb/ft^2/hr	---	---	---	---	---	---	---
FEEDS							
Steam/Coal, lb/lb	---	0	.28	.25	.14	.18	.12
O_2/Coal, lb/lb	---	---	.65	.60	.62	.56	.55
Air/Coal, lb/lb	---	3.5	---	---	---	---	---
PRODUCT STREAM VOLUME % (DRY)							
CO	24.2	29.7	49.8	49.6	53.3	53.9	55.5
H_2	9.4	13.2	34.3	34.5	33.8	33.3	33.1
CH_4	1.6	1.5	2.1	2.5	2.4	2.4	2.0
C_2H_4	---	---	0.2	0.3	0.2	0.5	0.4
C_2H_6	---	---	---	---	---	---	---
CO_2	6.0	3.5	12.4	12.1	9.5	9.3	8.2
N_2+Ar.	58.8	48.0	1.1	1.0	0.7	0.6	0.8
H_2S	100-200 PPM sulfur	<5 PPM sulfur	---	---	---	---	---
$COS+CS_2$					---	---	---
SO_2			---	---	---	---	---
H_2O, lb/lb Coal	---	---	---	---	---	---	---
Naphthas, lb/lb Coal	---	---	---	---	---	---	---
Tar, lb/lb Coal	---	---	---	---	---	---	---
Tar Oil, lb/lb Coal	---	---	---	---	---	---	---
Crude phenols, lb/lb Coal	---	---	---	---	---	---	---
NH_3, lb/lb Coal	---	<5 PPM	---	---	---	---	---
HCN, lb/lb Coal	---	---	---	---	---	---	---
Particulates, lb/lb Coal	---	---	---	---	---	---	---
GAS RATE, SCF/LB COAL	---	---	30.5	30.5	30.5	30.5	30.5
HHV, BTU/SCF (DRY BASIS)	---	158	296	302	309	314	313
REFERENCE	3-18	3-2	3-3	3-3	3-3	3-3	3-3

Table 3-5. Representative Gasifier Raw-Gas Compositions

NAME	METC	METC	Lurgi	Lurgi	U-Gas	Winkler	Hygas	Hygas	Bi-Gas	Koppers-Totzek	Bi-Gas	Atom. Int.	Atom. Int.
TYPE	Fixed Bed	Fixed Bed	Fixed Bed	Fixed Bed	Fluid. Bed	Fluid. Bed	Fluid. Bed	Fluid. Bed	Entrained Bed	Entrained Bed	Entrained Bed	Molten Salt	Molten Salt
PRESSURE, psia	115	220	375	385	50-350	1 atm.	1165	1165	---	1 atm.	750-1420	---	1 atm.
PROD. TEMP., °F	1000	1200	1126	718	---	1300 (norm)	---	---	1800 (norm)	2700 (norm)	1500	---	---
MAX. TEMP., °F	2500	2400-2500	1800-2500 (norm)	1900-2500 (norm)	1900	1800 (norm)	1720	1720	2700 (norm)	3500 (norm)	---	---	1700-1800
COAL TYPE	W. Virginia Upper Freeport	New Mexico Sub Bituminous	Illinois #6 HVC Bituminous	Montana Sub Bituminous	Pitt. Seam Bituminous	Subbituminous	Pitt. #8	Montana Subbituminous	Illinois #6 HVC Bituminous	East. Coal HVC Bituminous	Wyoming Subbituminous	Kentucky	Kentucky #9
GASIFICATION MEDIA	Steam/Air	Steam/Air	Steam/O_2	Steam/O_2	Steam/Air	Steam/Air	Steam/O_2	Steam/O_2	Steam/Air	Steam/O_2	Steam/O_2 (N_2 Dilution)	Steam/Air	Steam/O_2
PRODUCT STREAM (VOLUME %, DRY BASIS)													
CO	20.8	16.0	17.3	15.1	19.3	22.0	23.8	26.1	20.2	52.76	18.5	24.2	49.8
H_2	17.0	19.0	39.1	41.1	13.2	14.0	30.2	30.7	14.6	35.54	35.8	9.4	34.3
CH_4	2.5	3.5	9.4	11.2	4.7	1.0	18.6	16.0	4.0	0.11	7.5	1.6	2.1
C_2H_4	---	0.3	0.7	0.5	---	---	---	---	---	---	---	---	---
C_2H_6	0.1				---	---	0.7	1.3	---	---	---	---	---
CO_2	8.3	12.6	31.2	30.4	10.0	7.0	24.5	24.1	9.2	10.1	22.6	6.0	12.4
N_2+Ar	51.0	48.4	1.2	1.2	52.1	56.0	0.1	0.2	51.0	0.9	15.6	58.8	1.1
H_2S	0.3	0.2	1.1	0.5	0.68	---	1.2	0.2	0.6	0.32	---	$1\text{-}2\times10^{-4}$	---
$COS+CS_2$	---	---	8×10^{-3}	15×10^{-3}	0.02	---			0.1	0.03	---		---
SO_2	---	---	---	---	---	---	---	---	---	0.003			---
H_2O, lb/lb Coal	0.21	0.64	---	---	---	---	---	---	---	---	---	---	---
Naphthas, lb/lb Coal	---	---	1.0×10^{-2}	0.86×10^{-2}	---	---	---	---	---	---	---	---	---
Tar, lb/lb Coal	0.02	0.034	3.8×10^{-2}	3.0×10^{-2}	---	---	---	---	---	---	---	---	---
Tar Oil, lb/lb Coal	---	---	3.5×10^{-3}	3.2×10^{-2}	---	---	0.4	0.4	---	---	---	---	0.2
NH_3, lb/lb Coal	---	---	4.0×10^{-6}	2.0×10^{-6}	---	---	0.5	0.4	0.4	---	---	---	---
HCN, lb/lb Coal	---	---	6.2×10^{-5}	6.0×10^{-6}	---	---	---	---	---	0.04	---	---	---
Particles, lb/lb Coal	0.02	0.17	5.6×10^{-3}	3.7×10^{-2}	---	---	---	---	---	.05	---	---	---
GAS RATE, SCF/LB COAL	50.6	46.9	36.8	35.3	53.4	---	---	---	77.3	33.5 (D)	---	---	---
HHV, Btu/SCF (DRY)	150	150	298	307	158	125	370	375	142	290	---	---	296
REFERENCE	3-4	3-1	3-1	3-1	3-9	3-1	3-2	3-2	3-1	3-15	3-16	3-18	3-2

Note: (D) indicates gas rate on dry coal basis.

3.1.3 Effect of Gasification Parameters on Raw-Gas Compositions

3.1.3.1 Gasifier Temperatures

The temperatures prevailing in coal gasifiers influence both the kinetics of the chemical reactions and the equilibrium conditions. Thus, gasifier temperatures exert a major influence on the gasifier raw-gas compositions.

One of the major effects of temperature on raw-gas composition is its effect on the kinetics of decomposition or cracking of the tars, oils, phenols, and hydrocarbons that might be produced by coal devolatilization. In gasifiers where the product gas is subjected to temperatures above approximately 1600^{0}F, these materials will be cracked to CO, CO_2 and CH_4, producing a relatively clean product raw gas. On the other hand, in fixed-bed gasifiers where the product gas is not subjected to these temperatures, significant quantities of these tars, oils, etc. will be present in the gasifier off-gas.

The major equilibrium effects of temperature on raw-gas compositions are summarized in Figure 3-2, where the thermodynamic equilibrium composition in the C-H-O system is presented as a function of temperature, pressure, and overall H/O atomic ratio. As indicated, high temperature operation favors the formation of H_2 and CO as compared to CO_2 and H_2O. Although equilibrium will not prevail exactly within the gasifier, the trends predicted by thermodynamics should be qualitatively reflected by the experimental compositions. Thus, higher gasifier temperatures tend to produce higher concentrations of CO and H_2 in the gasifier raw gas and lower concentrations of CO_2 and H_2O.

The equilibrium compositions in Figure 3-2 also show marked reductions in CH_4 concentration with increasing temperature. Thus, methane synthesis from CO plus H_2 or from C plus H_2 will be reduced as temperature is increased. However, as indicated above, temperature also affects the kinetics of the cracking reactions that produce CH_4 from coal pyrolysis products. Thus, at moderate temperatures of about 1600^{0}F, methane concentration in the gasifier raw gas is not affected much by gasifier temperatures. However, as temperatures are increased further, to about 2600^{0}F, methane decomposition to CO and H_2 occurs, and the methane concentration in the product gas is quite small.

3.1.3.2 Gasifier Pressure

The thermodynamic equilibrium compositions in Figure 3-2 show that increasing pressure suppresses the formation of H_2 and CO in favor of increased concentrations for CH_4, CO_2, and H_2O. The effect is most pronounced in the 1200-1600^{0}F temperature

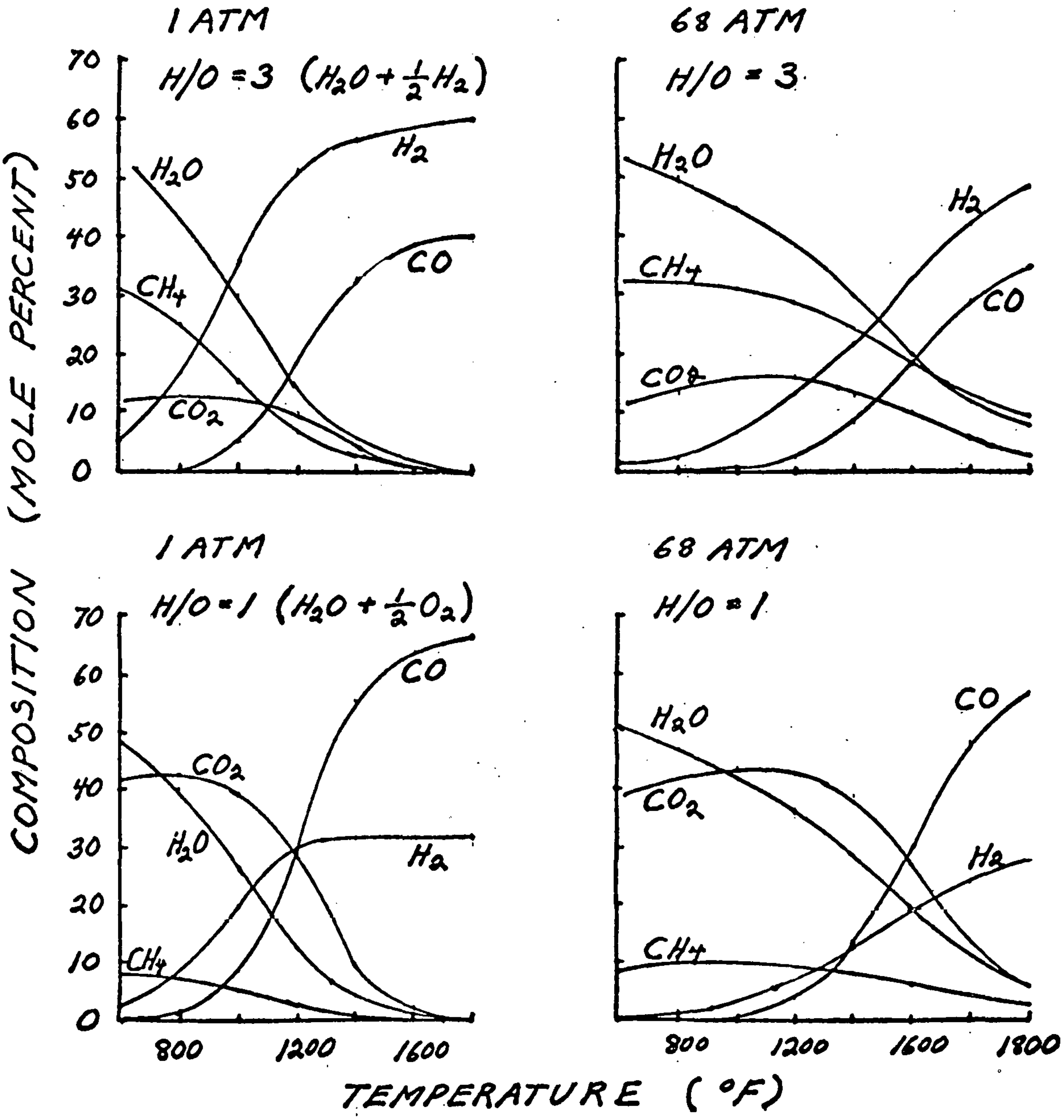


Figure 3-2, Equilibrium Compositions of C-H-O System range, where the effect of temperature on composition is also most pronounced. As temperatures are increased beyond 1800^{0}F, pressure has little effect, and the thermodynamically favored products are still CO and H_2, even at the higher pressures of practical interest.

High pressure also favors the formation of metal carbonyls and hydrogen cyanide. These are extremely hazardous materials, which, if formed, may present difficult downstream removal problems.

3.1.3.3 Gasifier Steam/Coal Ratios

The CO contents of gasifier raw-gas compositions are plotted versus gasifier steam/coal ratio in Figure 3-3 for all of the gasification cases given in Tables 3-1 through 3-4. The data show a general trend of decreasing CO concentration with increasing steam/coal ratio.

The reasons for this trend are two-fold. First, increasing the steam/coal ratio tends to decrease gasifier temperature because of the endothermicity of the steam-carbon reaction and the sensible heat capacity of unreacted steam. As discussed above, decreasing the gasification temperature tends to suppress the formation of CO. Second, the thermodynamic equilibrium compositions of Figure 3-2 show that increasing the overall H/O atomic ratio in the gasifier decreases CO concentration and increases H_2 concentration, and this tendency is also reflected by the CO concentration data plotted in Figure 3-3.

The H_2 contents of gasifier raw-gas compositions are plotted versus gasifier steam/coal ratio in Figure 3-4 for the same data base as above. These curves show that the H_2 content of the raw gas tends to increase with increasing steam/coal ratio even though gasification temperature is decreasing. The predominant effect here is the thermodynamic tendency for greater H_2 production as the overall H/O atomic ratio is increased.

3.1.3.4 Gasifier Oxidant/Coal Ratio

The CO content of the gasifier raw-gas compositions is plotted versus oxidant/coal weight ratio in Figures 3-5 and 3-6 for oxygen and air blowing, respectively. In both cases, the CO content increases with increasing oxidant/coal ratios, reflecting both the increased temperatures at increased oxidant/coal ratios and the increased thermodynamic tendency for CO production resulting from decreasing overall H/O atomic ratio (Figure 3-2). The smaller slope of the curve for air addition reflects N_2 dilution, both with respect to increased heat release per unit of oxidant (air) added and increased heat absorbing capacity of products.

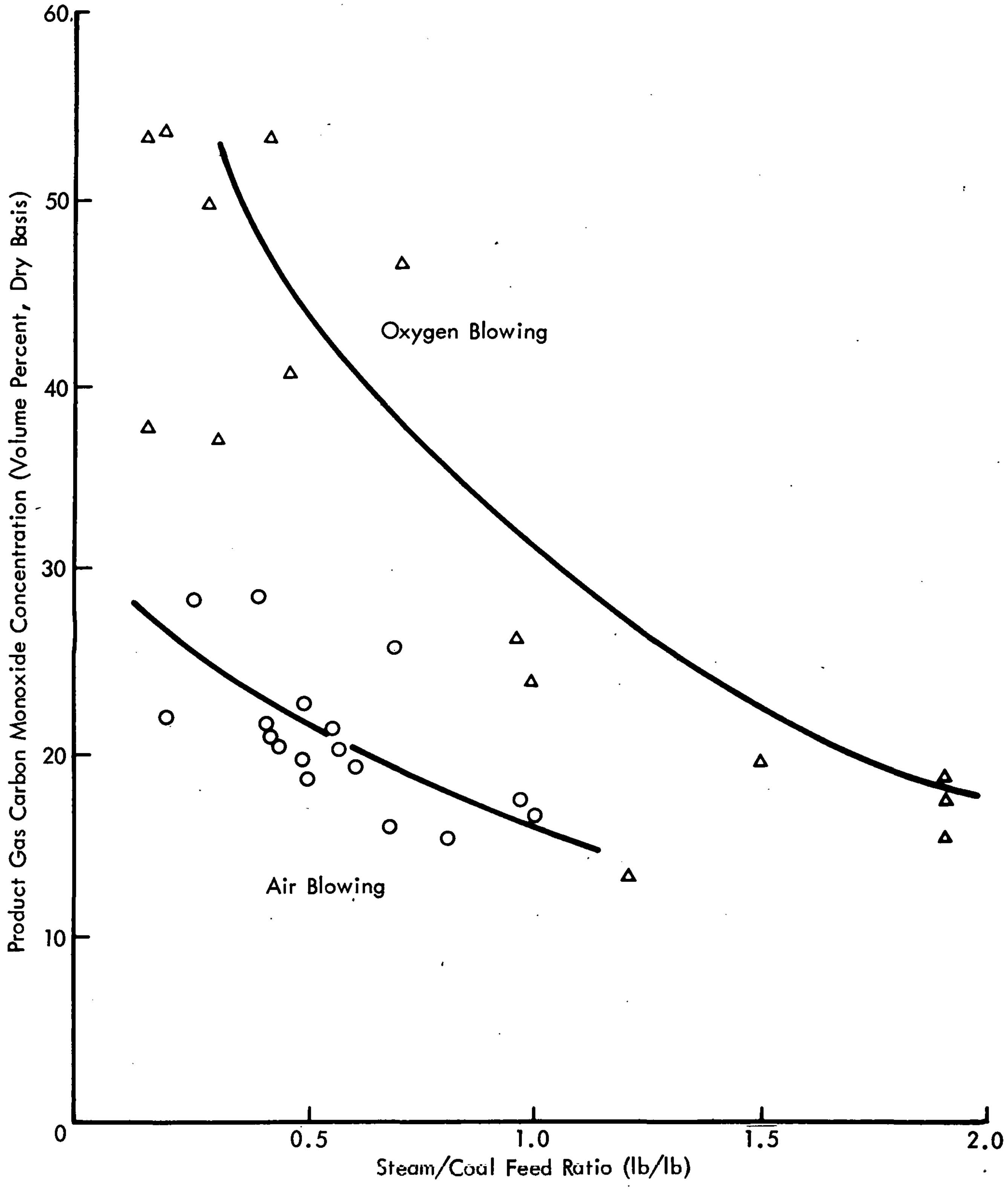


Figure 3-3. Carbon Monoxide Concentration in Gasifier Product Gas as a Function of Steam/Coal Feed Ratio

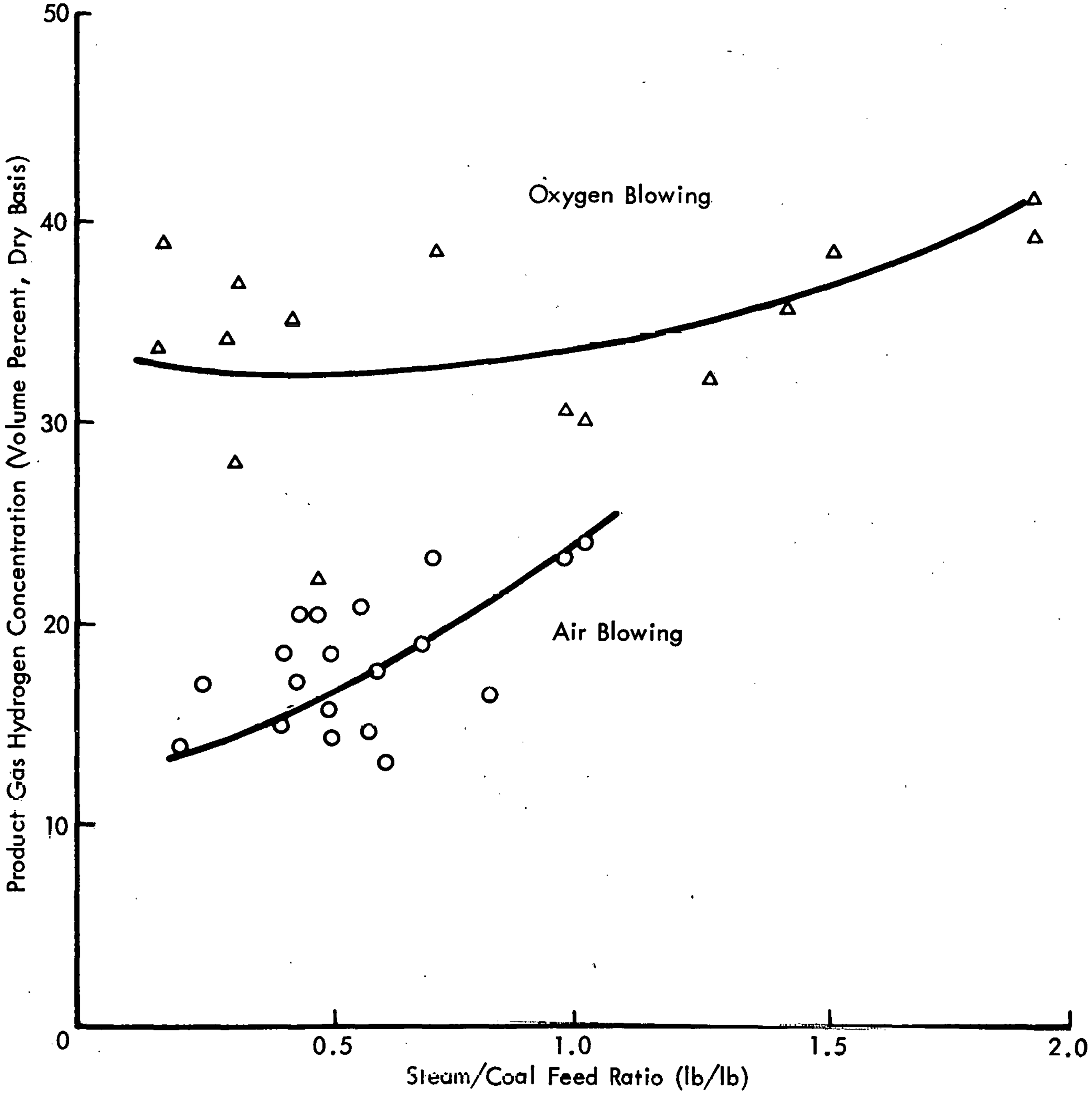


Figure 3-4. Hydrogen Concentration in Gasifier Product Gas as a Function of Steam/Coal Feed Ratio

