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Control of Hydrocarbon and Carbon Monoxide Emissions in the Tail Gases from Coal Gasification Facilities

J. F. Fisher
G. R. Peterson

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CHEMICAL TECHNOLOGY DIVISION

CONTROL OF HYDROCARBON AND CARBON MONOXIDE EMISSIONS IN THE
TAIL GASES FROM COAL GASIFICATION FACILITIES

J. F. Fisher
G. R. Peterson

Prepared for the
Division of Environmental Control Technology
Department of Energy

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CONTROL OF HYDROCARBON AND CARBON MONOXIDE EMISSIONS IN THE TAIL GASES FROM COAL GASIFICATION FACILITIES

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ABSTRACT

A study was made of the economics of various alternative methods of controlling emissions of CO and nonmethane hydrocarbons in the tail gases from a Lurgi substitute natural gas plant. Control of sulfur emissions was excluded from the scope of the study. Processes examined for decontaminating the tail gases included recovery and recycle methods as well as those that convert the contaminants to harmless products. The most recently proposed EPA emission standards for CO and nonmethane hydrocarbons were used as upper limits for the residual contaminants in the treated effluent. Limited assessments of the technical and economic feasibility of ten processes were made. Of the processes studied, the two most promising were found to be incineration in a coal-fired boiler and catalytic incineration. Neither of these methods has been employed commercially under the projected operating conditions, although both are employed in other industries to carry out the basic reactions involved. Total capital and operating costs on a 20-year discounted cash-flow basis with 100% equity financing and 12% annual after-tax return on investment were estimated to be 4¢ per 10^6 Btu of SNG for the coal-fired boiler and 5¢ per 10^6 Btu for the catalytic case. However, the uncertainties in the costs were greater than the indicated cost differentials. The cost of incineration in a gas-fired boiler using sulfur-free medium-Btu gas was estimated to be 11¢ per 10^6 Btu of SNG. All other routes examined were several times more expensive than these three methods.

As a result of the economic study presented, experimental studies on catalyst-aided incineration of typical tail gases will be initiated. Moreover, an industrial assessment of the impact and consequences of high tail-gas flow on the operating characteristics and design of a commercial boiler will be pursued.

1. INTRODUCTION

This report describes the results of a study of available and potentially available processes for the removal or destruction of CO and

nonmethane hydrocarbons in the vent gases of Lurgi-type high-Btu coal gasification plants.* Thermal incineration of the vent gases has heretofore been the principal process considered for this application. The primary purpose of this study was to determine whether there are environmentally acceptable alternatives to thermal incineration and, if so, whether they are economically attractive.

Examination of each alternative was based on its potential applicability in a Lurgi-type high-Btu gas plant using the Rectisol process* for acid-gas removal. The Lurgi process has been proposed for use in several large commercial plants for the production of substitute natural gas (SNG) from coal in the western United States. Standards were proposed in 1976 by EPA to regulate the emissions from such plants.¹ The large-volume vent-gas (tail-gas) streams from the gas-treating portions of a Lurgi SNG facility are composed mainly of CO₂ but may contain ~0.2% (2000 ppmv) CO and ~1% (10,000 ppmv) nonmethane hydrocarbons, as well as small amounts of sulfur compounds. The proposed EPA standards would limit the concentrations of CO and nonmethane hydrocarbons to not more than 200 ppmv and 100 ppmv, respectively. The same standards would also require that all sulfur emissions be in the form of SO_x and would place upper limits on the concentration of SO_x emitted. Thermal incineration in the presence of air converts the CO, hydrocarbons, and sulfur compounds to innocuous CO₂, water vapor, and SO_x, respectively. Incineration thus has the potential of meeting the proposed standards, provided the sulfur content of the tail gases and the fuel used in the incinerator is sufficiently low.