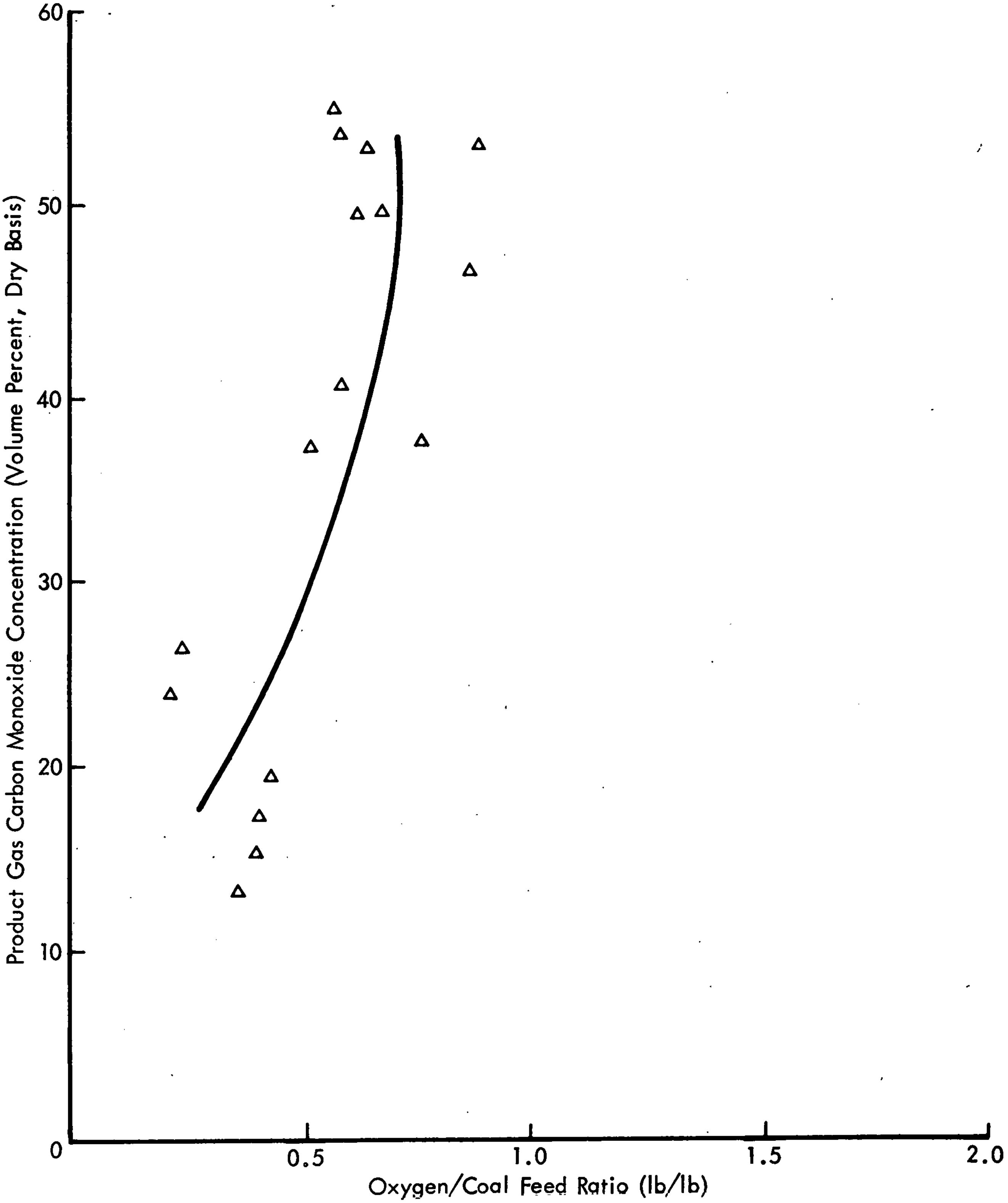


Figure 3-5. Carbon Monoxide Concentration in Gasifier Product Gas as a Function of Oxygen/Coal Feed Ratio

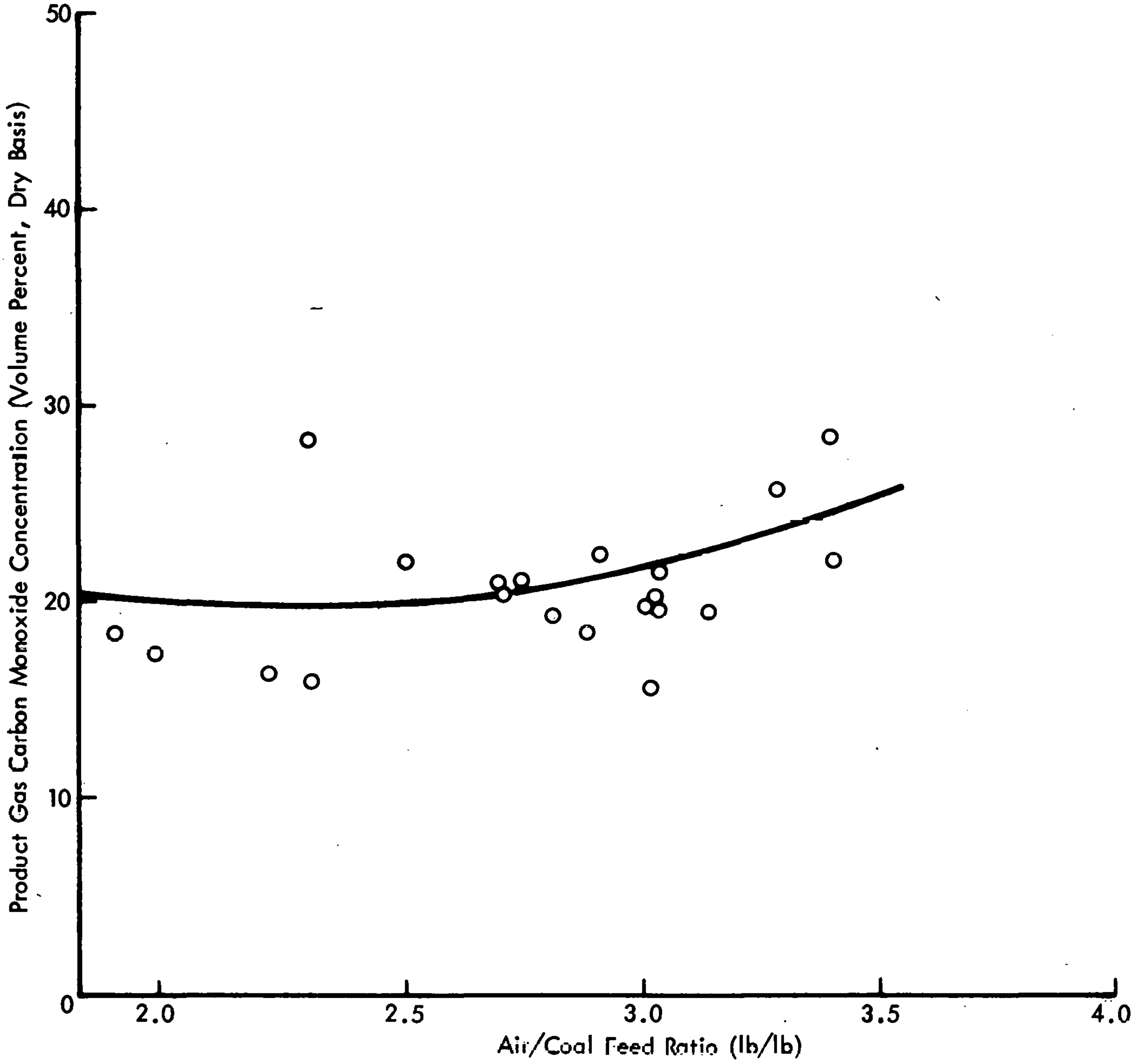


Figure 3-6. Carbon Monoxide Concentration in Gasifier Product Gas as a Function of Air/Coal Feed Ratio

The H_2 content of the gasifier raw-gas composition is plotted versus oxidant/coal weight ratio in Figures 3-7 and 3-8 for oxygen and air blowing, respectively. These data show that the H_2 content of the gasifier raw gas changes little or decreases slightly with increasing oxidant/coal ratio in spite of the accompanying higher temperatures. As in the variation of CO concentration with oxidant/coal ratio, the predominant effect here is the thermodynamic tendency for less H_2 production as the overall H/O atomic ratio is decreased (Figure 3-2).

3.1.3.5 Coal Type

There are two principal effects of coal type on gasifier raw-gas composition. First, the low-sulfur, Western subbituminous coals result in lower sulfur contents (H_2S, COS, etc.) in the gasifier raw gas in comparison to the high-sulfur-content, Eastern bituminous coals. Second, since the Western coals are generally more reactive, the gasifier can generally be operated at lower temperatures and higher overall H/O ratios. As indicated in the discussion above and the thermodynamic data of Figure 3-2, these conditions tend to produce higher H_2 and CH_4 concentrations and lower CO and CO_2 concentrations. In many cases, these tendencies are readily perceivable in the summary data presented in Table 3-5.

3.1.4 Effect of Gasifier Type on Raw-Gas Composition

There are four principal types of high-temperature, gas-solid contacting devices commonly used for the gasification of coal. These four types, with examples, are:

- Fixed-Bed Gasifiers
    - Lurgi
    - Wellman-Galusha
    - METC
    - Riley-Morgan
    - Wilputte
    - Woodall-Duckham
    - STOIC
    - Wellman-Incandescent
- Fluid-Bed Gasifiers
    - HYGAS
    - Synthane

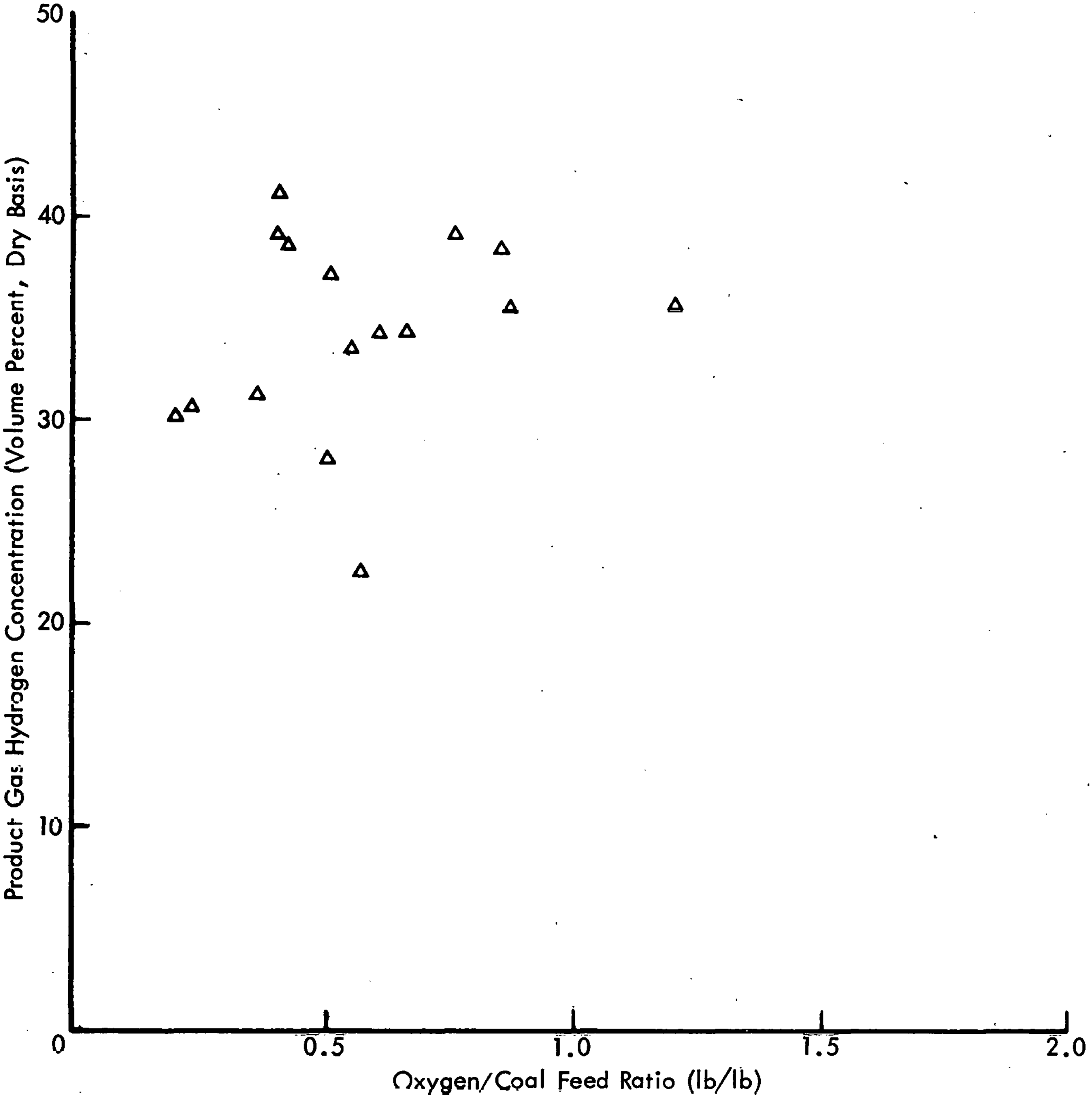


Figure 3-7. Hydrogen Concentration in Gasifier Product Gas as a Function of Oxygen/Coal Feed Ratio

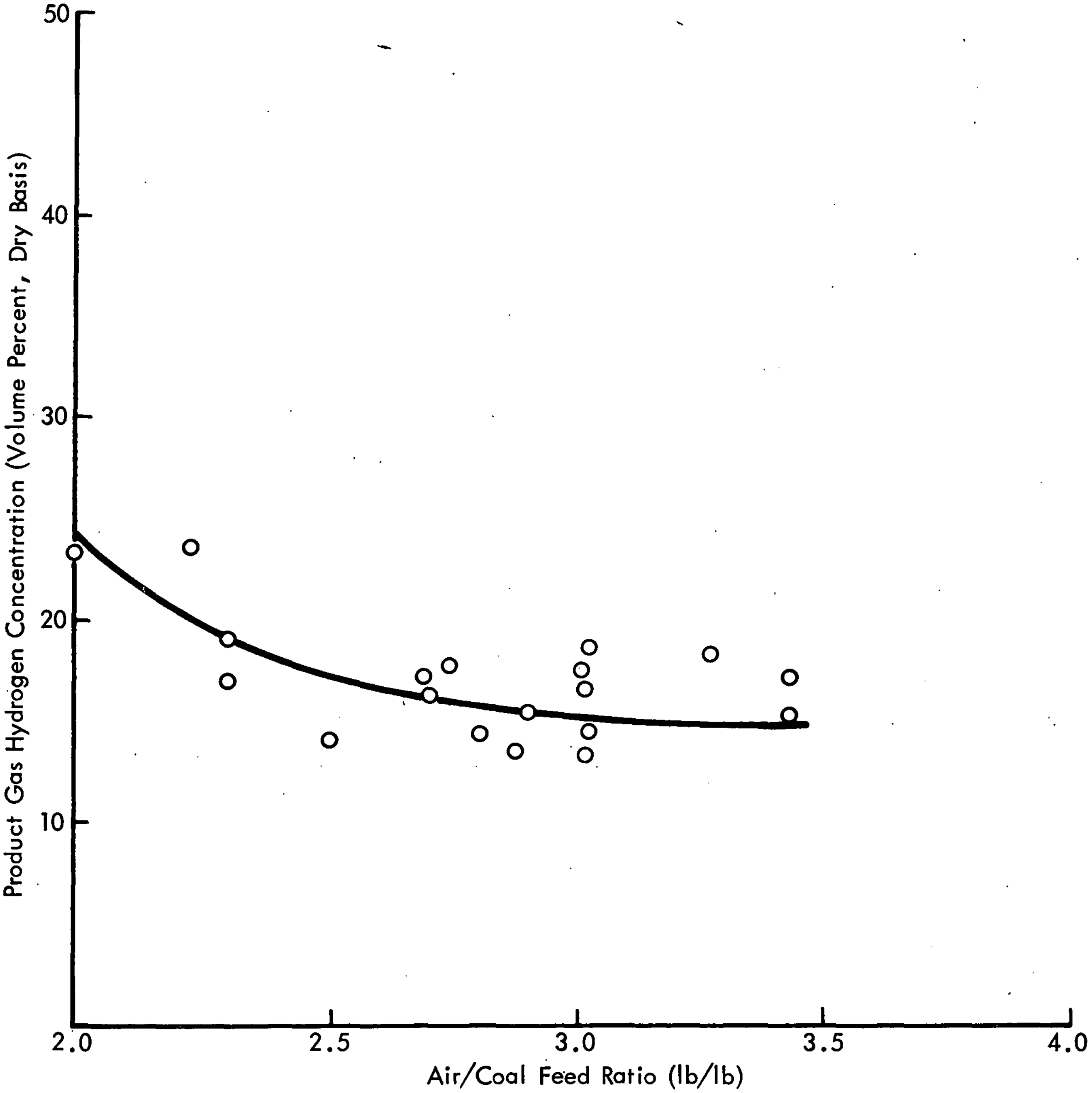


Figure 3-8. Hydrogen Concentration in Gasifier Product Gas as a Function of Air/Coal Feed Ratio

  - U-Gas
  - Winkler
- Entrained-Bed Gasifiers
  - Texaco
  - Koppers-Totzek
  - Shell-Koppers
  - Bi-Gas
- Molten-Salt Gasifiers
  - Atomics-International
  - M. W. Kellogg

In each type of gasifier, the relative flow patterns of the solid and gas streams are different, resulting in different temperature-time histories for the product gases. As indicated in the discussion above, these different temperature-time histories can result in significant differences in product gas composition from one gasifier type to another.

In fixed-bed gasifiers, the solid and gaseous streams generally flow countercurrent to one another, so the product gases are cooled from the gasification temperatures by the coal entering the reactor. As a result of this flow pattern, the tars, oils, and lighter hydrocarbons that are the products of the carbonization of the coal in the top portion of the bed are not cracked. Thus, these materials are present in the product raw gas. Also, nitrogen and sulfur compounds that might otherwise thermally decompose when exposed to higher temperatures will be present in the product raw gas of fixed-bed gasifiers. These components include ammonia, pyridines, hydrogen cyanide, carbon disulfide, carbonyl sulfide, thiophene, and mercaptans.

In a fluid-bed gasifier, the coal bed is fluidized by the high velocity gases passing up through the bed. The bed is thus maintained in a turbulent "boiling" state that provides excellent mixing and temperature uniformity throughout the reactor. Since the entire bed is maintained at a temperature close to the peak temperature encountered in a fixed-bed gasifier, the rates of gasification and coal throughput in the fluid-bed gasifier are considerably higher than they are for a fixed-bed gasifier.

Because the product gas temperature for the fluid-bed gasifier is considerably higher than that for a fixed-bed gasifier, much of the higher molecular weight compound are cracked and thus not present in the gasifier raw gas. Accordingly, the concentrations of tar, oils, hydrocarbons, nitrogen compounds, and sulfur compounds (except H_2S) will be much smaller in the product from a fluid-bed gasifier than in that from a fixed-bed gasifier.

Solid particle carryover with the product gas is a more severe problem with fluid-bed gasifiers than with fixed-bed gasifiers. The concentration of entrained particulates in the raw product gas can be as low as 2 percent and as high as 70 wt. percent. The particulate matter is more akin to a devolatilized char than it is to flyash, typically containing 50-80 percent carbon with the balance mostly ash.

In an entrained-bed gasifier, the gas and solids flow cocurrently through the reactor with the solid particles entrained in the gaseous flow. Because the residence time of coal in this type of gasifier is shorter than in other gasifiers, the gasification rate must be accelerated by use of higher temperatures and more finely divided coal. In general, an entrained-bed gasifier operates at higher temperatures than do fixed- or fluid-bed gasifiers; for example, the Koppers-Totzek gasifier operates at 3000-3500°F. As a result of the cocurrent flow, the highest temperatures occur near the exit of the gasifier.

Because of the high operating temperatures of entrained-bed gasifiers, essentially all the tars, oils, organic nitrogen compounds, and organic sulfur compounds are decomposed, and their concentrations in the product raw gas are essentially nil. The sulfur in the coal is converted to hydrogen sulfide. Organic nitrogen compounds are converted to ammonia and hydrogen cyanide. Since all of the fly-ash is entrained in the product gas as it leaves the gasifier, the ultimate removal of fine particulates from the product stream is a major concern with entrained-bed gasifiers.

In molten-salt gasifiers, coal, oxidant, and steam are injected into a bath of molten salt in which agitation is maintained by the kinetic energy of the gaseous reactant streams. High gasification rates are promoted by the moderately high (~1800°F) gasification temperature, the catalytic activity of the molten salt, and the high relative velocity between the coal trapped in the bath and the high velocity gas streams. The moderately high gasification temperature and the catalytic activity of the molten salt also eliminate any ammonia and tar formation, and additional advantages of molten-salt gasifiers are integral sulfur capture and the ability to gasify caking coals without pretreatment.

3.2 TRACE ELEMENTS

3.2.1 Availability of Data

3.2.1.1 Trace Elements in Coal

During the past few years, considerable information on trace elements in coal has been assembled and evaluated. (See References 3.20 - 3.24.) These data are usually presented as weight percent of the element in the coal without distinguishing between the molecular forms which may be present. Trace elements that commonly occur in U.S. coals and their concentration ranges are shown in Table 3-6. Except for sulfur, trace element concentration correlates only moderately with geographic location and not at all with coal rank.

Attari et al (3.40) have summarized the typical modes of occurrence of trace elements in coal, and these are given in Table 3=7. These modes of occurrence are merely indications of the common associations between the trace elements and other elements rather than specifications of exact compounds in the coal.

3.2.1.2 Fate of Trace Elements During Gasification

Very little data are available concerning the fate of trace elements during coal gasification. Limited experimental data have been collected in bench scale equipment simulating conditions in the Synthane (3.5, 3.34) and HYGAS (3.35) fluid-bed gasifiers. In the HYGAS experiments, the feed coals evaluated were Montana lignite and subbituminous and Illinois No. 6. Solid residues from the pretreater and hydrogasifier/electro thermal gasifier were analyzed, and the amounts of trace elements not recovered in those residues were assumed to report to the preheater offgas and to the main product raw-gas streams.

In the Synthane experiments, three runs were made with Illinois No. 6 coal. For each run, the trace element content was determined for the particulate, tar and condensate streams separated from the main gas stream and for the char exiting the gasifier. The fraction of each trace element appearing in each of the four streams was then computed from the total amount measured. A comparison of the total amount measured in the output streams to the amount in the feed coal revealed large imbalances for some elements in each run. Combining the data from the three runs on a weighted average basis seemed to improve data quality somewhat.