Many of the proposed gasification facilities use a coal-fired boiler to generate the steam and electric power required by the various process units within the facility. Such a boiler provides a convenient place for disposing and incinerating the vent gases. However, it is not clear that this method of disposal would be in compliance with the SO₂ limitations of the proposed EPA regulations, even if flue gas desulfurization were employed (see Appendix). It appears that the only feasible

* Trade name for Lurgi's low-temperature acid-gas absorption process.

way of meeting the proposed regulations is to incinerate the tail gases with a sulfur-free fuel; however, this procedure would be quite expensive because of the high cost of synthetic sulfur-free fuels. Based on these considerations, the objectives of the study were as follows:

1. To determine what processes are commercially available, or are in some stage of development, for the removal or destruction of CO and nonmethane hydrocarbons in the vent gases of Lurgi coal gasification plants using Rectisol acid-gas removal.
2. To assess the technical feasibility and cost of each process on the basis of the available commercial or experimental data.

Because the proposed EPA regulations have not yet been officially adopted, it was decided for purposes of this study to waive the requirement that all sulfur emissions be in the form of SO_x . This made it possible to consider a number of processes of potential interest other than incineration. When evaluating the results of the study, it should be kept in mind that most of the processes listed do not meet the proposed EPA sulfur standards and that incineration (either thermal or catalytic) is the only method presently available for ensuring that all sulfur emissions are in the form of SO_x .

2. SUMMARY OF RESULTS

Ten available or potentially developable processes for the control of CO and hydrocarbon emissions were identified. These are listed in Table 2.1 along with their estimated overall capital and operating costs in cents per 10^6 Btu of product. The costs represent the additional product cost due to the type of treating process used; that is, they represent the added cost relative to hypothetical base case in which the tail gases are simply vented to the atmosphere. Table 2.1 also gives a brief assessment of the technical feasibility of each process.

Incineration in a coal-fired boiler, at a cost of 4¢ per 10^6 Btu of product gas, is the least expensive process. Catalytic incineration (5¢/ 10^6 Btu) is its closest competitor; however, it is a much less proven process. Incineration with desulfurized synthesis gas (medium-Btu gas) costs 11¢/ 10^6 Btu; this is the base process used by EPA (by implication) in setting the proposed emissions standards. Both catalytic and direct incineration with the aid of desulfurized synthesis gas meet the tentative EPA criteria for SO_x emissions. Incineration in a coal-fired boiler meets both the letter and spirit of the law when low-sulfur western coals are fired, but may conflict with the law when high-sulfur coals are fired (see Appendix).

All other processes identified in this study were several times more expensive than the three incineration methods. The treated gases from the other processes will contain a few ppmv of H_2S and COS, which is in violation of EPA's tentative criterion that all sulfur be in the SO_x form.

Costs were calculated by the discounted cash-flow procedure using the method described by R. Skamser of C. F. Braun & Co.² Financing was assumed to be 100% equity with an annual after-tax rate of return of 12%. Fuel costs were assumed to be \$0.30/ 10^6 Btu for coal and \$3.50/ 10^6 Btu for treated SNG. Other details of the cost calculations are given in Sect. 4. Costs are estimated to be accurate within a range of about -25% to +50% of the stated value.

Table 2.1. Approximate cost of hydrocarbon and CO emissions control for Lurgi-type SNG plants^a

Process no.	Description of processes	Approximate cost (¢/10 ⁶ Btu SNG) ^b	Technical feasibility for this application
1	Incineration in a coal-fired boiler	4	Good
2	Incineration in a boiler using desulfurized medium-Btu gas	11	Good
3	Catalytic incineration	5	Unproved
4	Aqua Claus process	c	Unproved
5	Hot carbonate scrubbing	42	Doubtful
6	Cold water scrubbing	56	Doubtful
7	Cuprous ammonium solution absorption	16	Doubtful ^d
8	Adsorption	c	No practical adsorbent known
9	Cryogenic separation	64	Technically feasible
10	Porous membrane separation	c	Doubtful

^aMost of the processes listed here have not been demonstrated in this type of application and cannot be considered available for commercial use.