The first comprehensive attempt to determine the fate of trace elements in a full-size coal gasification facility was made by the Engineering Experimental Station

Table 3-6. RANGE OF TRACE ELEMENTS IN U.S. COALS BY GEOGRAPHICAL REGION (REF. 3.23)

ELEMENT - PPM ON COAL

REGION	Be	F	As	Se	Cd	Hg	Pb	B	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	Mo	Sn	Y	La	U	Br	Mn	P	Sb	Zr
Appalachia - Pa., Md. Va., W.V., Ohio. E. Kent., Tenn., Ala.	.6-4.1	10-190	3-59			.07-.41	4-14	4-50	2.4-44	4.1-25	.5-12	2.4-37	3.4-37	0-36	1.3-12	0-18	.4-8.7	0-2.1	6.6-28	0-25	10					
Eastern Interior - Ill. Ind., W. Kent	.6-7.6	50-167	8-45			.04-.49	H-14	13-198	8.7-67	5-54	1.2-10	5-37	3.1-25	0-53	1.5-8	.4-27	.6-8.5	.1-5	1-13	.2-24	10					
Illinois Basin*	.5-4	30-143	1.7-93	.45-7.7	.1-65	.03-1.6	4-218	12-224	16-78	4-54	2-34	8-68	5-44	10-5350	1.6-7.5	1-43	1-51	1-29				6-52	6-181	5-339	.2-8.9	12-133
Western Interior Iowa, Missouri, Kans. Oklahoma, Arkansas	.1-5.5	50-120	M-45			.19	4	2.5-180	4.7-44	4.4-38	.4-16	1.1-47	2.9-37	0-35	.5-7.3	0-30	0-7.3	0-5	1.7-27	0-37						
Western - Rocky Mountain and Pacific	<.1-3.1						5-10														10-160					
Southwest - 4 Corners Area	.0-	220	73	.50-3.9	0- .0-	.01-.25							1-15	1-17												
Northern Plains - Montana, N&S Dakota	.12-3.9	60-70				.07-.04-	7	78-201	5.3-29	2.6-19	.7-7	1.5-15	2.8-16	0-23	1.0-13	0-7	.1-3.4	.2-4.3	1.0-27	0-22	50-240					

*This data reported in Reference 3.22 is for the minimum and maximum values of 82 coals from Illinois, Indiana and Western Kentucky.

NOTES:

1) Range is for 90 or more of beds (of which 75% or more of coal in a columnar-sample was analyzed), omitting extreme values which appear to be exceptional.

2) The symbol 0 indicates below the limit of detection.

Table 3-7. TYPICAL MODES OF OCCURRENCE OF TRACE AND MINOR ELEMENTS IN COAL*

Element	Mode**	Element	Mode**
Sb	Sulfide	Mo	Sulfide
As	Oxide, sulfide	Ni	Sulfide
Ba	Carbonate, sulfate with Ca	N	OC
Be	OC	K	KCl, carbonate
Bi	Sulfide	Sm	SQ
B	OC, borate	Sc	Oxide
Cd	Sulfide	Se	POC, sulfide, iron selenides
Ca	Oxide, carbonate, sulfate	Si	Oxide, SQ
Cl	POC, sodium chloride	Ag	Element, sulfide, SQ
Cr	POC, oxide	Na	POC, carbonate
Co	POC, sulfide	Sr	POC, with Ca
Cu	$CuFeS_2$, sulfide	S	POC, sulfides, sulfates
F	CaF_2	Te	Iron tellurides
Ge	POC, carbonate	Th	SQ
Fe	Carbonate, sulfide, oxide	Sn	Carbonate, sulfide
Pb	Sulfide	Ti	POC, SQ
Li	SQ	V	OC
Mg	POC, carbonate, SQ	Yb	SQ
Mn	Carbonate in $CaCO_3$, SO	Zn	Sulfide
Hg	POC, element sulfide	Zr	Oxide, SQ

* Reference 3.40

** OC - organic contribution.
POC- partial organic contribution.
SQ - silicates, clay, quartz.

of the University of North Dakota in cooperation with the Natural Gas Pipeline Company of America (3.36). The coal used was a lignite from Mercer County, North Dakota, and the testing was carried out in the No. 13 Lurgi gasifier of the SASOL plant. Since the testing was privately funded, complete details are not available.

In this study, the concentration of trace elements in gasifier ash, oil, tar and quench liquor were analyzed, and the partitioning of the elements among each of the four output streams was computed from the total amount collected. Judging from the elemental balances, the overall data quality appears to be better than for the Synthane bench-scale experiments, but there are still significant imbalances for certain elements.

Other available experimental data from industrial-size gasifiers include Lurgi fixed-bed data from Sasolburg, South Africa, using South African subbituminous coal, and data from the Lurgi dry bottom gasifier in Westfield, Great Britain, using American Illinois No. 5 and Illinois No. 6 coals. Only a few trace elements were investigated in these studies and their results are summarized in Reference 3.28.

Recently, Radian Corporation (3.38, 3.39) released limited experimental data on the level of trace elements in grab samples of gasifier ash, cyclone dust, by-product tar, and quench liquor from an atmospheric, fixed-bed, single-stage gasifier. These data indicated that the levels of Pb, Hg, As, F and B were higher in the by-product tar than in the gas liquor, Se levels were essentially the same in the tar and gas liquor, and Hg levels in the tar were higher than those in the cyclone dust. More quantitative conclusions could not be drawn because of incompleteness of the available data.

To date, there are essentially no published data on the fate of trace elements in entrained-bed and molten-salt coal gasifiers.

3.2.1.3 Fate of Trace Elements During Coal Combustion

A large number of studies have analyzed the behavior of trace elements in coal-fired power plants (References 3.25 - 3.33). In general, these studies divide the elements into three groups according to the way they distribute themselves among the bottom ash, fly ash, and combustion flue gas. This partitioning is dependent on the boiling points of the compounds and can be described as follows:

- Group I
  Elements in this group form compounds with very high boiling points and are not volatilized in the combustion zone (2400-2900^{0}F). Concentrations of

these elements in the fly ash tend to be equal to the concentrations in the main bottom ash. Elements in this group are Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th and Ti.

- Group II

  These elements tend to volatilize in the combustion zone and condense on the fly ash as it cools. Concentrations in the fly ash are several times greater than in the main ash flow. Elements in this group are As, Cd, Cu, Ga, Mo, Pb, Sb, Se and Zn.

- Group III

  These elements volatilize and remain in the gas phase. Elements in this group include Br, Cl, F, Hg, and in some compounds, Se.

There are also a number of other elements with characteristics intermediate between Groups I and II. These elements, which include Be, Cr, Cs, Na, Ni, U, and V, are found to be only slightly concentrated in the fly ash.

The main concern with respect to trace elements in coal combustion is the release of volatile trace elements to the atmosphere as vapors and particulates (fly ash), especially as extremely fine particulates smaller than 0.5 microns that can be deposited in the respiratory/pulmonary tracts and chemically interact with body tissue. Natusch et al (3.29, 3.32) have reported preferential condensation/adsorption of Pb, Tl, Sb, Cd, Se, As, Zn, Ni, Cr and S on fly ash of decreasing particle size. Based on study results, a volatilization-condensation model was proposed to explain the phenomenon.

3.2.2 Data Summary

An extensive survey of the available literature has resulted in the compilation of seven sets of experimental data pertaining to the fate of coal trace elements during gasification (References 3.5, 3.34 - 3.41). This compilation is presented in Table 3-8 together with the types of gasifiers involved, their normal operating conditions, and the kinds of coal feed used.

For the most part, the available data are limited to only a few trace elements for which analyses were made. For the two instances (North Dakota Lignite - Lurgi Gasifier and Illinois No. 6 Bituminous - Synthane Gasifier) where more comprehensive data were reported, there were significant imbalances between the amounts of various trace elements in the coal feed and the total amounts recovered. These imbalances can be noted in Table 3-8 by comparing the elemental ppm's in the coal feed to the

Table 3-8. Volatility and Emission of Coal Trace and Minor Elements During Gasification

Coal Type	N. Dakota Lignite, Mercer County				Montana Lignite and Subbituminous			South African Subbituminous			Illinois #5			Illinois #6			Illinois #6			Illinois #6 Coal, King River Mine, Monroe Co.			
Gasifier Type	Lurgi, SASOL Test				Fluid-Bed, HYGAS			Lurgi, SASOL			Lurgi, Westfield			Lurgi, Westfield			Fluid-Bed, HYGAS			Fluid-Bed, Synthane			
Gasification Temperature	(1800-2500°F)				1700-1880°F			1800-2500°F			(1800-2500°F)			(1800-2500°F)			1700-1880°F			1686-1868°F			
Residence Time	(~ 1 Hour)				41 Min			~1 Hour			(~ 1 Hour)			(1 Hour)			17 Min			18 Seconds			
Gasifier Pressure	(300-465 psia)				1000-1200 psig			300-465 psia			(300-465 psia)			(300-465 psia)			1000-1200 psia			588 psi			
Element	ppm in Coal	ppm Recovered	% Volatilized	Emission	ppm in Coal	% Volatilized	Emission	ppm in Coal	% Recovery	% Volatilized	ppm in Coal	% Volatilized	Emission	ppm in Coal	% Volatilized	Emission	ppm in Coal	% Volatilized	Emission	ppm in Coal	ppm Recovered	% Volatilized	Emission
Ag, Silver	<0.1	0.11	0	0	0.24	4.65	0.011										0.1	63.0	0.063	0.011	<0.027	0 (0)	0
Al, Aluminum	5666	7087	1.3	92.1																3062	637	0.14 (79.2)	0.892 (2426)
As, Arsenic	8	9	9.2	0.83	18	51.8	9.33	NR	133	73.0 (64)	2.0	98.7	1.97	1.0	99.1	0.991	24	34.4	8.25	1.24	1.31	2.95	0.0386
Au, Gold	0.1^{c}	-	-	-																-	-	-	-
B, Boron	56	186	0.7	1.31	85	28.5	24.2	NR	40.3	10.6 (64)	307	80.9	248	132	57.5	76.0	200	11.1	22.2	86	148	46.5	69.0
Ba, Barium	616	945	3.3	31.2	1300	0	0										31	0	0	140	35.7	0.62 (74.8)	0.22 105
Be, Beryllium	0.27	0.67	0.9	6.03×10^{-3}	0.98	23.5	0.23	NR	3.11	62.3 (99)	2.0	13.0	0.26	1.6	21.2	0.34	1.0	23.0	0.231	1.1	1.35	0.12	1.63×10^{-3}
Bi, Bismuth	<0.1	0.19	100	0.19	0.72	43.8	0.315										1.1	52	0.572	<0.1	<0.29	2.85	$<8.27\times10^{-3}$
Br, Bromine	0.27	0.34	2.8	9.52x10-3				NR	35.6	89.9 (96.4)										0.16	0.52	0.37	1.92 $<10^{-3}$
Ca, Calcium	16200	20200	0.8	161.7	17000	0	0										3500	34.0	1191	>10000	-	-	-
Cd, Cadmium	<1	<0.38	14.5	<0.055	0.72	53.8	0.387	NR	76.6	47.7 (60)	<0.03	~13.0	$\sim3.9\times10^{-3}$	<0.03	~10	0.003	0.89	76.6	0.682	0.093	0.395	0.29	1.15×10^{-3}
Ce, Cerium	34.6	21.2	1.2 (39.3)	0.255 (13.6)				NR	72.1	0.144 (28)										27.7	14.2	0.13 (48.7)	0.0185 13.5
Cl, Chlorine	26.7	9.67	23.4 (72.3)	2.26 (19.3)	180	47.5	85.5	NR	97.2	47.5 (49)							2300	74.2	1706	129	310	98.0	304
Co, Cobalt	1.2	1.4	2.9	0.041	44	0	0				4.0	99.1	3.96	4.0	99.1	3.96	3.6	0	0	7.53	10.8	0.08	8.65×10^{-3}
Cr, Chromium	5.3	15.9	2.3	0.366	14	24	3.36				15.0	0	0	20	0	0	15	0	0	122	59.9	0.37 (51.0)	0.22 (62.4)
Cs, Cesium	4	1.0	1.0 (75.3)	0.01 (3.01)																0.17	0.207	0.15	3.1×10^{-4}
Cu, Copper	10.6	3.19	6.5 (71.9)	0.207 (7.63)	8.8	31.2	2.75				10.0	0	0	12	0	0	19	0	0	35.6	10.1	0.83 (71.7)	0.084 25.5
Dy, Dysprosium	0.67	0.88	0	0																1.08	0.93	0.08 (14.4)	7.44×10^{-4} 0.156
Er, Erbium	<0.1	0.44	0	0																1.76	0.194	0 (89)	0 1.57
Eu, Europium	0.4	0.45	1.3	5.85×10^{-3}																<0.32	>0.21	0.07	1.47×10^{-4}
F, Fluorine	29.3	31.6	33.2	10.49	71	36.5	25.9	NR	96.0	43.8 (46)	57	99.3	56.6	79	99.4	78.5	61.0	25.9	15.8	386	126	39.3 (80.1)	49.7 (309
Fe, Iron	7936	8782	1.0	87.8	9200	0	0										14000	7.49	1048	>8582	-	-	-
Ga, Gallium	5.3	5.9	0.6	0.0354																5.03	1.19	0.21 (76.4)	2.5×10^{-3} 3.84
Gd, Gadolinium	0.8	0.55	0 (31.3)	0 (0.250)																1.18	0.17	0.04 (85.4)	6.8x10-5 1.0
Ge, Germanium	0.27	0.23	2.5 (16.9)	5.75x10-3 0.0456	2.7	22.9	0.619										4.3	8.77	0.377	1.31	1.67	0.14	2.34×10^{-3}
Hf, Hafnium	<0.1	0.44	0	0																0.73	1.16	0.03	3.5×10^{-3}
Hg, Mercury	0.2	0.43	98.6	0.424	0.73	99	0.723	NR	77.4	48.3 (60)	0.2	99.3	0.198	1.1	99.6	1.09	0.12	96.2	0.116	0.1	0.070	81.8 (87.3)	0.057 (0.087)
Ho, Holmium	0.4	0.55	0	0																0.24	0.085	0 (64.4)	0 (0.155)

Table 3-8. Volatility and Emission of Coal Trace and Minor Elements During Gasification (Continued)

Coal Type	N. Dakota Lignite, Mercer County				Montana Lignite & Subbituminous			S. African Subbituminous			Illinois # 5			Illinois #6			Illinois #6			Illinois #6 Coal, King River Mine, Monroe Co.			
Gasifier Type	Lurgi, SASOL Test				Fluid-Bed, HYGAS			Lurgi, SASOL			Lurgi, Westfield			Lurgi, Westfield			Fluid-Bed, HYGAS			Fluid-Bed, Synthane			
Gasification Temperature	(1800-2500°F)				1700-1880°F			1800-2500°F			(1800-2500°F)			(1800-2500°F)			1700-1880°F			1686-1868°F			
Residence Time	(~1 Hour)				41 Min			~1 Hour			(~1 Hour)			(~1 Hour)			17 Min			18 Seconds			
Gasifier Pressure	(300-465 psia)				1000-1200 psig			300-465 psia			(300-465 psia)			(300-465 psia)			1000-1200 psia			588 psi			
Element	ppm in Coal	ppm Recovered	% Volatilized	Emission	ppm in Coal	% Volatilized	Emission	ppm In Coal	% Recovery	% Volatilized	ppm in Coal	% Volatilized	Emission	ppm in Coal	% Volatilized	Emission	ppm in Coal	% Volatilized	Emission	ppm in Coal	% Recovered	% Volatilized	Emission
I, Iodine	0.13	0.23	2.5	5.75×10^{-2}																0.35	0.087	1.51 (74.3)	1.01×10^{-3} 0.26
Ir, Iridium	0.1^c	-	-	-																-	-	-	-
K, Potassium	268	520	2.2	11.4	340	2.99	10.1										1700	0	0	>8582	-	-	-
La, Lanthanum	16	8.3	1.5 (48.9)	0.125 (7.82)																16.8	4.07	5.8 (77.2)	0.24 (12.9)
Li, Lithium	0.67	5	0.97	0.0485	5.8	0	0										33	0	0	0.64	14.5	0.11	0.016
Lu, Lutetium	<0.1	0.055	0	0																<0.08	0.083	0	0
Mg, Magnesium	3877	4690	0.9	42.2	5800	1.94	112										570	0	0	1659	1001	1.54 (40.6)	15.4 (674)
Mn, Manganese	70.7	84.5	0.8	0.676	8.9	6.25	0.556	NR	154	0.24 (0)	22	0	0	20	10	2	48	18.7	9.0	201	83.2	0.22 (58.6)	0.18 (118)
Mo, Molydenum	4	1.6	15.5 (66.2)	0.248 (2.64)	2.1	10.8	0.227				7.0	90.1	6.3	7.0	71.7	6.46	7.0	2.89	0.203	10.3	6.86	0.115 (33.9)	7.9×10^{-3} (3.52)
Na, Sodium	6994	6635	2.5 (7.5)	165 (524)	180	5.64	10.1										1400	0	0	1900	2619	1.03	27.0
Nb, Niobium	4	4.1	0.6	0.0246																4.7	2.32	0.116 (50.7)	2.7×10^{-3} (2.39)
Nd, Neodynium	2.7	2.0	2.5 (27.8)	0.05 (0.751)																17.7	3.42	0.13 (80.7)	4.46×10^{-3} (14.3)
Ni, Nickel	6.7	3.0	6.7 (58.2)	0.201 (3.9)	23	9.76	2.25	NR	154	0.45 (0)	32	0	0	14	0	0	15	5	0.75	20.4	7.65	0.65 (628)	0.0497 (12.8)
Os, Osmium	0.1^c	-	-	-																-	-	-	-
P, Phosphorous	236	395	3.5	13.6																111	344	0.17	0.58
Pb, Lead	2.7	7.2	11.7	0.842	1.9	47.0	0.894	NR	191	5.97 (0)	28	37.8	10.6	10	13.6	1.36	11	48.6	5.35	0.71	4.40	0.25	0.011
Pd, Palladium	0.1^c	-	-	-																-	-	-	-
Pr, Praseodynium	1.3	0.91	2.4 (31.7)	0.0218 (0.412)																7.3	1.33	0.14 (81.8)	1.86×10^{-3} 5.97
Pt, Platinum	<0.1	-	-	-																-	-	-	-
Rb, Rubidium	6.7	4.0	3.0 (42.1)	0.12 (2.82)																85.9	11.6	0.09 (86.4)	1.2×10^{-3} (74.3)
Re, Rhenium	<0.1^c	-	-	-																-	-	-	-
Rh, Rhodium	<0.1^c	-	-	-																-	-	-	-
Ru, Ruthenium	<0.1^c	-	-	-																-	-	-	-
S, Sulfur	12000	-	88.3	10600	990	66.6	659										38000	79.6	30250	36400	721	1.50 (98.0)	10.8 (35690)
Sb, Antimony	0.27	0.44	0	0	1.2	22.2	0.266	NR	79.5	49.6 (60)	0.2	0	0	0.1	82	0.082	1.1	36	0.396	0.13	0.275	0	0
Sc, Scandium	8	3.7	2.0 (54.7)	0.074 (4.37)																6.46	3.66	0.03 (43.3)	1.1×10^{-3} 2.8

Table 3-8. Volatility and Emission of Coal Trace and Minor Elements During Gasification (Continued)

Coal Type	N. Dakota Lignite, Mercer County				Montana Lignite & Subbituminous			S. African Subbituminous			Illinois #5			Illinois #6			Illinois #6			Illinois #6 Coal, King River Mine, Monroe Co.			
Gasifier Type	Lurgi, SASOL Test				Fluid-Bed, HYGAS			Lurgi, SASOL			Lurgi, Westfield*			Lurgi, Westfield			Fluid-Bed, HYGAS			Fluid-Bed, Synthane			
Gasification Temperature	(1800-2500°F)				1700-1880°F			1800-2500°F			(1800-2500°F)			(1800-2500°F)			1700-1880°F			1686-1868°F			
Residence Time	(~1 Hour)				41 Min			~1 Hour			(~1 Hour)			(~1 Hour)			17 Min			18 Seconds			
Gasifier Pressure	(300-465 psia)				1000-1200 psig			300-465 psia			(300-465 psia)			(300-465 psia)			1000-1200 psia			588 psi			
Element	ppm in Coal	ppm Recovered	% Volatilized	Emission	ppm in Coal	% Volatilized	Emission	ppm in Coal	% Recovery	% Volatilized	ppm in Coal	% Volatilized	Emission	ppm in Coal	% Volatilized	Emission	ppm in Coal	% Volatilized	Emission	ppm in Coal	% Recovered	% Volatilized	Emission
Se, Selenium	0.4	-	86.2	0.345	1.7	66.6	1.13				9.0	-	-				13	41.1	5.35	1.27	1.56	10.3	0.16
Si, Silicon	9114	13400	3.1	417	13000	7.61	989										20,000	0	0	> 10000	-	-	-
Sm, Samarium	1.07	0.78	1.4 (28.1)	0.011 (0.301)	0.51	1.44	7.34×10^{-3}										0.74	0	0	1.61	0.3	0.68 (81.4)	2×10^{-3} (1.31)
Sn, Tin	0.27	0.44	0	0	1.9	5.88	0.111										2.0	51.8	1.03	0.65	0.45	0.26 (31.5)	1.17×10^{-3} (0.205)
Sr, Strontium	1729	1428	0.3 (17.7)	4.28 (305)	350	34.3	120										37	0	0	7.70	19.7	1.30	0.257
Ta, Tantallum	<0.1	0.02	0	0																0.61	0.234	0.065 (61.6)	1.52×10^{-4} (0.376)
Tb, Terbium	0.67	0.33	0 (50.7)	0 (0.34)																0.12	0.113	0 (5.52)	0 6.62×10^{-3}
Te, Tellurium	0.27	-	88.9	0.24	0.42	43.2	0.182										8.1	40.7	3.3	<0.19	<0.045	0 (76.2)	0 (0.145)
Th, Thorium	4	5	1.1	0.055																4.56	1.81	0.16 (60.3)	2.9×10^{-3} (2.75)
Ti, Titanium	193	46.4	11.4 (78.7)	5.29 (151)	320	0	0										770	2.91	22.4	825	590	0.13 (28.6)	0.767 (236)
Tl, Thallium	<0.1	0.55	0	0																<0.12	<0.064	8.7 (51.2)	5.57×10^{-3} (0.06)
Tm, Thulium	<0.1	0.055	0	0																0.24	0.048	0 (80.1)	0 (0.19)
U, Uranium	4	0.83	6.2 (80.5)	0.0515 (3.22)																2.49	2.27	0.04 (9.05)	9.08×10^{-4} (0.255)
V, Vanadium	21.3	16.7	1.0 (22.4)	0.167 (4.77)	67	20	13.4	NR	72.0	0.09 (28)	21	25.0	5.25	29	6.58	1.91	17	17.3	2.96	57.8	31.3	0.09 (45.7)	(26.4)
W, Tungsten	<0.1	0.22	0	0																<0.04	>1.54	0.18	2.77×10^{-3}
Y, Yttrium	13.3	35.5	0.5	0.178																13.4	9.03	0.06 (33.0)	(4.48)
Yb, Ytterbium	<0.1	0.44	0	0	0.36	10.9	0.0394										0.56	8.0	0.0448	0.34	0.51	0.05	(2.55×10^{-4})
Zn, Zinc	6.7	1.5	25.3 (83.3)	0.38 (5.58)	13	26.0	3.39				200	30.4	60.8	43	1.83	0.79	49	26.1	12.8	41.4	2.59	0.631 (37.7)	15.6
Zr, Zirconium	85.3	58	1.0 (32.7)	0.58 (27.8)	25	11.3	2.84										35	0	0	8.53	6.71	0.12 (21.4)	1.82

Footnotes: Numbers in Parentheses are Calculated Based on Coal Feed Analysis

Numbers "Not" in Parentheses are Based on Distribution in Recovered Effluent Streams recovered ppm's reported relative to the coal feed. Possible reasons for these imbalances include:

- Errors in the chemical analyses
- Accumulation of material in the process piping and vessels
- Chemical interaction between the process stream and the process piping and vessels
- The introduction of trace elements in the quench/wash water

As indicated above, data were available for three individual runs with Illinois No. 6 Bituminous coal in the Synthane gasifier. Because the elemental balances for these individual runs were so poor, the data from all three runs were averaged to produce the single data column in Table 3-8. The averaged data exhibit significantly better elemental balances than do the individual runs.