^bCost includes both capital and operating charges. Additional details are given in Table 4.1.

^cInsufficient data to permit cost estimation in this application.

^dThis process removes only CO.

Technical feasibility has been fairly well established for the thermal incineration processes (processes 1 and 2), but not for the other processes. Catalytic incineration has been demonstrated in other applications, but its feasibility and catalyst life in this application are still undetermined. However, catalytic incineration is one of the few processes that is potentially capable of meeting the proposed EPA restrictions in regard to sulfur emissions.

Absorption and cryogenic processes have been well demonstrated in other applications, but their usefulness in this application is questionable. The feasibility of adsorption and membrane diffusion processes is conjectural at this time.

In the case of incineration in a coal- or gas-fired boiler, the large flows of inert vent gases could have an appreciable effect on the boiler operation, and the boiler would have to be designed to take such loads into account.

3. BASIS FOR THE STUDY

3.1 Gas Flows and Compositions

Published information on the WESCO plant, a typical proposed Lurgi SNG plant with an output of 250×10^6 scfd, was used as the basis for defining the flow rates and compositions of the various vent-gas streams.³⁻⁵ The WESCO plant will convert 19,540 tons of as-received low-sulfur western U.S. coal to SNG each day. The coal contains 0.8% sulfur, 21% ash, and 17% moisture and has a higher heating value of 8400 Btu/lb. The boiler plant will burn an additional 4320 tons of coal per day. Daily by-product production will be 880 tons of tar (0.5% sulfur), 440 tons of tar oil (0.25% sulfur), 200 tons of naphtha (0.2% sulfur), 130 tons of phenol, and 142 tons of sulfur.

Fig. 3.1 shows a schematic flowsheet of the relevant portions of the WESCO plant and gives approximate flow rates and compositions of the gas streams of interest. Raw synthesis gas (stream 1) is treated in a Rectisol unit to remove H_2S . The sulfur-rich acid-gas stream from the Rectisol unit (stream 2) goes to an H_2S concentrator to increase the H_2S concentration to ~70% and to reduce the hydrocarbon contaminants to a low level, thus permitting a more favorable mode of operation of the Claus plant. The dilute acid-gas stream from the Rectisol unit (stream 4) contains ~1% H_2S and is treated in a Stretford plant. Tail gases from the Claus and the Stretford plants (streams 8 and 7, respectively) are incinerated in the coal-fired boiler. A flue-gas desulfurization unit with a design removal efficiency of 90% provides SO_2 removal from the boiler stack gases (see Appendix). The large low-sulfur tail-gas stream from the Rectisol plant (stream 3) is combined with the tail gases from the SNG drying step (stream 11) and burned in an incinerator fired with low-sulfur fuel oil.

Streams used in this study for the purpose of analyzing alternative processes are the vent gases from the Rectisol and Stretford processes (streams 3 and 7 on the diagram). The Claus plant off-gas, stream 8, is relatively small compared to the other two and hence was omitted for the sake of simplicity. Its inclusion would have had no effect on the results of the study.

COMPONENT, LB-MOLES/HOUR	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
CO ₂	33250	1300	15150	15700	140	1160	16700	140	100	100	(500)	100
H ₂ S	506	347	0.5	159	345	2.6	2.5	1.9	0.0	0.0	0.0	0.0
COS	5.5	2.5	0.5	2.3	0.3	2.2	2.3	0.1	0.7	0.7	0.0	0.0
CO	14550	7	30	35	7		35		14550	34	0	30
H ₂	41300	8	35	40	8		40		44720	200	0	195
CH ₄	11500	42	85	104	4	38	104	3	11350	27000	0	27000
C ₂ H ₄	440	33	67	82	1	32	82	0	325		0	0
C ₂ H ₆	650	52	106	129	1	51	129	0	400		0	0
N ₂	300	0	0	0	0	0	0	0	300	300	0	300
TEMP. °F	100	100	100	100	100	100	100	250	100	100	130	100
PRESS. PSIA	2	24	15	17	22	17	15	15	450	420	15	1200
10 ³ scfm	668	11.3	97.5	108.7	3.2	8.1	107.7	0.9	452.7	174.1	0.06	174

Fig. 3.1. WESCO-Lurgi acid-gas removal and hydrocarbon control.