Using the above data base, calculations were made to determine the percentages of a given element that did not leave the gasifier with the bottom ash or char, but was rather carried overhead with the product raw gas. This percentage, which is reported in Table 3-8 as "percent volatilized," was calculated as follows.

For cases where the total amount of a trace element recovered was less than or equal to the amount in the coal feed, the percent volatilized was calculated as:

$$\text{Percent volatilized} = 100 \left[1 - \frac{C_{char}}{C_{coal}} X_{char} \right]$$

where:

C_{char} = concentration of the trace element in the bottom ash or char

C_{coal} = concentration of the trace element in the coal feed

X_{char} = weight fraction of the coal feed appearing as bottom ash or char

For cases where the total amount of a trace element recovered exceeded the amount in the coal feed, the percent volatilized was calculated as

$$\text{Percent volatilized} = 100 \left[1 - \frac{W_{char}}{W_{recovered}} \right]$$

where:

W_{char} = weight of trace element in the bottom ash or char

$W_{recovered}$ = total weight of trace element recovered in all the effluent strea

The percent volatilized is thus indicative of the total amount of trace element exiting the gasifier in the product raw gas. The trace elements in this stream may be present as gaseous species or condensed species, and the condensed species may or may not be associated with fly ash particles.

Quantities of trace elements in the product raw gas have been calculated by multiplying the fraction volatilized by either the ppm of the trace element in the coal feed or the total ppm, relative to the coal feed, in all of the effluent streams analyzed. These quantities of trace elements in the product raw gas are designated "emission" in Table 3-8 since they represent the total amount indicated to be present in the gasifier product raw gases for the experimental studies analyzed.

3.2.3 Trace Elements Consistently Appearing in Gasifier Raw Gas

Using the data base presented above, a rationale has been developed for identifying those elements consistently appearing in the gasifier raw gas. Figure 3-9 identifies those trace elements for which 10 percent or more of either the amount in the coal feed or the total amount recovered appears in the product raw gas. If such an element is so identified in more than 50 percent of the cases in which analyses for that element were made, then that element is identified as one consistently appearing in the gasifier raw gas. Elements so identified are:

As B Be Bi Cd
Ce Cl F Ge Hg
Mo Pb S Sb Se
Te Ti V Zn Zr

It is recognized that the criteria used for this designation are somewhat arbitrary. Also, this designation does not take into consideration the concentration of the trace elements in the feed coal. Thus, certain elements, such as Na and K, have not been identified by this criteria, but because their concentrations in the feed coals are so large, their concentration in the product raw gas will probably be larger than that for many of the elements identified above. Thus, an additional identification is made in Figure 3-9 of those elements appearing in the feed coal in concentrations of 50 ppm or more. Elements that have been consistently so identified are:

Al B Ca Cl
F Fe K Mg
Na S Si Ti

Coal Type	N. Dakota Lignite Mercer County			Montana Lignite and Subbit.			S. African Subbituminous			Illinois No. 5			Illinois No. 6			Illinois No. 6			Illinois No. 6 Monroe County		
Gasifier Type	Lurgi, SASOL			HYGAS			Lurgi, SASOL			Lurgi Westfield			Lurgi Westfield			HYGAS			Synchane		
Gasification Temperature	(1800-2500°F)			1720-1880°F			(1800-2500°F)			(1800-2500°F)			(1800-2500°F)			1720-1880°F			1686-1868°F		
Residence Time	(~1 Hour)			41 Min			(~1 Hour)			(~1 Hour)			(~1 Hour)			17 Minutes			18 Seconds		
Gasifier Pressure	(300-465 psia)			1000-1200 psia			(300-465 psia)			(300-465 psia)			(300-465 psia)			1000-1200 psia			600 psia		
Element	A	C	V	A	C	V	A	C	V	A	C	V	A	C	V	A	C	V	A	C	V
Ag, Silver	X			X												X		▨	X		
Al, Aluminum	X	●																	X	●	▨
As, Arsenic	X		▩ 9.23	X		▨	X	NR	▩	X		▨	X		▨	X		▨	X		
Au, Gold	X																				
B, Boron	X	●		X	●	▨	X	NR	▨	X	●	▨	X	●	▨	X	●	▨	X	●	▩
Ba, Barium	X	●		X	●											X			X	●	▨
Be, Beryllium	X			X		▨	X	NR	▨	X		▨	X		▨	X		▨	X		
Bi, Bismuth	X		▩	X		▨										X		▨	X		
Br, Bromine	X						X	NR	▩							X	●		X		
Ca, Calcium	X	●		X	●											X	●	▨	X		
Cd, Cadmium	X		▩	X		▨	X	NR	▩	X		▨	X		▨	X		▨	X		
Ce, Cerium	X		▨				X	NR	▨										X		▨
Cl, Chlorine	X		▩	X	●	▨	X	NR	▩							X	●	▨	X	●	▩
Co, Cobalt	X			X						X		▨	X		▨	X			X		
Cr, Chromium	X			X		▨				X			X			X			X	●	▨
Cs, Cesium	X		▨																X		
Cu, Copper	X		▨	X		▨				X			X			X			X		▨
Dy, Dysprosium	X																		X		▨
Er, Erbium	X																		X		▨
Eu, Europium	X																		X		
F, Fluorine	X		▩	X	●	▨	X	NR	▩	X	●	▨	X	●	▨	X	●	▨	X	●	▩
Fe, Iron	X	●		X	●											X	●		X	●	
Ga, Gallium	X																		X		▨
Gd, Gadolinium	X		▨																X		▨
Ge, Germanium	X		▨	X		▨										X		▨	X		
Hf, Hafnium	X																		X		
Hg, Mercury	X		▩	X		▨	X	NR	▩	X		▨	X		▨	X		▨	X		▩
Ho, Holmium	X																		X		▨
I, Iodine	X																		X		▨
Ir, Iridium	X																				
K, Potassium	X	●		X	●											X	●		X	●	
La, Lanthanum	X		▨																X		▨
Li, Lithium	X			X												X			X		
Lu, Lutetium	X																		X		
Mg, Magnesium	X	●		X	●											X	●		X	●	▨
Mn, Manganese	X	●		X			X	NR		X			X		▨	X		▨	X	●	▨
Mo, Molydenum	X		▩	X		▨				X		▨	X		▨	X			X		▨
Na, Sodium	X	●		X	●											X	●		X	●	
Nb, Niobium	X																		X		▨
Nd, Neodynium	X		▨																X		▨
Ni, Nickel	X		▨	X		▨	X	NR		X			X			X			X		▨
Os, Osmium	X																				
P, Phosphorous	X	●																	X	●	
Pb, Lead	X		▩	X		▨	X	NR		X		▨	X		▨	X		▨	X		
Pd, Palladium	X																				
Pr, Praseodymium	X		▨																X		▨
Pt, Platinum	X																				
Rb, Rubidium	X		▨																X		▨
Re, Rhenium	X																				
Rh, Rhodium	X																				
Ru, Ruthenium	X																				
S, Sulfur	X	●	▩	X	●	▨										X	●	▨	X	●	▨
Sb, Antimony	X			X		▨	X	NR	▩	X			X		▨	X		▨	X		
Sc, Scandium	X		▨																X		▨
Se, Selenium	X		▩	X		▨										X		▨	X		▩
Si, Silicon	X	●		X	●											X	●		X	●	
Sm, Samarium	X			X												X			X		▨
Sn, Tin	X			X												X		▨	X		▨
Sr, Strontium	X	●	▨	X	●	▨										X			X		
Ta, Tantalum	X																		X		▨
Tb, Terbium	X		▨																X		
Te, Tellurium	X		▨	X		▨										X		▨	X		▨
Th, Thorium	X																		X		▨
Ti, Titanium	X	●	▩	X	●											X	●	▨	X	●	▨
Tl, Thallium	X																		X		▨
Tm, Thulium	X																		X		▨
U, Uranium	X		▨																X		
V, Vanadium	X		▨	X		▨	X	NR	▨	X		▨	X		▨	X		▨	X	●	▨
W, Tungsten	X																		X		
Y, Yttrium	X																		X		▨
Yb, Ytterbium	X			X		▨										X			X		
Zn, Zinc	X		▩	X		▨				X	●	▨	X		▨	X		▨	X		▨
Zr, Zirconium	X	●	▨	X		▨										X			X		▨

▨ More than 10% Volatilized Based on Feed Coal

▩ More Than 10% Volatilized Based on Both Feed Coal and Total Recovered

A - Analysis Made Where X

C - Concentration in Feed Coal in Excess of 50 ppm Where ●

NR - Not Reported

V - Volitility

Figure 3-9. Frequency of Appearance of Trace Elements in Coal Gasifier Product Raw-Gas

The elements underlined were not identified by the volatility criteria above.

3.2.4 Stable Molecular Forms for Trace Elements

A knowledge of the compounds of the trace elements existing in the gasifier raw gas is necessary for predicting their ultimate fate in subsequent processing steps. Unfortunately, there are no data available in the literature that define what these compounds are, so the following thermodynamic estimates have been relied upon.

Attari et al (3.40) determined the thermodynamically stable compounds of the trace elements in the chemical and physical environment of the hydrogasifier of the Hygas process. These stable compounds are given in Table 3-9. These authors also investigated the effects of variability in gasifier operating conditions on the relative stability of potential trace element compounds and concluded that a change of ± 20 percent in temperature or pressure from normal levels does not affect the ultimate form of the elements. Thus, to a first approximation, the stable compounds listed in Table 3-9 can be considered generally applicable.

Table 3-9 indicates that many of the trace elements will be present as sulfides and hydrides as well as in elemental form. In many cases, these modes of occurrence are more volatile than the oxides generally produced during coal combustion. In a more limited thermodynamic study of the compounds of the trace elements, Case et al (3.41) also concluded that these more volatile species would be favored over the higher oxides that are commonly the constituents of combustion fly ash.

Table 3-9. THERMODYNAMICALLY STABLE FORMS OF ELEMENTS IN THE HYGAS GASIFIER*

Element	Compound**
Sb	S
As	E,H
Ba	C
Be	0
Bi	E,S
B	F
Cd	S
Ca	S
Cl	HCl
Cr	S
Co	S
Cu	S
F	HF
Ge	H
Fe	S
Pb	S
Li	C
Mg	S
Mn	S
Hg	E,S
Mo	S
Ni	S
N	H
K	C
Sm	0
Se	H
Si	0
Ag	S,E
Na	C
Sr	C
S	H
Te	H
Sn	E,Cl
Ti	0
V	0
Yb	0
Zn	S
Zr	0

* Reference 3.40

**C = carbonate; E = element; H = hydride; 0 = oxide; S = sulfide

4.0 GAS CLEANING

4.1 DESCRIPTION OF APPROACH

As indicated in Section 2.0, the only gasifier raw-gas contaminants that are known with certainty to have adverse affects of fuel cell performance are sulfur compounds. However, it is expected that particulates and tars, oils, etc., will also degrade fuel cell performance. Accordingly, the following two major requirements have been established for the clean-up systems evaluated in this study:

- Reduce total product-gas sulfur content to <1 ppm
- Reduce the concentration of particulates, tars, oils etc. to very low levels.

The approach adopted here has been to synthesize gas clean-up systems capable of meeting these requirements for two representative gasifier raw-gas compositions. The first composition, designated Type 1 Gas, is representative of a typical product raw gas from a fixed-bed gasifier operating at relatively low pressure, i.e., 175 psia. The second composition, designated Type 2 Gas, is representative of a typical product raw gas from a fluid-bed or entrained-bed gasifier, also operating at about 175 psia. In comparison to Type 1 Gas, Type 2 Gas would have a lower CH_4 content and higher CO and H_2 content, and thus it is more suitable for fuel cell operation.

Concentrations of the major gas stream constituents (on a wet basis) in both Type 1 and Type 2 gases are given in Table 4-1. Compositions are given for both air and oxygen blowing, and although subsequent discussions refer specifically to the oxygen blown case, the results are equally applicable to air blown gasifier compositions.

Table 4-2 lists the major gas stream contaminants expected to be present in the Type 1 and Type 2 Gas. As indicated, the major difference between these two product gases is the presence of naphthas, phenols, tars and tar oils in the Type 1 Gas and their virtual absence from the Type 2 Gas. The presence of these compounds impacts the selection of gas clean-up system components.

Except for RSH and C_4H_4S, the compositions given in Table 4-2 were estimated mainly from the data given in Tables 3-1 to 3-4. No quantitative data could be found for RSH and C_4H_4S, and the concentrations were crudely estimated to be approximately one tenth the COS $+CS_2$ levels.

Two types of gas clean-up systems have been synthesized for analysis. The first, a low temperature system employing state-of-the-art technology, has been

TABLE 4-1. MAJOR GAS STREAM CONSTITUENTS FOR TYPE 1 AND TYPE 2 GASES

Constituent	Gas Composition, Wet Basis (Mole Percent)			
	Type I Gas		Type 2 Gas	
	Oxygen Blown	Air Blown	Oxygen Blown	Air Blown
CO	9.2	13.3	25.7	19.0
CO_2	14.7	13.3	15.8	6.2
H_2	20.1	19.6	32.2	11.7
H_2O	50.2	10.1	23.1	11.5
CH_4	4.7	5.5	2.4	0.5
N_2	0.73	37.5	0.8	51.1
H_2S COS	0.37	0.7	0.3	0.1

Table 4-2 GASIFIER RAW GAS CONTAMINANTS

	Concentration (lb/SCF x 10^6)	
	Type 1 Gas	Type 2 Gas
$COS + CS_2$	25	25
RSH	2	2
C_4H_4S	2	2
NH_3	0.1	0.08
HCN	2	2
Naphthas	300	0
Tar and Tar Oil	2000	0
Crude Phenols	100	0
Particulates	1000	2000

analyzed for cleaning both the Type 1 and Type 2 Gases. The second clean-up system, which operates at higher temperature and employs technology in the developmental stage, has been analyzed for cleaning only the Type 2 Gas. The presence of heavy hydrocarbons in the Type 1 Gas makes it unsuitable for processing in the high temperature clean-up system.

Each of the clean-up systems has been synthesized by combining specific process modules, each designed to perform a particular cleaning function. These functions are:

- Primary Particulate Removal
- Secondary Particulate and Nitrogen Compound Removal
- Heavy Hydrocarbon or Tar Condensation
- Acid Gas Removal
- Hydrodesulfurization
- Trace Sulfur Removal

There are many process options available for each of these functions, and these are surveyed below. However, to illustrate the degree of clean-up achievable and the associated energy penalties, it was sufficient to analyze only a single representative process option for each function in the two basic flow sheets.

4.2 DESCRIPTION OF GAS CLEANING PROCESS OPTIONS

4.2.1 Primary Particulate Removal

The use of cyclones constitutes the principal option for either high or low temperature particle removal. These units have been in use in the chemical industry for many years, primarily for coarse particle removal and to a certain extent for fines removal. Because of their relatively high collection efficiency, cyclones can handle gases with high particle loadings, and while they are seldom adequate alone, they are almost always used as a precleaner to be followed by secondary collection devices. Tangential-entry cyclones are commercially available in diameters ranging from about 4 to 20 in. with capacities ranging from 30 to 130,000 ft^3/min, respectively. For larger gas flows, two or more cyclones are paralleled.

Figure 4-1 shows a typical curve of cyclone collection efficiency as a function of particle size. As can be seen, collection efficiency is greater than 99 percent for particles larger than about 15 microns and falls off to about 50 percent for 2 micron particles. The total pressure loss through the cyclone ranges from 0.2 - 0.4 percent.

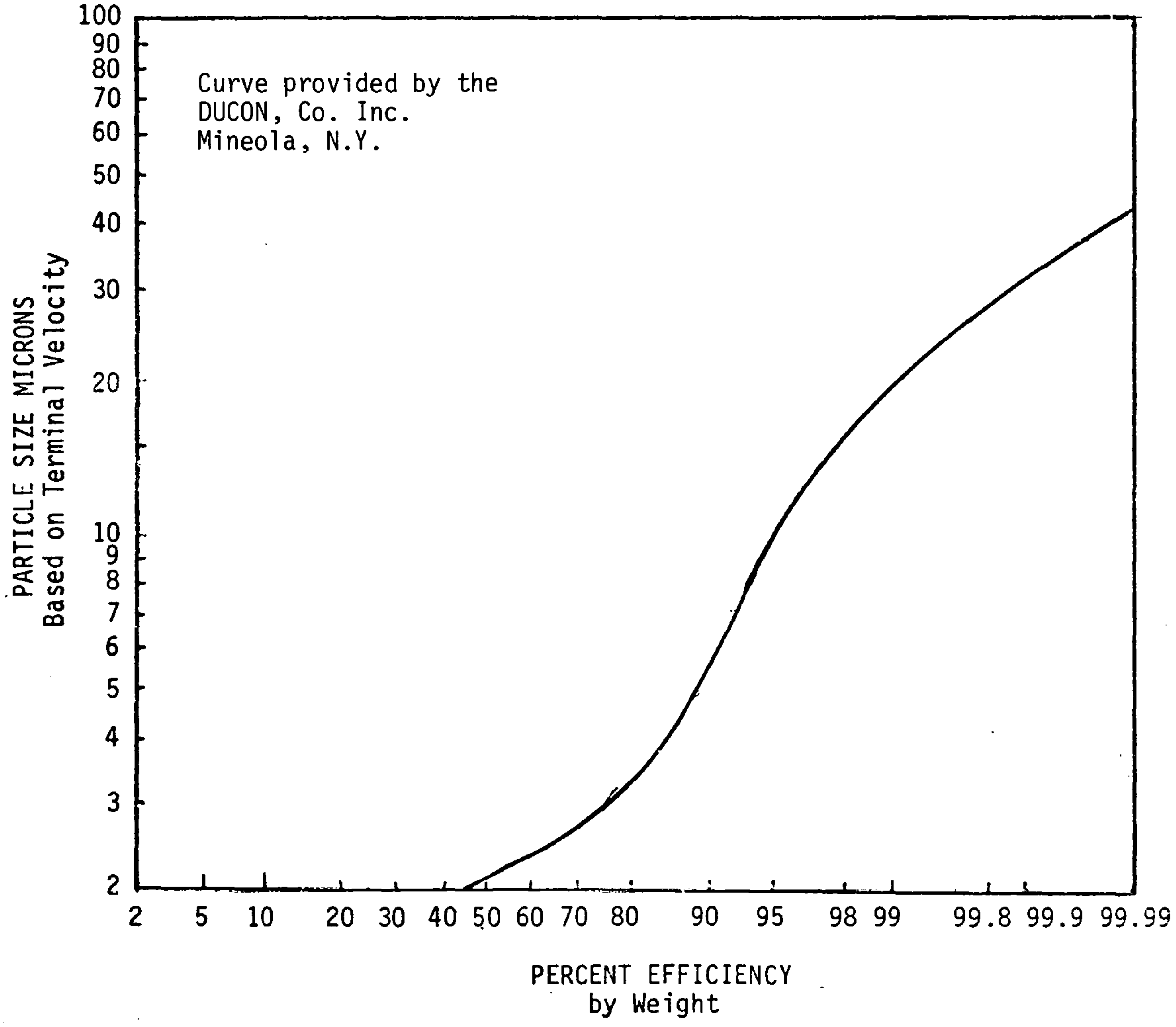


Figure 4-1. Cyclone Fractional Efficiency Curve.

4.2.2 Secondary Particulate and Nitrogen Compound Removal

4.2.2.1 Gas Scrubbers

Gas scrubbers constitute the principal option for low temperature secondary particulate and nitrogen compound removal. A flow diagram for a typical gas scrubber system is shown in Figure 4-2.

Gas leaving the primary particle removal cyclones first enters the venturi scrubber where it contacts a recirculating absorbing medium of aqueous solution saturated with ammonium salts. The atomized aqueous solution impinges upon the gas in the venturi throat, and essentially all particles larger than 0.5 micron are removed by inertial impaction.

The gases leaving the venturi scrubber enter Zone 1 of a high pressure (170 psig), multi-stage absorber, where they are contacted with recirculating water from the stripper in order to accomplish the removal of bulk ammonia, trace metals, and any particulates not captured by the upstream cyclones and venturi scrubber. In addition to the water absorption of NH_3, reaction of H_2S, CO_2 and HCN to form various ammonium salts will also occur as indicated below:

$$NH_3 + H_2O + H_2S \longrightarrow NH_4S$$

$$NH_3 + H_2O + HCN \longrightarrow NH_4CN$$

$$NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$$

Zone 1 of the scrubber can be designed to effect complete removal of HCN.

From Zone 1 of the scrubber, the gases enter Zone 2 for complete removal of residual trace amounts of NH_3, so that the off-gas from the absorber is completely free of NH_3. This zone of the absorber is also generally a multi-stage unit, and in this case, the absorbing medium is an ammonium phosphate solution recycled from an NH_3 recovery process such as U.S. Steel's Phosam Process.