3.2 Emissions Standards

EPA has proposed standards (November 1976) for allowable emissions of sulfur and hydrocarbons from Lurgi SNG plants.¹ The standards are unusual in that they place limits on contaminants in specific tail-gas streams from the gas-treating section of the plant rather than on the total emissions from the plant complex. With respect to the Rectisol plant tail gases, the proposed regulations require that all sulfur compounds be emitted as SO_x and that the allowable emission of nonmethane hydrocarbons be limited to 100 ppmv.

EPA limits are compared with the WESCO design in Table 3.1. Some of the individual streams in the WESCO design exceed the proposed EPA standards. However, if the EPA standards were applied on a total facility basis, the total sulfur emissions would be within the allowable limits.

New Mexico regulations limit H_2S emissions from gasification plants to 10 ppmv and limit the sum of H_2S , COS, and CS_2 emissions to 100 ppmv. Table 3.2 summarizes the WESCO plant emissions and the applicable New Mexico regulations. Emission standards for nonmethane hydrocarbons and CO are defined by their impact on the ambient air quality. Under New Mexico regulations, it is feasible to use coal- or oil-fired boilers as incinerators. Allowable SO_2 emissions from the boiler are calculated according to the following equation:

$$W = E_o Q_o + E_c Q_c + E_g Q_g .$$

The variables used in this equation are defined as follows:

W = total allowable SO_2 emission, lb/hr;

E_o = allowable emission from oil, lb/ 10^6 Btu of oil fired;

Q_o = heat released by the oil based on the higher heating value,
 10^6 Btu/hr;

E_c = allowable emission from coal, lb/ 10^6 Btu of coal fired;

Q_c = heat released by the coal based on the higher heating
 value, 10^6 Btu/hr;

Table 3.1. Comparison of various streams in WESCO SNG plant with proposed EPA emission standards^a

Tail-gas contaminants	WESCO SNG plant ^b	Proposed EPA standards ^c
<u>Sulfur</u>		
Stream (7) ^d , Stretford tail gas	150 ppmv H ₂ S 135 ppmv COS	30 ppmv No limit
Stream (8), Claus tail gas	13,000 ppm H ₂ S + SO ₂	250 ppmv
Stream (3), sulfur-free Rectisol tail gas	30 ppmv H ₂ S 30 ppmv COS	30 ppmv No limit
<u>Nonmethane hydrocarbons</u>		
Stream (7), Stretford tail gas	12,000 ppmv	100 ppmv
Stream (3), sulfur-free Rectisol tail gas	12,000 ppmv	100 ppmv
Stream (8), Claus tail gas	Low; no data	100 ppmv
<u>Carbon monoxide</u>		
Stream (7), Stretford tail gas	2000 ppmv	200 ppmv
Stream (3), sulfur-free Rectisol tail gas	2000 ppmv	200 ppmv
Stream (8), Claus tail gas	Low; no data	200 ppmv
<u>Methane</u>		
Stream (7), Stretford tail gas	6000 ppmv	No limit
Stream (3), sulfur-free Rectisol tail gas	5000 ppmv	No limit

^aProposed EPA standards, November 1976.

^bConcentrations shown are before incineration.

^cLimits for sulfur compounds are given preincineration values, but incineration is required.

^dStream numbers refer to Fig. 3.1.