The saturated solution of ammonium salts and captured particulates collect at the bottom of the absorber. Some of this solution is recirculated to the venturi, and the balance, after solids separation, is sent to an atmospheric pressure steam stripper. The stripped solution (i.e. water) is recirculated to Zone 1 of the absorber while the stripper overhead, containing NH_3, H_2S, CO_2, and HCN, is directed to the ammonia recovery unit.

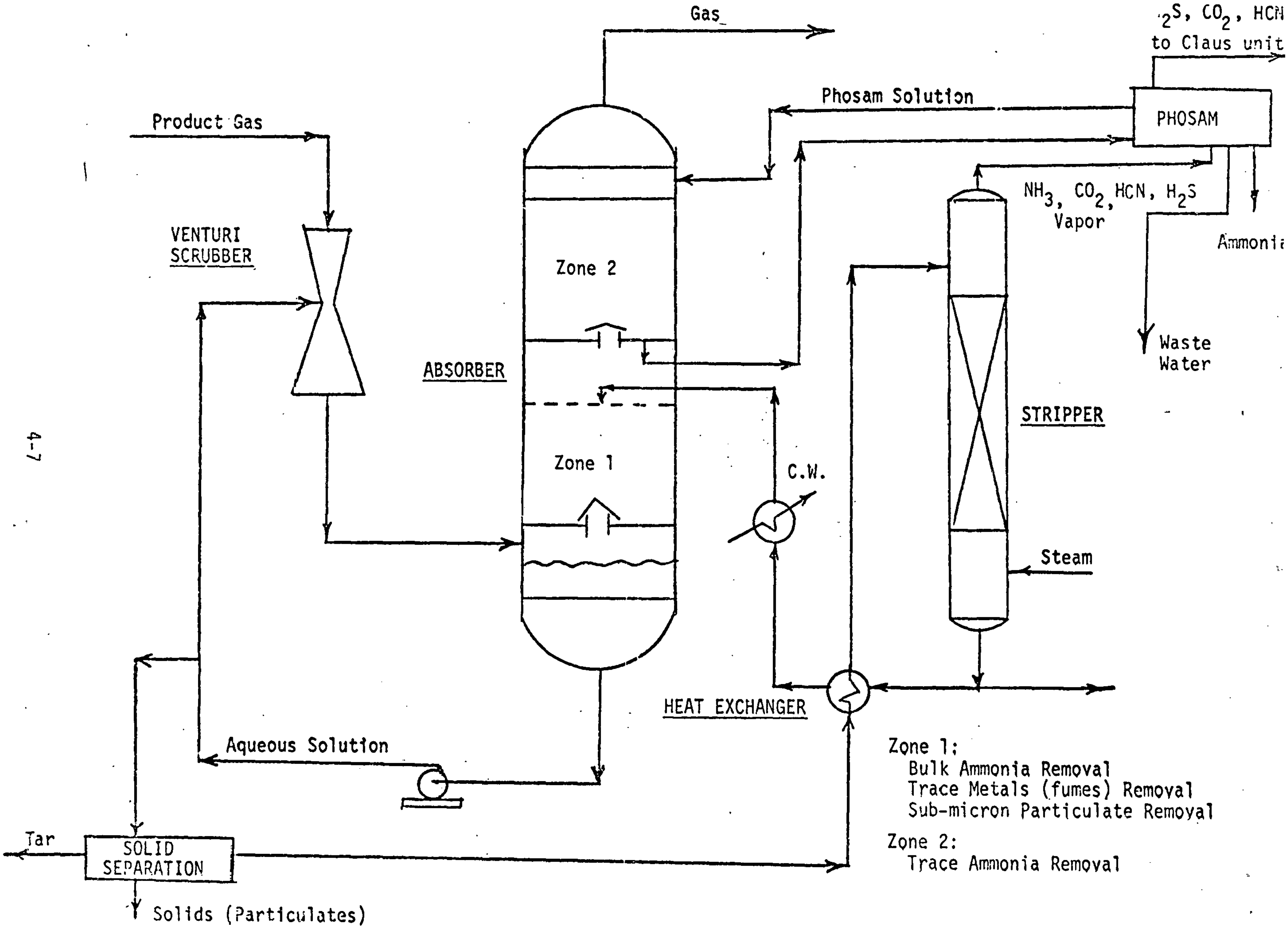


Figure 4-2. Gas Scrubber System

There are several possible contacting configurations for the absorber. These include:

- Plate columns
- Packed beds
- Spray towers
- Centrifugal scrubbers
- Baffle and Secondary-Flow Scrubbers
- Impingement-and-Entrainment Scrubbers
- Mechanically-Aided Scrubbers
- Moving-Bed Scrubbers

4.2.2.2 High Temperature Particulate Removal

There are several processes available today and under development for the secondary removal of particulates from high temperature gas streams. Table 4-3, taken from reference 4.55, lists these systems together with their developmental status, probable operating conditions, and projected efficiencies. The commercial processes include:

- Electrostatic Precipitators
- Gravel Bed Filters
- Pebble Bed Filters
- Ceramic Filters
- Porous Metal Filters

Techniques under development are:

- Silica Fibers
- Metal Fibers
- Panel Bed Filters
- Sand Bed Filters

Table 4-3. HIGH TEMPERATURE PARTICULATE REMOVAL SYSTEMS*

Collector Type	Manufacturer	Maximum Projected Collection Efficiency	Operating Conditions		Status
			Operated °F/PSIG	Projected °F/PSIG	
Electrostatic Precipitators	Research Cottrell and Others	>99	900/15	1700/300	Commercial
Silico Fibers	J. P. Stevens	99.9	-	1500/High	Developmental
Metal Fibers	Brunswick Corp.	99.9	800/15	1500/High	Developmental
Gravel Bed Filter	Rexnord	80	900/High	2000/300	Commercial
Panel Bed Filter	Squires	99.9	1600/15	2000/High	Developmental
Sand Bed Filter	Ducon	99	900/15	1500/High	Developmental
Pebble Bed Filter	Combustion Power Co.	>90	750/15	1500/High	Commercial
Ceramic Filters	Norton Co.	>99	3450/15	-	Commercial
Porous Metals	Mott Metallurgical Corp.	98	900/15	1500/High	Commercial

*Taken from Reference 4.55

4.2.3 Acid Gas Removal

4.2.3.1 Low Temperature Acid Gas Removal Processes

The primary function of acid gas removal systems is to clean the gas of H_2S and CO_2. Prior to entering the acid gas removal system, the gaseous stream will generally have been treated to remove particles, NH_3 and organic nitrogen compounds. Also any tars, oils, tar acids, phenols, and cresols will have been removed in the upstream scrubbers.

The low temperature acid gas removal systems can generally be classified as:

- Physical absorption processes
- Chemical absorption processes
- Direct conversion processes

These classifications of acid gas removal systems are discussed in the paragraphs below.

The physical absorption processes for acid gas removal are summarized in Table 4-4. These processes employ organic solvents to physically absorb or hold sulfur compounds without chemical reaction. The solvent is regenerated by heat, pressure reduction, or gas stripping and is recycled while the concentrated acid gas stream is further processed for sulfur recovery. In general, these processes are sensitive to partial pressure effects and are most applicable for treating gases at high pressure and low temperatures ($<100^{\circ}F$) where large quantities of sulfur components must be removed. They are also favored where a high degree of selectivity of H_2S over CO_2 is required. Many processes will effectively remove COS, CS_2, and mercaptans, and many will also remove other minor gas impurities such as NH_3 and HCN. However, in selective acid gas processing, COS may report with the CO_2 rich stream and not be removed with the H_2S.

The Rectisol and Selexol processes are presently being used for coal gas desulfurization: Rectisol at the SASOL coal gasification plant in South Africa, and Selexol in the proposed BiGas coal gasification pilot plant.

The chemical absorption processes for acid gas removal are summarized in Table 4-5. These processes employ a reagent in aqueous solution to react with and chemically bind sulfur components. These components are released through heating and pressure reduction and are further processed for sulfur recovery while the lean solvent is returned to the absorber. Because absorption is by chemical means, these

Table 4-4.

Physical Absorption Processes for H_2S Removal

Process (Developer)	Media	H_2S in Cleaned Gas (PPM)	Temp. (°F)	Press.	Selectivity w.r.t. CO_2	Commercial Status	Remarks	References
1. Sulfinol (Shell)	Sulfolane $(CH_2)_4$ SO_2 + DIPA (di-isopropanolamine)	4	80-120	High	Low	34 plants in U.S. & Canada (7/71)	(1) Stable Media (2) Removes H_2S, CO_2, COS, Mercaptans, Aromatics, High Hydrocarbons (3) Low circulation rates (4) Low corrosion (5) Low vaporization losses (6) Expensive media (7) Widely accepted (8) Physical/chemical absorption	(4.3)(.5)(.6)(.14)(.29)(.46)
2. Selexol (Allied)	Dimethyl ether of polyethylene glycol (DMPEG)	< 1	20-80	High	Good	Used in Bigas pilot plant	(1) Low solvent circulation (2) Low degradation with COS, CS_2, & Mercaptans removal (3) Low corrosion (4) Low vaporization losses (5) Capable of dehydrating gas if water is removed during regeneration (6) Expensive solvent (7) Absorbs heavy hydrocarbons	(4.3)(.5)(.6)(.29)(.46)
3. Fluor Solvent (Fluor)	Propylene Carbonate	4	40-80	High	Moderate	Commercial	(1) Selexol remarks apply	(4.3)(.6)(.29)(.46)
4. Purisol (Lurgi)	n-methyl 2-pyrrolidone (NMP or M-pyrol)	2	70-100	High	Good	Several plants in Europe	(1) Selexol remarks apply (2) Widely accepted in Europe.	(4.11)(.3)(.5)(.6)(.29)(.46)
5. Rectisol (Lurgi)	Methanol	1	< 0	High	Good	Used at SASOL & proposed for use in El Paso, WESCO, & American Natural Gas coal gasification plants	(1) Selexol remarks apply except: (2) Refrigeration may be required (3) Low solvent cost (4) Low freezing point advantageous in cold climates	(4.3)(.6)(.29)(.48)
6. Amisol (Lurgi)	Methanol + DEA (diethanolamine)	-	70	High	Low	-	(1) Particularly suitable for gases with low or medium CO_2 & H_2S contents (2) physical/chemical absorption	(4.29)(.35)(.46)
7. Estasolvan (Friedrick Uhde)	Tri-n-butylphosphate (TBP)	-	80-120	High	Moderate	-	(1) Selexol remarks apply	(4.3)(.6)(.44)(.46)
8. MCA (Union Oil)	Methyl Cyanoacetate (MCA)	-	-	High	Moderate	-	-	(4.29)(.40)

Taken from Reference 4.55

Table 4-5.

Chemical Absorption Processes for H_2S Removal

Process (Developer)	Media	Reaction(s)	Media Capacity	H_2S		Utility Requirement	Temperature (°F)	Pressure	Selectivity w.r.t. CO_2	Commercial Status	Remarks	References
				Initial Conc	Final Conc							
Alkanolamines												
1. MEA	Monoethanolamine 15% solution	$HO-(CH_2)_2-NH_2+H_2S \rightleftharpoons [HO-(CH_2)_2-NH_3]SH$	1:2.5-3.5 mol H_2S: mol MEA	Low to Med.	-	2.5:1 Steam: H_2S	80-120	-	Low	Wide use	(1) Inexpensive solvent (2) Absorption is temp. sensitive (3) Degrades with CS_2,COS,O_2 (4) MEA is easily reclaimed (5) Ineffective removal of Mercaptans (6) Most widely used for sour gas treating (7) Low absorption of hydrocarbons (8) High vaporization loss	(4.11)(.5)(.6)(.40)(.46)
2. DEA	Diethanolamine 22-27% solution	$(HOC_2H_4)_2NH_2+H_2S \rightleftharpoons (HOC_2H_4)_2NH_3HS$	Lower than MEA	-	-	Low steam	100-130	-	Better than MEA but still low	Wide use in Canada	(1) Resists degradation with CS_2,COS (2) Low vaporization loss (3) Higher circulation rates (4) Higher solvent cost (5) Otherwise comparable to MEA	(4.11)(.5)(.6)(.40)(.47)
3. SNPA:DEA	Diethanolamine 20-30% solution	Similar to DEA	1:0.9-1.3 mol H_2S: mol DEA	11-35% Acid gases	0.05-0.15 gr/100 scf	Less than MEA	100-130	H_2S part. P min 4 atm 600-1100 psig	Low	Several in operation	(1) No corrosion problems (2) Very low foaming tendency	(4.3)(.5)(.6)(.41)(.46)
4. Econamine (Fluor, Jefferson Chem. Co.)	Diglycolamine [DGA or 2(2 amino-ethoxy) ethanol] $NH_2(CH_2)_2O(CH_2)_2OH$ 65-70% solution	-	1:3.4-4 mol H_2S: mol DGA 5-7 scf/gal	1.5-2% min.	$<\frac{0.25\ gr}{100\ scf}$ & <0.01 vol. %CO_2	Low	70-100	-	Low	15 plants (7/71); Hygas pilot plant	(1) Not irreversibly degraded by COS,CS_2; Degradation products reclaimed at 380°F (2) Low freezing point is advantageous in cold climate (3) Expensive solvent (4) Low circulation rate (5) Low absorption of heavy hydrocarbons (6) Lower volatility	(4.3)(.5)(.6)(.41)
5. Trencor-M	Noble metal catalyst methyldiethanolamine (MDEA)+ inorganic salts	$(HOC_2H_4)_2NCH_3+H_2S$ $(HOC_2H_4)_2NHCH_3.HS$	-	-	4 ppm	-	550 Cat. 100-150 abs.	atm - 1000 psig	Low	-	(1) High CO_2 streams may require pretreatment (2) Used mainly for off-gas pollution control (3) Degraded by HCN	(4.29)(.38)(.40)(.46)(.50)
6. Sulfiban (Black, Sivalls & Bryson)	Alkanolamine based solution	-	-	$\frac{500gr}{100SCF}$	$\frac{10gr}{100SCF}$	-	-	-	-	Will be used in coke oven gas desulfurization in U.S.	(1) O_2 results in degradation of solvent (2) Resists degradation with COS, CS_2, HCN	(4.45)
7. ADIP (Shell)	DIPA (di-isopropanolamine)	$(CH_3CH(OH)CH_2)_2NH+H_2S \rightarrow (CH_3CH(OH)CH_2)_2NH_2.HS$	1:1.6 mol H_2S: mol DIPA	-	5-100 ppm	1-3:1 Steam:H_2S; .01-.04 kwh: lb H_2S	100-140	Atm - 1000 psig$^+$	Low	-	(1) Not corrosive (2) Low vaporization loss (3) Absorbs some COS (4) Non-foaming solvent (5) HCN & O_2 result in degradation	(4.11)(.14)(.29)(.41)(.50)
8. SCOT (Shell Claus Off-Gas Treatment)	Cobalt/Molybdenum catalyst DIPA	-	-	-	200-500 ppm	34 kw, 6400 lb/hr steam 2.9 x 10^6 Btu/hr fuel gas for tail gas from 100 LT/D Claus install.	570 Cat.	Atm	Low	Plants built worldwide	(1) Best applied for off-gas pollution control (2) Sour water stream produced (3) Recycles off-gas as H_2S to Claus (4) Non-corrosive to carbon steel	(4.14)(.15)(.16)(.17)(.41)
Carbonates												
9. Hot Pot (Bureau of Mines)	Potassium Carbonate (K_2CO_3) 25-35% solution	$K_2CO_3+H_2S \rightleftharpoons KHS+KHCO_3$ $COS+H_2O \rightarrow CO_2+H_2S$	High	5-8%	-	Steam: H_2S 2.5:1	200-250	300 psig min.	Low	-	(1) CO_2 presence needed for operation (2) Removes COS, CS_2, but not Mercaptans (3) Not good if acid gas is to be processed in Claus plant (4) Low vapor loss (5) Can be used if gas contains particulates (6) Solution does not degrade significantly (7) Low absorption of HC	(4.5)(.6)(.40)
10. Catacarb (Esso R&E)	K_2CO_3, with amine borates as catalyst	Similar to Hot Pot	Higher than Hot Pot	5-50%	-	Lower than Hot Pot	150-250	100-1000 psig	Low	39 plants worldwide (8/71)	(1) Catalyzed version of Hot Pot, with similar advantages and disadvantages (2) Catalyst increases the solution activity of K_2CO_3	(4.4)(.6)(.40)(.41)(.46)
11. Benfield	K_2CO_3, with DEA as catalyst	Similar to Hot Pot	Higher than Hot Pot	5-50%	200 ppm (one stage)	2.5:1 Steam:H_2S	150-250	100-2000 psig	Moderate	Wide use outside U.S.; Synthane pilot plant	(1) Good removal of CO_2,H_2S,COS (2) Low corrosion (3) Catalyzed version of Hot Pot (4) Low solubility of hydrocarbons (5) Removes HCN, some CS_2 (6) Low solvent degradation	(4.11)(.6)(.29)(.40)(.41)(.46)(.50)
12. Vacuum Carbonate (Koppers)	Na_2CO_3	$Na_2CO_3+H_2S \rightleftharpoons NaHS+NaHCO_3$	-	$\frac{500gr}{100SCS}$	30gr/100SCF	Low steam	80-100	-	-	Used for coke gas desulf in U.S.	(1) No degradation with COS,CS_2 (2) Low solubility for HC (3) O_2 will degrade solution forming SCN^- + $S_2O_3^=$ which must be purged	(4.40)(.45)(.46)
Other												
13. Alkaline liquors (UOP Firma Carl Still, Collin, tri-potassium phosphate)	NH_3,NaOH, K_3PO_4	$2NaOH+H_2S \rightarrow Na_2S+2H_2O$	High	Low	$<\frac{50\ gr}{100\ scf}$ (NH_3)	-	-	-	Low	-	(1) High circulation rate (2) Wastewater may be a problem (3) UOP process byproduce sodium thiosulfate	-
14. Alkazid (BASF) "M" "DIK" "S" solutions	Aqueous solution of Potassium salts of weak organic acids, Potassium-di-methyl aminoacetic acid	$(CH_3)_2C(NH_2)COOK+H_2S \rightarrow KHS+(CH_3)_2C(NH_2)COOH$	-	-	10-50 ppm	2-3:1 Steam:H_2S	70-120	Atm - 1000 psig	Low	-	(1) Very low vaporization loss (2) Low solubility for hydrocarbons (3) Not degraded by COS and CS_2 (4) Doesn't absorb COS,CS_2, or Mercaptans (5) Degraded by HCN + O_2	(4.11)(.29)(.40)(.46)

Taken from Reference 4.55

processes are insensitive to the partial pressure of H_2S in the fuel gas.

The chemical absorption processes are generally characterized by low selectivity for H_2S over CO_2, a low affinity for heavy hydrocarbons, low corrosion rates, and high utility requirements. COS, CS_2, O_2, and HCN tend to form degradation products with the solvent, although some alkanolamines resist degradation and some degradation products can be reclaimed. These processes have low temperature applications (<150°F) and have found extensive use in petroleum refineries and natural gas fields for removal of H_2S and CO_2 from sour gas streams. A DGA system is presently in use at the Hygas coal gasification pilot plant.

There are several aqueous carbonate processes used for chemical absorption of H_2S. In general, these processes offer low to moderate selectivity for H_2S over CO_2, hydrolysis of the COS and CS_2 to H_2S thereby removing these components, less absorption of hydrocarbons than physical solvents, and less solution degradation and utilities requirements compared to physical absorption systems. These processes can accept feed gas temperatures up to 250°F. The Benfield Process is the most widely used hot carbonate system and is in use at the Synthane coal gasification pilot plant.

The direct conversion processes for acid gas removal are summarized in Table 4-6. Most of these processes are based on oxidation-reduction reactions. These processes do not remove CO_2 from the feed gas, so they are very selective for H_2S. They do not remove COS or CS_2, and HCN in the feed gas tends to form degradation products. Some success in treating these degradation products has been reported.

Direct conversion processes have been used most widely in Europe. Applications there have included H_2S and sulfur recovery from manufactured gas, coal gas, and coke oven gas.

4.2.3.2 High Temperature Sulfur Compound Removal Systems

High temperature systems for sulfur removal (principally H_2S) are not commercially available although several processes are being developed. Most of the active work involves the use of limestone or dolomite, iron oxides, molten salts, or liquid metals as absorbants. Metal sulfides form in these systems from the chemical reaction of the absorbant with sulfur compounds in the gas. The gas is passed through a bed of solid absorbent or a spray of liquid absorbant. The degree of desulfurization depends on the chemical equilibria for the particular system.