Table 3.2. Comparison of emissions from WESCO SNG plant with New Mexico emission regulations

Tail-gas contaminants	WESCO SNG plant	New Mexico regulations
<u>Sulfur and sulfur compounds (except SO₂)</u>		
Stream (7), Stretford tail gas	150 ppmv H ₂ S 135 ppmv COS	All streams: 100 ppmv max. H ₂ S + CS ₂ + COS, but the H ₂ S content must be ≤10 ppmv (Section 673). ^a Nonsulfur contaminants: ≤10 ppmv HCN (Section 674), ≤5 ppmv HCl (Section 675), ≤25 ppmv NH ₃ (Section 677).
Stream (8), Claus tail gas	13,000 ppmv H ₂ S + COS	
Stream (3), sulfur-free Rectisol tail gas	30 ppmv H ₂ S 30 ppmv COS	
<u>Sulfur as SO₂</u>		
Streams (3) + (7) + (8)	0.20 lb SO ₂ /10 ⁶ Btu heat input	0.34 lb SO ₂ /10 ⁶ Btu heat input to boiler (Section 682) ^b 0.008 lb sulfur equivalents/10 ⁶ Btu contained fuel value to gasification plant (Section 680)
<u>Nonmethane hydrocarbons</u>		
Stream (7), Stretford tail gas	12,000 ppmv	0.19 ppmv max. (Section 201 - C, 7) ^c (ambient)
Stream (8), Claus tail gas	Low; no data	
Stream (3), sulfur-free Rectisol tail gas	12,000 ppmv	
<u>Methane</u>		
Stream (7), Stretford tail gas	6000 ppmv	No regulations
Stream (3), Claus tail gas	5000 ppmv	
<u>Carbon monoxide</u>		
Stream (7), Stretford tail gas	2000 ppmv	8.7 ppmv (Section 201 - C, 4) ^c (ambient)
Stream (8), Claus tail gas	Low; no data	
Stream (3), sulfur-free Rectisol tail gas	2000 ppmv	

^aAdopted Sept. 14, 1973.^bAdopted Dec. 31, 1974.^cAmbient air quality standards adopted June 2, 1974. No compound-specific regulations covering C₂+ and CO emissions from gasification plants.

E_g = allowable emission from gas, lb/10⁶ Btu of gas fired; and

Q_g = heat released by the gas based on the lower heating value,
10⁶ Btu/hr.

In using this equation, the allowable values E_o , E_c , and E_g would be specified by the regulatory agency.

4. PROCESS DESCRIPTIONS AND COST ESTIMATES

4.1 Basis and Accuracy of Cost Estimates

Table 4.1 summarizes the various processes and presents a breakdown of the estimated costs. As mentioned earlier, these costs represent the additional or incremental cost compared to a hypothetical base case in which the tail gases are simply released to the atmosphere. The cost of this 2.50×10^8 -scfd Lurgi SNG plant is about \$1.5 billion.⁶ The costs are broken down into: estimate incremental capital investment, capital charges, fuel cost, catalyst cost, other costs including power and labor, and a total yearly incremental capital and operating cost. Total yearly costs are also reported on a cents-per- 10^6 Btu basis. As indicated in the table, the economics is based on a 20-year discounted cash-flow calculation using 100% equity financing and an annual aftertax rate of return of 12%.

The cost estimates are rather approximate. Overall accuracy limits are estimated to be in the range of -25% to +50%. In some cases, the plant costs were scaled from reported costs for generally similar systems. The clean fuel gas-fired incinerator cost was scaled from a gas-fired boiler cost developed for Coalcon.⁷ This estimate agreed with the value developed by the J. Zink Company.⁸ The incinerator is essentially a 20-MW boiler.