Table 4-6.
Direct Conversion Processes for H_2S Removal

Process	Sponsor	Media	Reaction	Media Capacity	% Eff'cy	H_2S Initial Conc (gr/100 scf)	H_2S Final Conc (ppm vol)	Regeneration - Media and Reaction	Utility Requirement	Temperature (°F)	Selectivity w.r.t. CO_2	Commercial Status	Remarks	References
1. Stretford	U.K. N.W. Gas Board, Ralph M. Parsons, J.F. Pritchard	Na_2CO_3 Anthraquinone - Disulfonic acid (ADA) Sodium metavanadate	5-Stage (pH 8.5) $H_2S+Na_2CO_3 \rightarrow NaHS+NaHCO_3$ $NaHS+NaHCO_3+2NaVO_3 \rightarrow S+Na_2V_2O_5+Na_2CO_3+H_2O$	Low	-	10-700	<1	ADA $(O_2) \rightarrow$ ADA, O_2 provides Redox couple $Na_2V_2O_5 \rightarrow NaVO_3$	-	Ambient to 120	Good	Over 50 units worldwide (7/71)	(1) Chemicals are stable (2) High purity sulfur is produced (3) Greatest acceptance in U.K. (4) Small sodium thiosulfate purge (5) Does not remove COS, CS_2 or mercaptans	(4.11)(.2)(.7) (.8)(.19)(.29) (.30)(.41)(.46)
2. Holmes-Stretford	-	See Stretford	-	-	-	50-3000 ppm Vol	<5	-	-	-	Good	MERC pilot plant	(1) Modification of basic Stretford (2) Polysulfide wash removes HCN before absorber (3) $SCN^- + S_2O_3^=$ in water reduced to $H_2S + Na_2CO_3$ for recycle	(4.13)(.42)
3. Beavon	Ralph M. Parsons, Union Oil	Cobalt/Molybdenum Catalyst H_2	$H_2S, SO_2, COS, CS_2 \xrightarrow[Co/Mo]{H_2} H_2S$ $H_2S \xrightarrow[Stretford]{} S$	-	-	1-3%	<250	-	300 kw, 156 x 10^6 Btu/d fuel gas, 660 lb/hr steam for 100 LT/D Claus install.	550-750 cat 70-120 abs	Good	-	(1) Add-on for pollution control (2) Stretford remarks apply	(4.8)(.10)(.18) (.30)(.40)(.41)
4. Cleanair	J.F. Pritchard & Texas Gulf Sulfur Co.	-	$H_2S, SO_2, COS, CS_2 \xrightarrow{cooling} H_2S+CO_2+S$ $H_2S \xrightarrow[Stretford]{} S$	-	-	-	<250	-	580 kw, 32.4 x 10^6 Btu/d fuel gas, 1200 lb/hr steam for 150 LT/D Claus install.		Good	-	(1) Add-on for pollution control (2) Stretford remarks apply	(4.8)(.20)(.11) (.40)
5. Takahax	Tokyo Gas Co. & Ford, Bacon and Davis	Na_2CO_3 1,4 - naphthaquinone 2 - sulfonate sodium	$Na_2CO_3+H_2S \rightarrow NaHS+NaHCO_3$ $RO_2SO_3Na+NaHS+NaHCO_3 \rightarrow R(OH)_2SO_3Na+Na_2CO_3+S$	-	-	-	<10	$R(OH)_2SO_3Na+1/2\ O_2 \rightarrow RO_2SO_3Na+H_2O$	-	-	Good	60 Units in Japan	(1) Similar to Stretford and Thylox but no arsenic	(4.3)(.7)(.40) (.41)(.46)
6. Giammarco-Vetrocoke (G-V)	-	Na_2CO_3 arsenic activated	$Na_3AsO_3+3H_2S \rightarrow Na_3AsS_3+3H_2O$ $Na_3AsS_3+3Na_3AsO_4 \rightarrow 3Na_3AsO_3S+Na_3AsO_3$ $Na_3AsO_3S \rightarrow Na_3AsO_3+S$		-	1000	<.5	$Na_3AsO_3+1/2\ O_2 \rightarrow Na_3AsO_4$	-	100-300	Good	Used in Europe for coke gas desulf.	(1) Flow scheme similar to Stretford (2) Sulfur produced will contain arsenic	(4.11)(.2)(.7) (.32)(.41)(.46)
7. Thylox	Koppers	Na_2CO_3, As_2O_3	$Na_4As_2S_5O_2+H_2S \rightarrow H_2O+Na_4As_2S_6O$	High	-	Low	10-20	$Na_4As_2S_6O+1/2\ O_2 \rightarrow Na_4As_2S_5O_2+S$	Low	100	Good	-	(1) Sulfur produced will contain arsenic (2) U.S. use limited to treating coke oven gas (3) Used in Europe for treating coke oven gas and manufactured gas (4) High thiosulfate formation	(4.11)(.1)(.2) (.5)(.7)(.40) (.46)
8. Townsend	-	Aqueous solution of organic solvent i.e., triethylene glycol	$S+O_2 \xrightarrow{\Delta} SO_2$ (absorbed in solvent) $SO_2+2H_2S \rightarrow 2H_2O+3S$	-	-	-	-	-	-	100-250	Good	Pilot plant 7/71	(1) Does not remove COS or CS_2	(4.8)(.3)(.7) (.31)(.40)(.46)
9. Nalco	Nalco Howe-Baker Weyerhaeuser	Proprietary acidic solution	Acidic solution reacts directly to convert H_2S to S	-	99	-	-	O_2 regenerated - no froth formed - sulfur recovered by centrifugation	-	-	Good	Pilot plant	-	(4.3)(.7)(.46)
10. C. H. Deal	Shell	Sulfolane, ferrous salt catalyst & pyridine carboxylic acid chelating agent	$S+O_2 \rightarrow SO_2$ $SO_2+2H_2S \rightarrow 2H_2O+3S$	-	-	-	-	-	-	-	Good	-	(1) Similar to Townsend	(4.2)(.7)(.3) (.46)
11. Manchester, Ferrox, Gluud		Ferric Hydroxide in sodium or ammonium carbonate solution	$Na_2CO_3+H_2S \rightarrow NaHS+NaHCO_3$ $Fe_2O_3 \cdot 3H_2O+3NaHS+3NaHCO_3 \rightarrow Fe_2S_3 \cdot 3H_2O+3Na_2CO_3+3H_2O$	-	85^+	-	-	$2Fe_2S_3 \cdot 3H_2O+3O_2 \rightarrow 2Fe_2O_3 \cdot 3H_2O+6S$	-	100	Good	Obsolete	(1) Process is obsolete - replaced by Stretford (2) HCN & O_2 degrade solution to $SCN^- + S_2O_3^=$	(4.24)(.2)(.7) (.40)(.46)
12. Catahan	Rhodia, Inc.	Ferric ion with organic chelating agent & stabilizing agent for pH 6-10	Fe^{+++}(chelated) $+H_2S \rightarrow Fe^{++} + H^+ + S$	-	-	-	-	$Fe^{++} + O_2 \xrightarrow[regen.]{in\ situ} Fe^{+++}$	-	-	-	-	-	(4.8)
13. Konox	-	Na_2FeO_4	$4Na_2FeO_4+6H_2S \rightarrow 4NaFeO_2+4NaOH+4H_2O+6S$	-	99.5	950 ppm Vol	4	$4NaFeO_2+4NaOH+3O_2 \rightarrow 4NaFeO_4+2H_2O$	-	-	-	-	(1) Add-on for pollution control (2) Thiosulfate purge is small	(4.36)
14. Perox	Koppers	Ammonia solution with quinones	-	-	-	-	20-100	-	-	-	Good	-	(1) Used for coal gas purification in Europe	(4.11)(.2)(.7) (.46)
15. Sulfox	UOP	NH_4OH absorption catalytic oxidation	$NH_4OH+H_2S \rightarrow NH_4HS+H_2O$	-	-	-	10-100	$NH_4HS+1/2\ O_2 \xrightarrow{cat} NH_4OH+S$	-	-	-	-	(1) Produces ammonium sulfate bleed stream	(4.34)
16. Fumaks	-	Ammonia & picric acid	-	-	-	-	-	-	-	-	-	-	(1) Used in coke oven gas desulfurization outside of U.S.	(4.45)
17. Lacy-Keller	-	Unidentified	Chemical solution reacts with H_2S & RSH to form colloidal sulfur which is flocculated out	-	-	-	-	-	-	-		-	(1) May not be economical for treating more than 1 LTPD sulfur (2) Solution very corrosive	(4.2)(.3)(.7) (.37)(.40)

Taken from Reference 4.55

Table 4-6. (Continued)

Direct Conversion Processes for H_2S Removal

Process	Sponsor	Media	Reaction	Media Capacity	% Eff'cy	H_2S Initial Conc (gr/100 scf)	H_2S Final Conc (ppm vol.)	Regeneration - Media and Reaction	Utility Requirement	Temperature (°F)	Selectivity W.r.t. CO_2	Commercial Status	Remarks	References
18. Freeport	-	Amine catalyst in molten sulfur	$S+O_2 \xrightarrow{\Delta} SO_2$ (mixed with gas) $SO_2+2H_2S \rightarrow 2H_2O+3S$	-	-	-	-	-	-	-	-	-	-	(4.3)
19. Lo-Cat	Air Resources, Inc.	Proprietary organo - metallic catalyst	H_2S oxidized to S which precipitates	-	95+	5ppm-100%	-	Reduced metal ions regenerated by O_2	-	Ambient	-	-	(1) Will treat 20-200,000 CFM	(4.33)
20. IFP (Solution Claus)	IFP	Polyalkyline glycol, alkali salt of a carboxylic acid	$S+O_2 \rightarrow SO_2$ $SO_2+2H_2S \rightarrow 2H_2O+3S$	-	99.4	-	1500-2000	-	60 kw (140 T/D Claus) 261 kw (200 T/D Claus) 1100#/hr steam (200 T/D Claus)	200-300	Good	16 commercial plants world-wide	(1) Very high purity sulfur (99.7%) produced in pilot plant (2) First commercial plant in Japan (7/71) (3) Extremely simple process (4) Does not remove COS or CS_2 (5) Add - on for polution control	(4.7)(.31)(.21) (.29)(.30)(.46)
21. Claus		Bauxite or iron ore catalyst	$S+O_2 \rightarrow SO_2$ $SO_2+2H_2S \rightarrow 2H_2O+3S$	-		15-100%	-	-	6 lb steam/lb sulfur, .04 kwh/lb sulfur	700-750	-	-	(1) Process is oldest commercial process (2) Most economical for removal of most of the sulfur (3) Tail gas must be cleaned up to meet air stnds. (4) Many variations of basic flow scheme	(4.11) (4.50)
22. Direct Oxidation	Pan American Petrol Corp.	-	Direct oxidation of H_2S with O_2 over bauxite catalyst	-	70-85	2-15%	-	-	-	-	-	6 installations	(1) Used for acid gas streams too low in H_2S to support noncatalytic oxidation (2) Adversely affected by unsaturated HC	(4.2)(.39)

Taken from Reference 4.55

The absorbant is subsequently removed for regeneration or disposal, but generally, economics dictate that the absorbant be regenerated for reuse. Table 4-7 lists the high temperature sulfur removal systems currently under development.

4.2.4 Hydrodesulfurization

Most of the sulfur compounds in the fuel gas can be removed by the acid gas removal processes described above. However, some sulfur compounds, i.e., carbonyl sulfide (COS), carbon disulfide (CS_2) and mercaptans (RSH) will still be present to varying extents, and these must be removed to meet the ultimate goal of total sulfur concentration reduction to < 1 ppm. Since the final trace sulfur removal step (described below) is very effective for H_2S removal but only marginally effective for COS, CS_2 or RSH removal, this hydrodesulfurization step may be required to convert these compounds to H_2S. The chemical reactions involved are:

$$COS + H_2 \longrightarrow CO + H_2S$$

$$CS_2 + H_2 \longrightarrow C + H_2S$$

$$RSH + H_2 \longrightarrow R + H_2S$$

$$C + H_2O \longrightarrow CO + H_2$$

$$CS_2 + H_2O \longrightarrow CO + H_2S$$

$$COS + H_2O \longrightarrow CO_2 + H_2S$$

Experience with hydrodesulfurization in the petroleum industry as well as DOE experience hydrotreating coal gasification products (4.54, 4.55) indicates that there should be no problem in effecting the conversion of COS, CS_2 and RSH required to reduce total sulfur concentration in the product to 1 ppm. However, thiophene, which may also be present in the gasifier raw gas, is more difficult to hydrogenate, and experiments are needed to establish that it can be converted with high enough efficiency to meet the total sulfur specification of ≤ 1 ppm. Existing experimental studies of catalytic hydrodesulfurization of thiophene suggest that the high conversion levels that will be required here (4.56-4.58) should be achievable.

4.2.5 Trace Sulfur Removal

Processes for trace sulfur removal are summarized in Table 4-8. These processes all involve the physical or chemical absorption of sulfur compounds on a solid

Table 4-7.
High Temperature Desulfurization Processes

	Process (Developer)	Absorbent	Temperature F	Pressure	Efficiency of S Removal		Regeneration Conditions		Form of Sulfur Recovery	Status	Remarks
					% Removal	Residual, PPM	Agent	F			
1.	Molten Salt (Battelle Northwest)	Molten Carbonates	1100 - 1700	Atmospheric	95	350	Steam + CO_2	1100	H_2S	Pilot	(1) Removes both particulates and H_2S. (2) Process not demonstrated at high pressures. (3) Alkali metal carryover a problem.
2.	Iron Oxide (Bureau of Mines)	Sintered pellets of Fe_2O_3 (25%) + fly ash. *	1000 - 1500	Insensitive to variations in pressure	95	350	Air	1500	SO_2	Pilot	(1) SO_2 offgas instead of H_2S is a disadvantage.
3.	Iron Oxide (Babcock and Wilcox)	Thin iron plates.	800 - 1200	Insensitive to variations in pressure	99	75	Air	1200	SO_2	Experimental	(1) Laboratory scale tests maximum operating temperature 1400F. (2) SO_2offgas instead or H_2S.
4.	Consolidation Coal	Half calcined dolemite	1500 - 1800	200 psia	95	350	Steam + CO_2	1200	H_2S	Pilot	
5.	Air Products	Calcined dolemite	1600 - 2000	Insensitive to variations in pressure	95	350	Steam + CO_2	1200	H_2S	Abandoned	(1) Poor regenerability of dolemite, coke deposition in fixed load, high energy consumption.
6.	IGT - Meissner	Molten Metal	900		98	150	-	-	-	Conceptual	(1) Proprietary system.

Taken from Reference 4.55

*Support for Fe_2O_3 can be either fly ash or silica.

TABLE 4-8. PROCESSES FOR TRACE SULFUR REMOVAL

	Process		
	Activated Carbon	Sponge Iron	Zinc Oxide
Temperature Range, °F	80-150	80-120	650-750
Effective Removal of:*			
H_2S	Yes	Yes	Yes
COS	Yes	Yes	Yes
CS_2	?	No	No
Mercaptans	Yes	No (2.5ppm)	No
Thiophene	No	No	No (60%)

*"No" means the absorbant will not remove the specific component to a level less than 1 ppm.

absorbant. In the case of sponge iron, once the absorbant becomes saturated, it is discarded, but in the activated carbon and zinc oxide processes, the absorbant can be regenerated. Usually, however, economics favor discarding these absorbants as well.

All of the processes in Table 4-8 are effective in removing H_2S and COS, but their ability to remove thiophene, mercaptans, and CS_2 is limited. As discussed above, mercaptans, CS_2 and thiophene should be hydrolyzed to H_2S prior to trace sulfur removal.

The minimum H_2S concentration leaving the trace sulfur removal step is determined by the chemical equilibrium for the particular absorption process involved. For the sponge iron and zinc oxide processes, the absorption chemical reactions are:

Sponge Iron: $Fe_2O_3 + 3H_2S \rightleftharpoons Fe_2S_3 + 3H_2O$

Zinc Oxide: $ZnO + H_2S \rightleftharpoons ZnS + H_2O$

For the water concentrations prevailing in typical cleaned gas compositions, the equilibrium gas composition for the sponge iron process operating at 77°F would contain less than 5×10^{-14} ppm H_2S. For the zinc oxide process operating at 750°F, the minimum H_2S concentration achievable in the product gas is about 0.05 ppm, corresponding to a gas stream saturated with water vapor at 135°F. Further reductions of water vapor in the product stream would permit lower H_2S concentrations.

The actual mechanism of sulfur removal by activated carbon has not been clearly established. It is believed that desulfurization of the gas is accomplished by a combination of chemical absorption and physical adsorption. Thus, the H_2S in the gas reacts with the metal oxide activators in the carbon to form metal sulfide while COS, CS_2, and mercaptans are probably physically adsorbed on the carbon particles. Natural gas has been purified with activated carbon to produce an H_2S concentration of 0.2 ppm.

4.3 DESCRIPTION OF GAS CLEAN-UP SYSTEMS

Three cases have been analyzed to determine the impact of gas clean-up systems on gasifier product composition and the associated energy penalties. These are:

- Case 1:

  Type 1 gas and state-of-the-art low temperature gas clean-up

- Case 2:

  Type 2 gas and state-of-the-art low temperature gas clean-up

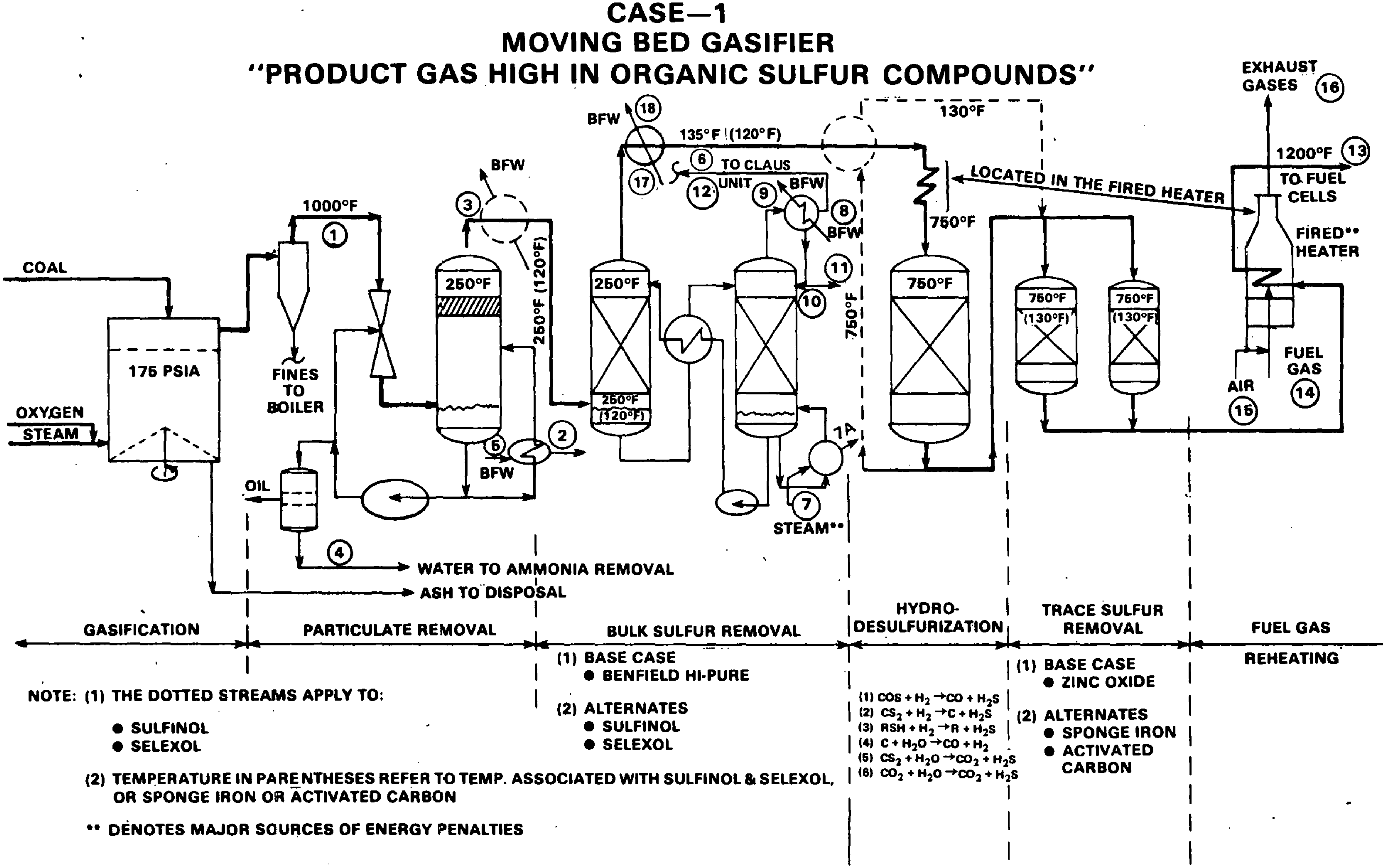
- Case 3:

  Type 2 gas and hot gas clean-up technology currently in the developmental stage

The clean-up system flow sheets for these three cases are described below together with their impact on gas composition. In all cases, the gasifier operating pressure is assumed to be 175 psia, with the fuel cells operating at about 150-160 psia.

4.3.1 Case 1

The flow diagram for the Case 1 clean-up system is given in Figure 4-3, and the stream properties are given in Table 4-9. The gasifier off-gases first pass through cyclones, where primary particulate removal is effected, and from there pass to a wet scrubbing system as described in Section 4.2.2.1 above. In the scrubbing system, oils, residual particulates and nitrogen compounds are removed. From the scrubbing system, the gases enter the Acid Gas Removal Unit.



CASE—1
MOVING BED GASIFIER
"PRODUCT GAS HIGH IN ORGANIC SULFUR COMPOUNDS"

BULK SULFUR REMOVAL

(1) BASE CASE
- BENFIELD HI-PURE

(2) ALTERNATES
- SULFINOL
- SELEXOL

HYDRO-DESULFURIZATION

(1) $COS + H_2 \rightarrow CO + H_2S$
(2) $CS_2 + H_2 \rightarrow C + H_2S$
(3) $RSH + H_2 \rightarrow R + H_2S$
(4) $C + H_2O \rightarrow CO + H_2$
(5) $CS_2 + H_2O \rightarrow CO_2 + H_2S$
(6) $CO_2 + H_2O \rightarrow CO_2 + H_2S$

TRACE SULFUR REMOVAL

(1) BASE CASE
- ZINC OXIDE

(2) ALTERNATES
- SPONGE IRON
- ACTIVATED CARBON

NOTE: (1) THE DOTTED STREAMS APPLY TO:
- SULFINOL
- SELEXOL

(2) TEMPERATURE IN PARENTHESES REFER TO TEMP. ASSOCIATED WITH SULFINOL & SELEXOL, OR SPONGE IRON OR ACTIVATED CARBON

** DENOTES MAJOR SOURCES OF ENERGY PENALTIES

Figure 4.3. Flow Diagram, Case 1

Stream No.		1	2	3	4	5	6	7	7A	8	9	10	11	12	13	14	15	16	17	18
Temperature (°F)		1000	150	250	250	110	135	281	281	110	150	230	230	230	1200	250	77	350	110	150
Pressure (PSIA)		175		175				50							165	15	175	15		
Total Flow Rate (lb mols/hr)		100	1855	50.1	39.9	1855	35.2	75	75	1518	1518	60.27	3.07	15.03	41.9	3.58	* 11.54	** 13.90	219	219
CONSTITUENTS	CO	9.2		9.2			9.2								9.2	0.78				
	CO_2	14.7		14.7			0							14.7	0			1.17		
	H_2	20.1		20.1			20.1								20.1	1.72				
	H_2O	50.2	1855	10.27	39.9	1855	0.528	75	75	1518	1518	60.27	3.07		0.53	0.61		3.10	219	219
	CH_4	4.7		4.7			4.7								4.7	0.40				
	N_2	0.73		0.73			0.7								0.7	0.07	9.12	9.23		
	H_2S	0.37		0.37		4 ppm								0.37	0.1 ppm	0				
Flow Rate (10^3 lb/hr)		1.88	33.4	1.24	.718	33.4	0.404	1.35	1.35	27.3	27.3	1.085	0.055	0.658	0.524	0.044	0.335	0.379	3.95	3.95

*Contains O_2 = 2.42 mols/hr
**Contains O_2 = 0.40 mols/hr

Table 4-9 . Stream Properties, Case 1

As discussed in Section 4.2.3 above, there are many commercial acid gas removal processes available, such as Benfield Hi-Pure, Hot Carbonate, Sulfinol, Selexol, etc. The Benfield and Hot Carbonate processes operate at 250° F and are more effective in removal of organic sulfur compounds, such as COS, CS_2 and mercaptans than are the Sulfinol and Selexol processes that operate at 120° F. The extremely low levels of sulfur content that are required in the clean gas dictate the selection of a process that effectively removes the organics. Accordingly, the Benfield Hi-Pure process was chosen for evaluation here because of its commercially proven performance in hydrolyzing organic sulfur compounds. This process is selective for H_2S absorption, but when sufficient residence time is provided to permit hydrolysis equilibrium, the percent CO_2 removal can be essentially the same as the H_2S removal. Since H_2S is removed down to approximately 4 ppm, for simplicity, it was assumed that essentially all of the CO_2 is removed. The presence of trace quantities of CO_2 is insignificant since it is only a diluent, not a contaminant.

The absorbed acid gases are stripped from the absorbing solution with steam and sent to a Claus unit for sulfur recovery, and the lean solution is recycled to the absorption column. Consumption of steam in the steam stripper constitutes a major energy penalty. Consistent with commercial experience, the steam for this analysis was taken to be saturated at 50 psia and the water reflux ratio in the steam stripper was set at 4:1. It should be noted that along with H_2S and CO_2, part of water vapor in the fuel gas stream also condenses in the absorber and is bled off after condensation (Stream 11).

The fuel gas from the acid gas removal step is cooled to 135°F to reduce the water vapor content to a value low enough to permit the eventual reduction of H_2S to <1 ppm in the zinc oxide absorbers. After being cooled the gas is reheated to 750°F in the convection section of the fired heater and sent to the hydrodesulfurization step of the process where the trace sulfur compounds COS, CS_2, mercaptans, and thiophene, react with hydrogen in a catalyst bed at 750°F to produce H_2S. As previously discussed, thiophene hydrogenation is not commercially proven, but we have assumed here that sufficient thiophene hydrogenation will occur so that the total sulfur content of the product will be <1 ppm. The fuel gas, carrying traces of H_2S, is then directed to the trace sulfur removal stage for which several commercial processes are available. The zinc oxide adsorption process operates at 750°F whereas sponge iron and activated carbon adsorption can be carried out at 130°F. Since the fuel gas is already at 750°F and the zinc oxide process would be more effective in removing any thiophene not hydrogenated, the zinc oxide process was selected. It was assumed that the usual commercial practice would be followed of discarding spent zinc oxide beds rather than regenerating them.

The H_2S concentration entering the zinc oxide absorbers is 4 ppm and the design exit concentration is 0.1 ppm. The minimum H_2S concentration achievable with the water concentration set by equilibrium at 135°F is 0.05 ppm.

The clean fuel gas at 750°F is then heated in a direct fired heater to 1200°F with heat supplied by burning a portion of the fuel gas with 20 percent excess air.

4.3.2 Case 2

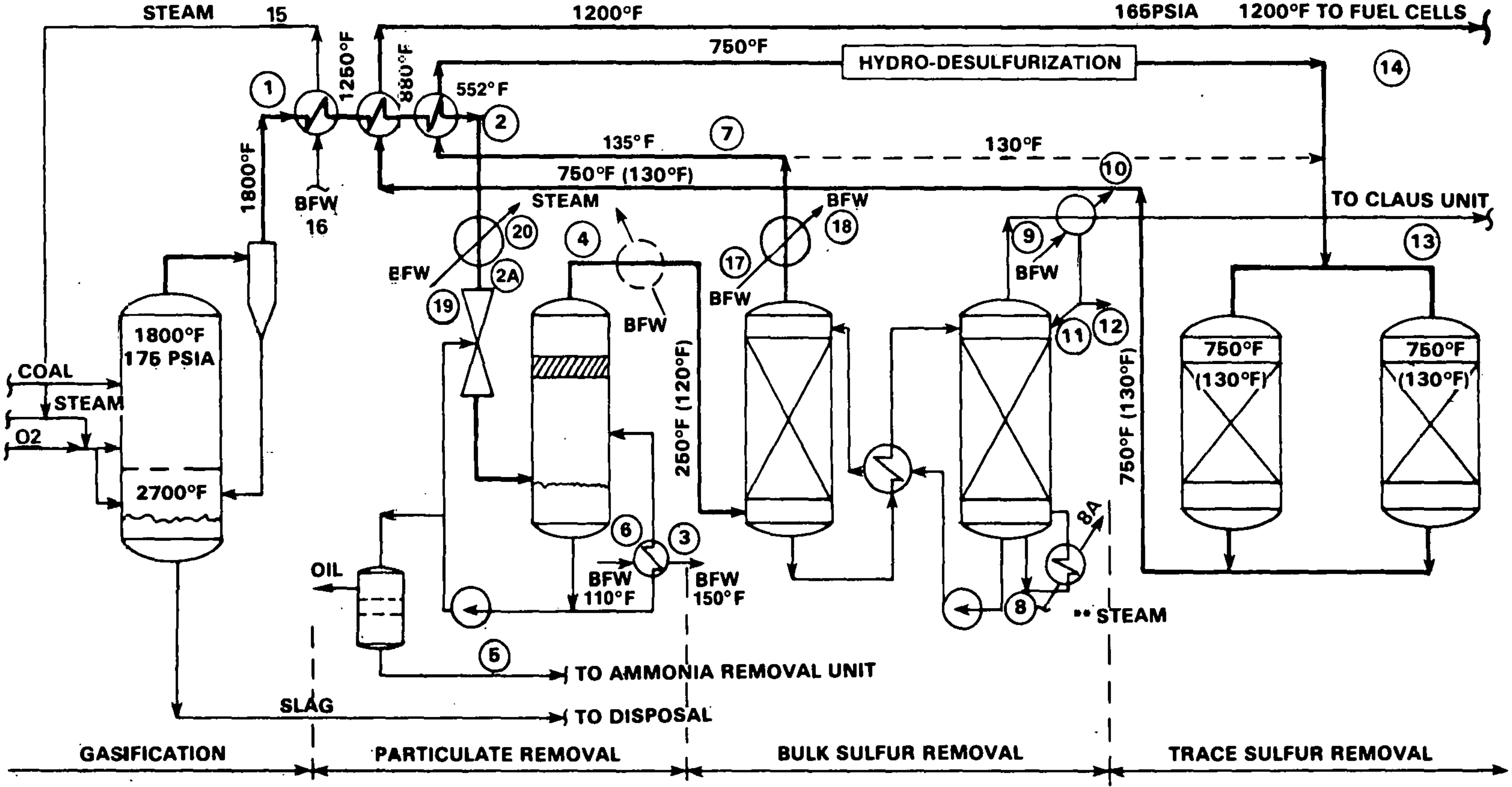
The flow diagram for the Case 2 clean-up system is given in Figure 4-4, and the stream properties are given in Table 4-10. In this case the fuel gas leaves the gasifier at 1800°F and 175 psia. Cyclones are used as primary particulate removal devices, and the fuel gas is subsequently cooled in four heat exchangers. Saturated steam at 175 psia is generated from BFW at 77°F in the first heat exchanger, and the second heat exchanger raises the temperature of the cleaned fuel gas from 750°F to 1200°F. The third heat exchanger raises the fuel gas temperature from 250°F to 750°F prior to its entering the trace sulfur removal step while 80 psia saturated steam is generated in the fourth heat exchanger. The temperature of the gasifier raw fuel gas leaving the fourth heat exchanger is 350°F.

The cooled raw gas is then subjected to secondary particulate removal by wet scrubbing and then enters the acid gas removal process step, as discussed in Case 1. The fuel gas then passes through the hydrodesulfurization step and is finally cleaned in the zinc oxide absorption process, as discussed in Case 1, before being heated to 1200°F by the incoming raw fuel gas. The final sulfur content of the fuel gas is 0.1 ppm assuming that thiophene is effectively removed by the combination of hydrodesulfurization and ZnO adsorption.

4.3.3 Case 3

The flow diagram for the Case 3 clean-up system is given in Figure 4-5, and the stream properties are given in Table 4-11. The fuel gas leaving the gasifier at 1800°F and 175 psia passes through the high temperature particulate removal step that consists of cyclones and advanced, developmental-stage electrostatic precipitators projected to operate at 1800°F. The coal fines separated from the raw gas are burned in the boilers.

CASE—2
HIGH TEMPERATURE GASIFIERS
LOW ORGANIC SULFUR CONTENT



BULK SULFUR REMOVAL

(1) BASE CASE
- BENFIELD HI-PURE

(2) ALTERNATES
- SULFINOL
- SELEXOL

TRACE SULFUR REMOVAL

(1) BASE CASE
- ZINC OXIDE

(2) ALTERNATES
- SPONGE IRON
- ACTIVATED CARBON

NOTE: (1) THE DOTTED STREAMS APPLY TO:

- SULFINOL
- SELEXOL

(2) TEMPERATURE IN PARANTHESES REFER TO TEMP. ASSOCIATED WITH SULFINOL & SELEXOL, OR SPONGE IRON OR ACTIVATED CARBON

** DENOTES MAJOR SOURCES OF ENERGY PENALTIES

Figure 4.4. Flow Diagram, Case 2

Table 4-10. Stream Properties, Case 2

Stream No.		1	2	2A	3	4	5	6	7	8	8A	9	10	11	12	13	14	15	16	17	18	19	20
Temperature (°F)		1800	552	350	150	250	250	110	135	281	281	110	150	230	230	230	1200	370	110	110	150	110	312
Pressure (PSIA)		175	175	175		175											165	175				80	80
Total Flow Rate (lb mols/hr)		100.3	100.3	100.3	280	93.1	7.2	280	62.0	80	80	1620	1620	64.3	3.31	16.07	62.0	29.34	29.34	380	380	8.21	8.21
CONSTITUENTS	CO	25.7	25.7	25.7		25.7			25.7								25.7						
	CO_2	15.8	15.8	15.8		15.8										15.8	0						
	H_2	32.2	32.2	32.2		32.2			32.2								32.2						
	H_2O	23.1	23.1	23.1	280	15.9	7.2	280	0.93	80	80	1620	1620	64.3	3.31		0.93	29.34	29.34	380	380	8.21	8.21
	CH_4	2.4	2.4	2.4		2.4			2.4								2.4						
	N_2	0.8	0.8	0.8		0.8			0.8								0.8						
	H_2S	0.27	0.27	0.27		0.27			4 ppm							0.27	0.1 ppm						
Flow Rate (10^3 lb/hr)		1.97	1.97	1.97	5.03	1.82	.13	5.03	0.83	1.44	1.44	34.7	34.7	1.16	.06	.70	0.86	.53	.53	6.83	6.83	0.15	0.15

CASE - 3
High Temperature Gasifiers
Advanced High Temperature Gas Clean-up

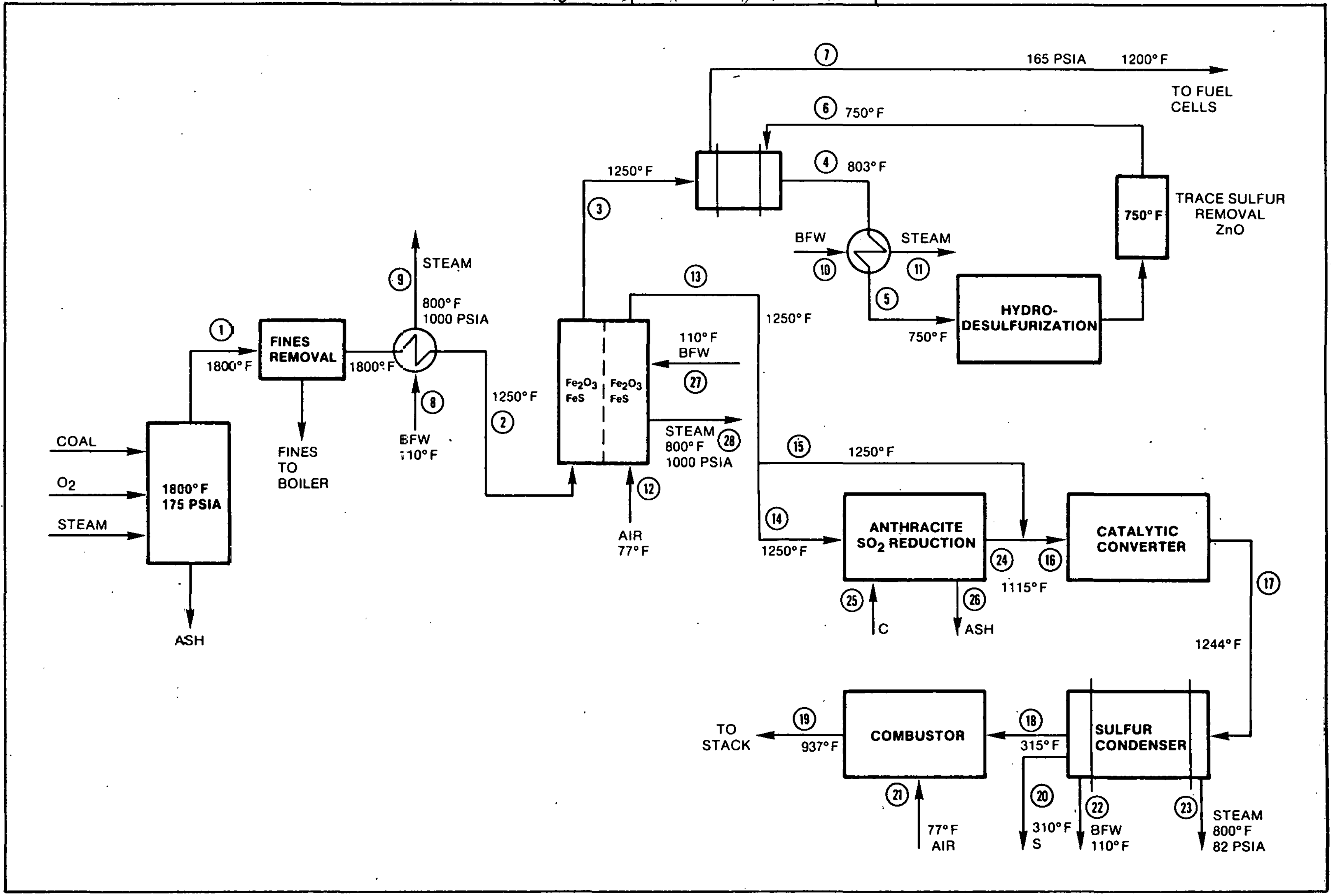


Figure 4.5. Flow Diagram, Case 3

Table 4-11. STREAM PROPERTIES, Case 3

	Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
	Temperature (°F)	1800	1250	1250	800	750	750	1200	110	800	110	750	77	1250	1250	1250		1244	315	937	310	77	110	800	1115	77	1115	110	800
	Pressure (PSIA)	175						165	1000	1000	1000	1000	17							15		15	82	82				1000	1000
	Total Flow Rate (lb mols/hr)	100	100	99.7	99.7	99.7	99.7	99.7	25.7	25.7	1.94	1.94	1.94	1.94	1.31	0.634	2.07	1.87	1.74	2.21	0.1253	0.267	0.617	0.617	1.44			2.22	2.22
CONSTITUENTS	CO	25.7	25.7	25.7	25.7	25.7	25.7	25.7									0.088	0.088	0.088						0.088				
	CO_2	15.8	15.8	15.8	15.8	15.8	15.8	15.8									0.088	0.213	0.213	0.300					0.088				
	H_2	32.2	32.2	32.1	32.1	32.1	32.1	32.1																					
	H_2O	23.1	23.1	23.5	23.5	23.5	23.5	23.5	21.9	21.9	1.94	1.94											0.617	0.617				2.22	2.22
	CH_4	2.4	2.4	2.4	2.4	2.4	2.4	2.4																					
	N_2	0.8	0.8	0.8	0.8	0.8	0.8	0.8					1.687	1.687	1.136	0.550	1.687	1.687	1.687	1.897		0.2106			1.136				
	O_2												0.256							0.0093		0.0560							
	H_2S	0.27	0.27	0.0138	0.0138	0.0138	0.44 ppm	0.44 ppm																					
	COS	0.011	0.011	0.011	0.011												0.083								0.083				
	CS_2	0.004	0.004	0.004	0.004												0.042								0.042				
	S_2																0.0026	0.128	0.0029		0.1253				0.0026				
	SO_2													0.256	0.173	0.084	0.084			0.0029									
	C																									0.300			
	Ash																									0.19*	0.19*		
	Flow Rate (10^3 lb/hr)	1.97	1.97	1.96	1.96	1.96	1.96	1.96	0.394	0.394	0.035	0.035	0.056	0.064	0.043	0.021	0.067	0.067	0.067	0.067	0.008	0.008	0.011	0.011	0.046	0.0038	0.0002	0.040	0.040

*lb/hr

The raw fuel gas is then cooled to 1150°F in a boiler generating 800°F superheated steam at 1000 psia and directed to a high temperature bulk sulfur removal step, assumed here to be the iron oxide absorption process operating at 1250°F with beds alternating between absorption and regeneration cycles.

The H_2S concentration leaving the iron oxide absorber is set by the following chemical reaction equilibrium:

$$2H_2S + H_2 + Fe_2O_3 \rightleftarrows 2FeS + 3H_2O$$

For the feed stream composition prevailing here, the H_2S removal accomplished by the iron oxide absorber is 94.9 percent.

From the iron oxide absorber, the fuel gases pass through the product heater and a boiler producing 750°F superheated steam at 1000 psia to the hydrodesulfurization step where COS, CS_2, mercaptans and thiophene are converted to H_2S. From the hydrodesulfurization step, the products pass through the ZnO absorber and finally through the product heater to the fuel cells.

As indicated above, the minimum H_2S concentration achievable in the ZnO absorber is set by the water vapor concentration in the product stream. Because the fuel gases are not cooled below 750°F in Case 3, the water vapor content of the product gases is not reduced below its value in the gasifier raw gases. Under these conditions, the minimum H_2S concentration achievable is 0.44 ppm. If the combination of hydrodesulfurization and ZnO absorption removes all of the thiophene, then the 0.44 ppm H_2S concentration represents the total sulfur content of the fuel gas product. Lower H_2S concentrations from a hot gas cleanup system should be achievable if a lower water vapor content in the gasifier raw gas can be achieved.

For cases 1 and 2, NH_3 and HCN removal are accomplished in the wet scrubber. Since there are no wet scrubbers in Case 3, the NH_3 and HCN concentrations in the product gas are not reduced below their values in the gasifier raw gas. Thus, the product gases contain 0.08 and 2 lb/MMSCF of NH_3 and HCN, respectively. If this NH_3 and HCN are completely converted to NO in the combustor downstream of the fuel cells, the resulting fuel derived NOX emission would be about 0.009 lb/MMBTU, well below the EPA regulated limit of 0.7 lb/MMBTU. Whether additional thermal NOX generation would raise the total NOX emissions above the regulated limit depends upon the design of the combustor.

The iron oxide regeneration is accomplished by air oxidation at 1200°F, and the SO_2 in the tail gas is reduced to elemental sulfur using the Resox process. Here, part of the SO_2 is reduced by carbon in an anthracite bed to form COS, CS_2 and S_2, and the COS and CS_2 are then reduced to S_2 by the remaining SO_2. Approximately 98 percent of the elemental sulfur is condensed, and the remaining gaseous sulfur is burned to SO_2 and sent to the stack. This emission amounts to about 0.04 lb SO_2/MMBTU, well within the regulated limit of 1.2 lb SO_2/MMBTU.

4.3.4 Cleaned Gas Compositions

The cleaned gas compositions are summarized in Table 4-12 for the three cases described above. In all cases, tars, oils, and particulates are completely removed and the total sulfur content is reduced to <1 ppm.

4.4 FATE OF TRACE ELEMENTS IN CLEAN-UP SYSTEMS

In order to assess the probable fate of the trace elements in the gas cleanup systems, physical properties have been assembled for the stable trace element compounds identified in Table 3-9 above. These physical properties are presented in Table 4-13.

The boiling and melting point data for the thermodynamically stable compounds listed in Table 4-13 indicate that the less volatile species, i.e., As, Be, Bi, Cd, Hg, Mo, Pb, Sb, Ti, V, Zn, Zr, Ca, Fe, Mg, and some Na and K, will condense with coal tar vapor as an aerosol or condense/adsorb on the surfaces of gasification particulates at temperatures of 1000°F and below. As indicated above, these particulates will then be removed in the cyclones and scrubbing systems of Cases 1 and 2 above. In Case 3, where cyclones and electrostatic precipitators are used for particle removal, some fines may not be removed, so some of these elements may be present in minute amounts in the product gas of Case 3.

The solubility data in Table 4-13 indicate that Cl, F, Na, K and some sulfur will be removed from the gasifier raw gas in the scrubbing systems of Cases 1 and 2. However, since the scrubbing solution is recycled for repeated usage, quantities of soluble elements may accumulate. In Case 3, where wet scrubbing is not employed, these elements will be present in the cleaned product gas.