The same procedure could be followed only in part in the coal-fired boiler case. The plant capacity from the convection section through the stack gas cleanup was simply scaled up by 50%. This corresponds to the increase in the gas flow rate through the boiler caused by the introduction of the tail-gas streams into the fire box. The cost was then scaled up using an exponent of 0.6. Costs for modifying the radiant section of the furnace and the possible cost increases in coal grinding were not estimated. These could best be established through a detailed study by a qualified boiler manufacturer or engineering firm specializing in such studies. The costs of the radiant section were arbitrarily increased in proportion to the flue-gas flow rate. It was assumed that there was no loss in combustion efficiency. Scale-up was based on coal-fired boiler costs that were reported for Coalcon.⁷

Table 4.1. Incremental capital and operating costs for selected effluent treatment processes applied to a 2.50×10^8 -scfd Lurgi SNG plant^a

Process no.	Name	Estimated capital investment (\$10 ⁶)	Capital and operating costs (\$10 ⁶ /year) ^b						Total cost (¢/10 ⁶ Btu)
			Capital charges	Fuel ^c	Steam ^d	Catalyst	Other	Total	
1	Incineration in coal-fired boiler	9	2.2	(0.2) ^e	0		1.7	3.7	4
2	Incineration in medium-Btu, gas-fired boiler	6	1.5	12.0	(5.0)		1.5	10.0	11
3	Catalytic oxidation	14	3.5	0	(1.8)	0.3	2.6	4.6	5
4	Aqua Claus								f
5	Hot carbonate scrubbing	38	9.4	(8.0)	19		17.9	38.3	42
6	Cold water scrubbing	66	16.3	(8.0)	8		23.4	39.7	44
7	Cuprous ammonium solution absorption	20	4.9	(0.2)	2		7.9	14.6	16
8	Adsorption								f
9	Cryogenic separation	100	24.7	(8.0)	13		28.7	58.4	64
10	Porous membrane separation	75	18.5	0	6				f

^aBasis: 20-year discounted cash-flow method with 100% equity financing and 12% return on equity after taxes.

^bCosts and production rate based on 365 days/year. Capital charges are based on an annual fixed charge rate of 24.7%.

^cCoal at \$0.30/10⁶ Btu; medium-Btu gas (synthesis gas) at \$3.50/10⁶ Btu; recycled (contaminated) fuel gas credited at \$3.00/10⁶. Product SNG was estimated at \$4.00/10⁶ Btu.

^dSteam (900 psig, 825°F) is estimated at \$1.35/10³ lb.

^eNumbers in parentheses indicate credit.

^fInsufficient data to permit cost estimation.

The accuracy of estimates made for the hot carbonate acid-gas absorption system is approximately the same as that for the coal-fired boiler. The costs available were those of the standard, single-stage acid-gas removal process. The proposed two-stage process relies on the relative rates of absorption of H_2S and CO_2 in the first stage for the selective removal of H_2S and on a partial CO_2 flash after the second stage for removal of the dissolved hydrocarbons. In the absence of operating data for these alternatives, the sizes of additional process equipment could only be roughly estimated.

The costs of most of the other processes were based on approximate heat and material balances and shortcut methods of equipment sizing (based on mass or heat flows). This procedure was applied to the cold-water acid-gas absorption, cryogenic separation, and adsorption processes. The most uncertain cost in the analysis is that for membrane separations. General Electric's projection^{9,10} for the manufacture of membranes on a commercial scale was employed without alteration. Membranes with surface areas of a few square feet have been prepared, but the application contemplated here would require surface areas of over 8 million square feet. Costs for the adsorption and membrane separation cases were developed only to give an indication as to whether such systems have sufficient potential to justify further development for this application.

Accuracy limits for the energy-related operating costs are believed to be in the range of -20% to +30%.

4.2 Detailed Process Descriptions

In this section, the processes are discussed from the standpoint of their additional capital and operating requirements and equipment modifications in comparisons with the hypothetical base case.