	Composition in Mol Percent		
	Case 1	Case 2	Case 3
CO	26.1	41.4	25.6
CO_2	0	0	15.8
H_2	57.1	51.9	32.0
H_2O	1.5	1.5	23.4
CH_4	13.4	3.9	2.4
N_2	2.0	1.3	0.8
Total Sulfur	< 0.1 ppm	< 0.1 ppm	<1 ppm
NH_3	0	0	1.5 ppm

Table 4-12. Clean Gas Compositions

Table 4-13. Physical Properties of Trace Element Compounds and Their Possible Fate in Gas Clean-up Systems

COMPOUND	MELTING POINT, °C	BOILING POINT, °C	SOLUBILITY IN WATER IN GRAMS/100 C.C.			POSSIBLE REMOVAL IN CLEANUP SYSTEM*	
			COLD WATER	HOT WATER	OTHER REAGENTS	AS PARTICULATE/AEROSOL	BY SOLUBILITY
AS	$814^{36\ atm}$	subl 615	i	i	S HNO_3	YES	NO
ASH_3	-116.3	-55	20 c.c.	-	S $CHCl_3$, bz	NO	NO
BF_2	-56	-34	-			NO	NO
BeO	2530±30	Ca 3900	2×10^{-5} (20)		S conc H_2SO_4, fus KOH	YES	NO
Bi	271.3	1560 ± 5^{760}	i	i	S h H_2SO_4, HNO_3, aq reg; Sl S h Hcl	YES	NO
Bi_2S_3	d685	-	1.8×10^{-5} (18)		S HNO_3; i dil al	YES	NO
CdS	$1756^{100\ atm}$	subl in(N_2)980	0.00013^{18}	colloid	Sa; V S NH_4OH	YES	NO
Ce (?)							
HCl	-114.8	-84.9	$82.3^{(0)}$	$56.1^{(60)}$	327 cc al; S eth, bz	NO	YES
HF	-83.1	19.54	∞	VS		NO	YES
Ge_2H_6	-109	29; d215	d		S liq NH_3	NO	NO
Ge_3H_3	-105.6	110.5 d195	i	i	S CCl_4	NO	NO
GeH_4	-165	-88.5 d350	i	i	S liq NH_3, NaOCl, Sl S h HCl	NO	NO
Hg	-38.87	356.9	i	i	S HNO_3, i HCl	YES/NO	NO
HgS	subl 583.5		1×10^{-6} (18)		S aq reg, Na_2S; ial, HNO_3	YES	NO
Mo_2S_3	d1100	vol 1200			i conc HCl; d h HNO_3	YES	NO
PbS	1114		8.8×10^{-5} (18)		S a; i al, KOH	YES	NO
H_2S	-85.5	-60.7	437 c.c. $^{(0)}$	186 c.c. $^{(40)}$	9.54 c.c. $^{(20)}$ al; S CS_2	NO	YES
Sb_2S_3	550	Ca 1150	1.75×10^{-4} (18)	-	S al, NH_4SH, K_2S, HCl; i ac a	YES	NO
H_2Se	-60.4	-41.5	3.77^{4}	$270^{22.5}$	S CS_2, $COCl_2$	NO	YES/NO
TeH_2	-48.9	-2.2^{160}	VS	S	d al	NO	NO
TiO_2	1830-1850	2500-3000	i	i	S H_2SO_4, alk; i a	YES	NO
V_2O_3	d480		V Sl S		S HNO_3, HF, alk	YES/NO	?
ZnS	subl 1185		6.9×10^{-4} (18)		V S a; i ac a	YES	NO
$Zr\ O_2$	Ca 2700	Ca 5000	i	i	S H_2SO_4, HF	YES	NO
Al_2O_3	2072	2980	i		V Sl S a, alk	YES	NO
$3Al_2O_3\ 2SiO$	1920		i	i	i a, HF	YES	NO
CuS	d~2400		0.02^{15}d	0.048^{80}d	d a	YES	NO
FeS	1193-1199	d	6.2×10^{-4} (18)	d	S d a; i NH_3	YES	NO
FeS_2	1171		4.9×10^{-4}		d HNO_3, dil a	YES	NO
K_2CO_3	891	d	112^{20}	156^{100}	i al, acet	YES	NO
MgS	d>2000		d	d	S a, PCl_3	YES	NO
Na_2CO_3	851	d	7.1°	45.5^{100}	Sl S abs al; i acet	YES	NO
SiO_2	1723±5	2230	i	i	S HF, V Sl S alk	YES	NO

d - Decomposes
i - Insoluble
S - Soluble
VS - Very Soluble
Sl S - Slightly Soluble
h - Hot

c - Cold
acet - Acetone
a - Acid
al - Alcohol
alk - Alkaline
Subl - Sublimes
Vol - Volatilizes

bz - Benzene
fus - Fused
aq reg - Aqua Regia
dil - Dilute
conc - Concentrated
eth - Ethanol
ac a - Acetic Acid

*Applicable to cases I and II only.

The most volatile compounds, i.e., AsH_3, BF_2, Ge hydrides, H_2Se, TeH_2, exist as gases and are insoluble in water or alkali solutions. These elements will probably be present in the cleaned product gases of all three cases.

4.5 ENERGY PENALTIES

Figures 4-6, 4-7, and 4-8 show all of the input and output streams of the clean-up systems for each of the three cases described above. Also included in these figures are the temperatures and total energy contents for each of these streams. The total energy contents consist of the sensible and latent heats of the streams relative to 77°F together with whatever heat would be released by the complete combustion of the streams.

The first law of thermodynamics requires that the total energy input to a clean-up system equal the total energy output. However, because of irreversibilities in the system, the quality of the heat leaving the system will be degraded in comparison to the heat entering the system, so less work can be derived from the heat leaving the system than can be derived from the heat entering the system. It is this difference in realizable work, or work defect, that constitutes the energy penalty associated with a given clean-up system.

For any nonreactive stream entering or leaving a clean-up system, the maximum amount of work that could be derived from cooling this stream to T_2 is given by

$$W_{max} = \int_{T_2}^{T_i} \dot{m} \, C_p \, E_c \, dT + E_c \, \Delta H_c \qquad (1)$$

where

W_{max} = Maximum derivable work, Btu/hr

$\dot{m}$ = Stream mass flow rate, lb/hr

C_p = Stream heat capacity, Btu/lb, °F

E_c = Carnot engine efficiency

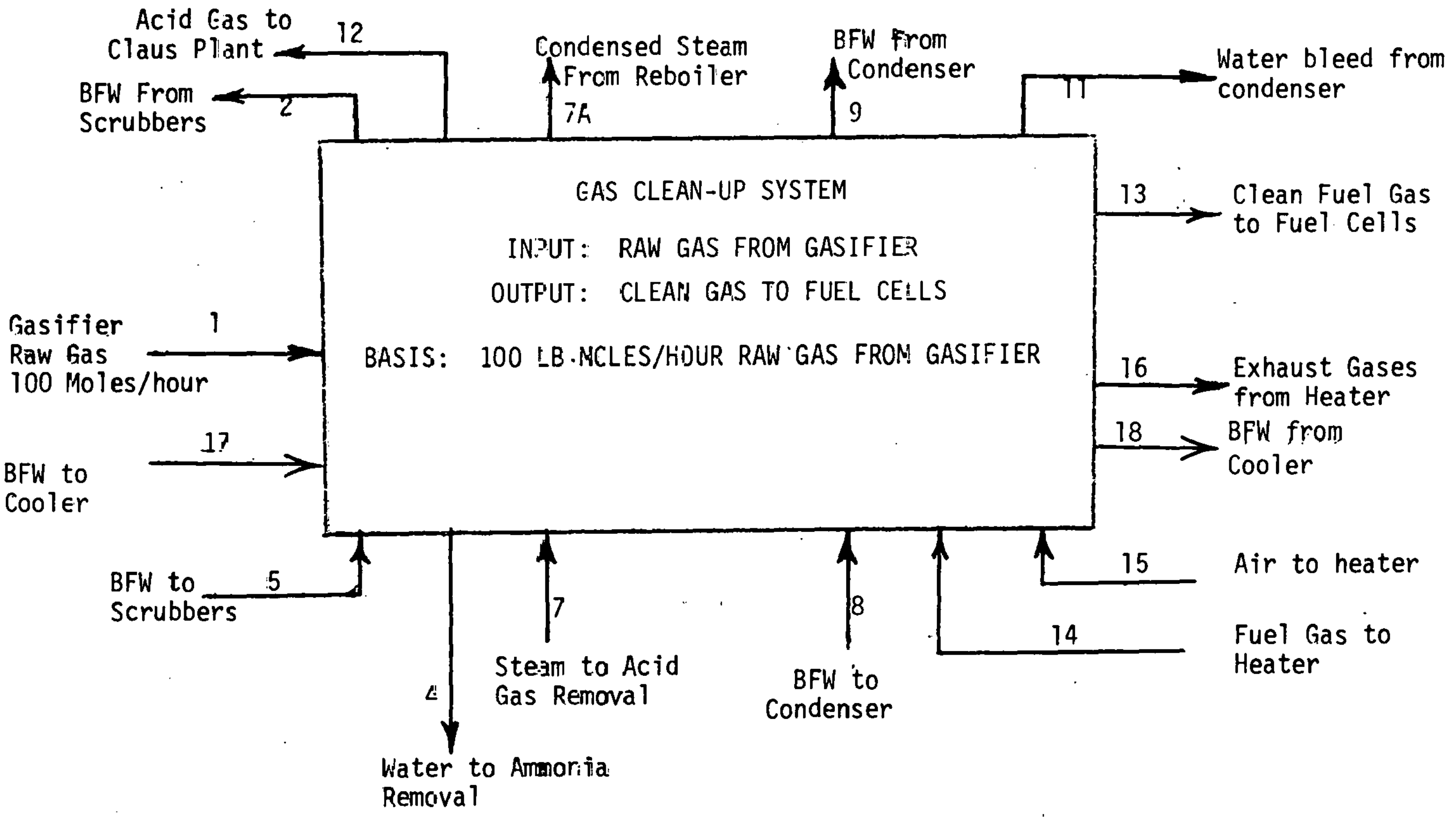
T = Stream temperature, °R

T_o = Ambient temperature, °R

T_i = Initial stream temperature, °R

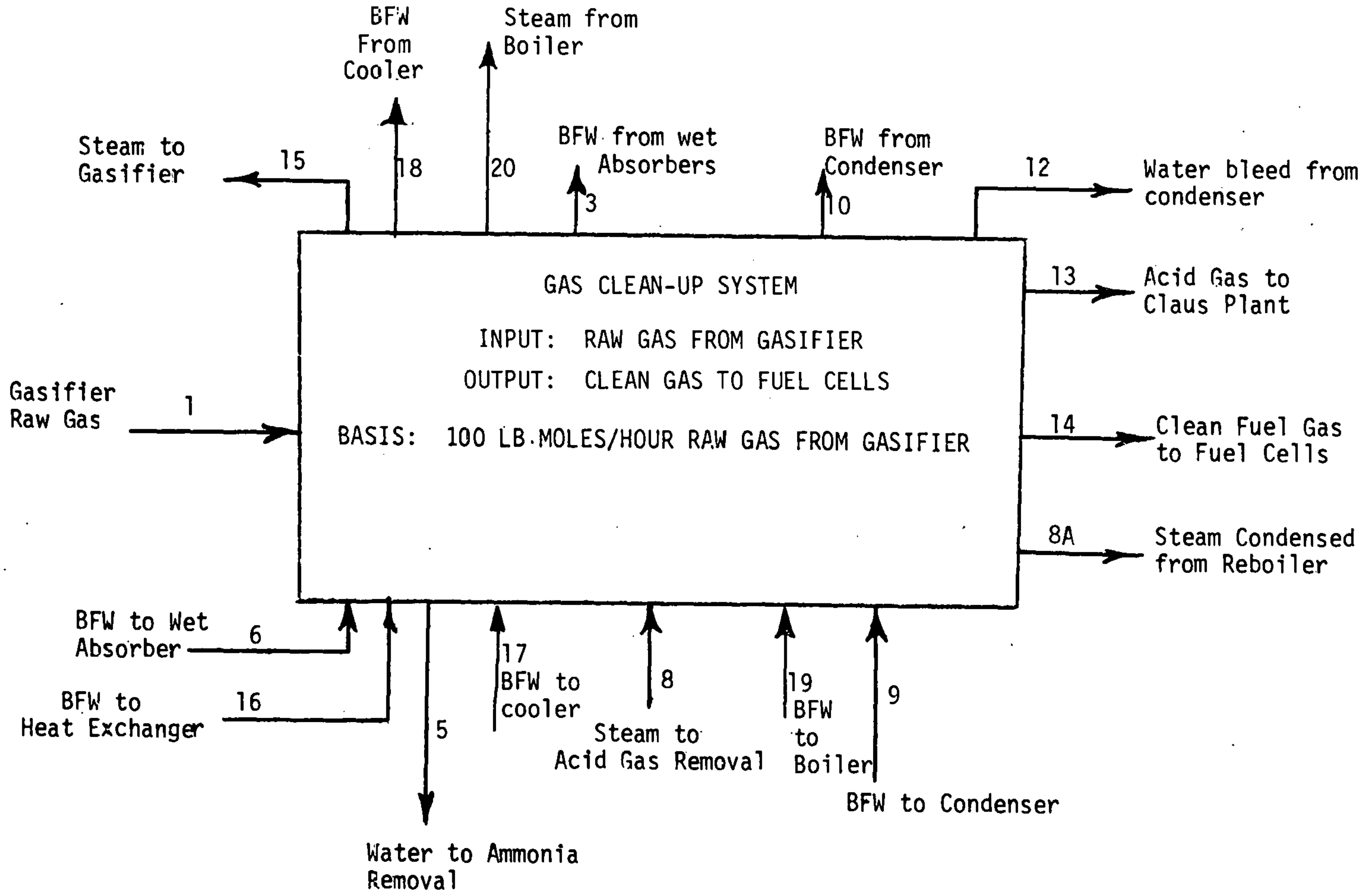
T_2 = Cool stream temperature, °R

ΔH_c = Heat released on condensation, Btu/hr



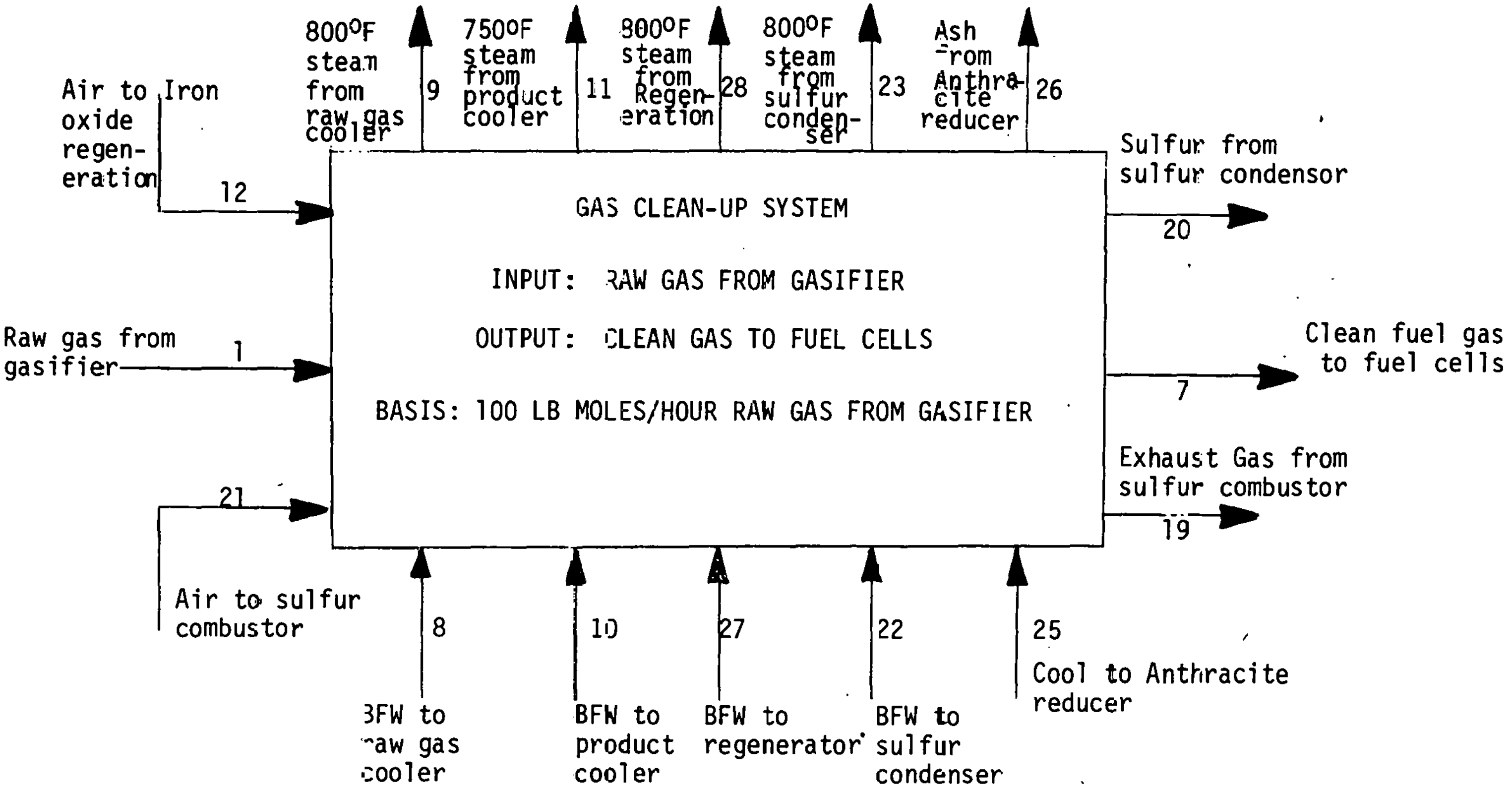
STREAM NO.	1	2	4	5	7	7A	8	9	11	12	13	14	15	16	17	18
THERMAL ENERGY (Q) 10^3 BTU/HR	7136	2435	124	1100	1524	277	1070	2369	8.5	21.7	5713	469	0	22.7	130	288
TEMPERATURE (°F) (AVAILABILITY TEMP)T_i	1000 (2500)	150 (150)	250 (250)	110 (110)	281 (281)	281 (281)	110 (110)	150 (150)	230 (230)	230 (230)	1200 (2500)	250 (2500)	77 (77)	350 (350)	110 (110)	150 (150)
ENERGY AVAILABILITY 10^3 BTU/HR	4436	152	16.5	22.5	385	42.2	31.6	148	1.0	2.6	3703	292	0	434	3.8	18.0

Figure 4-6 ENERGY BALANCE - Case 1



STREAM NO.	1	3	5	6	8	8A	9	10	12	13	14	15	16	17	18	19	20
THERMAL ENERGY (Q) 10^3 BTU/HR	9935	367	22.5	166	1626	296	1145	2533	9.1	23.2	8539	610	17.5	225	498	166	171
TEMPERATURE (°F) (AVAILABILITY TEMP) T_i	1800 (2500)	150 (150)	250 (250)	110 (110)	281 (281)	281 (281)	110 (110)	1 0 (1 0)	230 (230)	230 (230)	1200 (2500)	370 (370)	110 (110)	110 (110)	150 (150)	110 (110)	312 (312)
ENERGY AVAILABILITY 10^3 BTU/HR	6180	22.9	3.0	4.9	411	45.0	33.8	158	1.1	2.8	5501	192	0.5	6.6	31.1	4.9	47.2

Figure 4-7, ENERGY BALANCE - Case 2



STREAM NO.	1	7	8	9	10	11	12	19	20	21	22	23	25	26	27	28
THERMAL ENERGY (Q) 10^3 BTU/HR	10,000	9372	13.0	530	1.15	46.0	0	14.5	0.41	0	0.36	14.8	50.8	0.063	1.32	53.8
TEMPERATURE, (°F) (AVAILABILITY TEMP)T_i	1800 (2500)	1200 (2500)	110 (110)	800 (800)	110 (110)	750 (750)	77 (77)	937 (937)	310 (310)	77 (77)	110 (110)	800 (800)	77 (2500)	1575 (1575)	110 (110)	800 (800)
ENERGY AVAILABILITY 10^3 BUT/HR	6220	5829	0.38	267	0.034	20.9	0	5.9	0.070	0	0.011	7.4	31.6	0.028	0.039	27.1

Table 4-8, ENERGY BALANCE - Case 3

The Carnot efficiency, E_c, is given by

$$E_c = \frac{T - T_o}{T} \tag{2}$$

Also, we can define an average stream heat capacity over the internal T_i-T_2 by

$$m\,\bar{C}_p = \frac{Q}{T_i - T_2} \tag{3}$$

where

Q = The sensible heat content of the stream released on cooling from T_i to T_2

$\bar{C}_p$= An effective average heat capacity over the temperature interval

Taking T_2 to be the condensation temperature for a condensible stream and substituting equations (2) and (3) into (1) and integrating yields the following expression for the maximum work derivable from a nonreactive stream:

$$W_{max} = Q_{i-2}\left[1 - \frac{T_o}{T_i - T_2} \ln\left(\frac{T_i}{T_2}\right)\right] + \Delta H_c\left(\frac{T_2 - T_o}{T_2}\right) + Q_{2-o}\left[1 - \frac{T_o}{T_2 - T_o} \ln\left(\frac{T_2}{T_o}\right)\right] \tag{4}$$

To calculate W_{max} for a combustible stream, we can assume that the stream is combusted with air to produce a nonreactive stream with a higher temperature. Then, equation (4) can be used with this higher value for T_i to calculate W_{max}. By varying the air/fuel ratio, almost any value for T_i can be achieved as long as it is below the adiabatic flame temperature. However, for these calculations, we have assumed a T_i value of 2500^oF (2960^oR) for calculating W_{max} for combustible streams. This temperature is the maximum inlet temperature for utility gas turbines projected for several years in the future. As such, it is a reasonable upper limit to be used when calculating the amount of thermal energy that can be converted to work.

Values for maximum derivable work have been calculated for each of the streams entering and leaving the clean-up systems for the three cases analyzed, and these quantities are given in Figures 4-6, 4-7, and 4-8. Table 4-14 summarizes the total work entering and leaving each system, including electrical energy, and presents the work defects, or energy penalties. For cases 1 and 2 the electrical energy inputs were scaled from data provided by Drayo (4.49), while for Case 3, the electrical energy requirements for the electrostatic precipitators were computed to be negligible from data provided by Friscn (4.59).

The energy penalty is largest, 25.0 percent, for Case 1 in which the Type 1 gas is cleaned in the low temperature clean-up system. For Case 2, where Type 2 gas is cleaned in the low temperature system, the energy penalty

TABLE 4-14. Energy Penalties for Gas Clean-up Systems
(Basis: 100 Lb. Moles/Hour Raw Gas from Gasifier)

	Gas Clean-up Systems		
	Case 1	Case 2	Case 3
Work Available from Input Streams (Btu/hr x 10^{-3})	5181	6642	6277
Electric Power Inputs (Btu/hr x 10^{-3})	68	54	--
Total Available Energy Input (Btu/hr x 10^{-3})	5249	6696	6277
Work Available from Output Streams (Btu/hr x 10^{-3})	3939	5814	6197
System Efficiency (Percent)	75.0	86.8	98.7
Energy Penalty (Percent)	25.0	13.2	1.3

is reduced to 13.2 percent. The smallest energy penalty, 1.3 percent, is realized in Case 3 where the Type 2 gas is cleaned in the developmental, high-temperature, clean-up system.

It should be noted that in a real coal gasification/molten carbonate fuel cell plant, heat recovery for gasification, purification, and power generation will be integrated to achieve the highest possible overall thermal efficiency. The best way to compare clean-up system energy penalties would thus be to examine the optimized overall efficiency for plants incorporating each clean-up system. The method for computing energy penalty used here assumes that efficient use is made of the energy contained in all of the process streams leaving the clean-up system. To the extent that complete utilization of this energy is not achieved in a real plant, the energy penalties calculated here will be too low. Nevertheless, these values are certainly adequate for comparative purposes, and short of preparing a complete, integrated, energy balance for the entire power plant, the method used for computing these energy penalties is the most rational alternative available.

As indicated above, the calculations of energy penalties have been carried out only for oxygen blown gasification systems. For air blown systems, the energy penalties for Cases 1 and 2 should be somewhat larger since more heat is required to heat the nitrogen in the air blown systems from 250^{o}F to 1200^{o}F. For Case 3, which does not exhibit this source of energy penalty, the total energy penalties should be approximately the same for air and oxygen blown systems.

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