4.2.1 Incineration in a coal-fired boiler

The WESCO boiler flue-gas flow is ~85,000 lb-moles/hr before the tail gases are added. Incineration of the contaminated CO_2 streams will increase this flow by 45,000 lb-moles/hr. A schematic flow diagram for

this process is presented in Fig. 4.1. Incineration of the CO requires temperatures of $\sim 1800^{\circ}\text{F}$ in the radiant section of the boiler. The addition of the tail gases will drastically reduce the gas temperature in the radiant zone and will appreciably increase the emissivity of the flue gas. Before the tail gases enter the boiler, they should be pre-heated by exchange with the flue gas to avoid losses in the overall thermal efficiency and to avoid excessive cooling of the radiant zone. Reductions in the burning rate may be offset by grinding the coal feed to a finer consistency; however, the intensity of the flame in the burner zone will increase with a finer coal feed. Based on these considerations, it is apparent that the boiler design and efficiency could be appreciably affected by the introduction of the tail gases into the fire box. Computer programs for boiler design could probably be used to evaluate the effect of tail-gas incineration on the overall efficiency and cost.¹¹

As indicated in Table 4.1, the difference in capital cost for the coal-fired boiler case above the base case was estimated at \$9 million. The increased costs of the boiler, flue gas desulfurization unit, and electrostatic precipitator account for \$5.3 million, \$3.4 million, and \$0.3 million, respectively. These rough estimates were made by using scaling factors based on the increased throughput of flue gas.

The reduction of fuel consumption was estimated at \$0.2 million/year. This was based on an estimated 2.6×10^9 Btu of heat input per hr to the boiler in the base case, of which $\sim 3\%$ is consumed by the induced-draft fans and grinding mills and $\sim 3\%$ to 4% is used by the flue gas wet-scrubbing system.^{12,13} It was estimated that the increased energy requirements would be ~ 140 million Btu/hr and that the net recoverable energy from burning the CO and hydrocarbons would be ~ 200 million Btu/hr. This leads to an overall net saving of 60 million Btu/hr, or about \$0.2 million/year.

4.2.2 Incineration in a boiler fired with desulfurized medium-Btu gas

The flowsheet for this option is shown in Fig. 4.2. It was estimated that a temperature on the order of 1600 to 1800°F would be required for essentially complete combustion of the CO and hydrocarbons in the tail gases fed to the boiler.^{8,14} If the gases entering the

STREAMS 12A AND 12B REFLECT THE CONTRIBUTIONS OF THE CONTAMINATED AND THE NORMAL BOILER FLUE GAS STREAMS RESPECTIVELY.

APPROXIMATE STREAM FLOWS FOR EQUIPMENT SIZING, LB-MOLES/HOUR:

COMPONENT	3	7	10	11	12A	12B	13	14
H ₂ O	-	800			1381	9677		~25000
SO ₂	-	-			6	102		(ALLOWABLE 56)
CO ₂	15150	16700	31850		32875	14172		47047
H ₂ S	0.5	2.5	3		0	0		0
COS	0.5	2.3	3		0	0		0
CO	30	35	55		<200 PPM	<200 PPM		<200 PPM
H ₂	35	40	75		0	0		0
CH ₄	85	104	189		0	0		0
C ₂ H ₄	67	82	149		0	0		0
C ₂ H ₆	106	129	235		0	0		0
N ₂				72294	10190	62104		72294
O ₂				19227	800	3125		3925
COAL							4300* tons/day AS (RECEIVED)	
10 ³ scfm	97.5	112.7	205.2	576.6	285.1	561.8		934.1

* NORMAL COAL FEED RATE TO WESCO BOILER

Fig. 4.1. Incineration in coal-fired boiler.

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APPROXIMATE COMPONENT FLOWS FOR EQUIPMENT SIZING, LB-MOLES/HOUR:

COMPONENT	(3)	(7)	(10)	(11)	(12)	(13)	(14)
H ₂ O		800	800		4110		0.47 MM LB
SO ₂					6		(900#/825°F STEAM)
CO ₂	15150	16700	31850		33855		
H ₂ S	0.5	2.5	3		0		
COS	0.5	2.3	3		0		
CO	30	35	65		<200 PPM		
H ₂	35	40	75		0		
CH ₄	85	104	189		0		
C ₂ H ₄	67	82	149		0		
C ₂ H ₆	106	129	235		0		
N ₂				19325	19325		
O ₂				1200	1200		
MEDIUM-BTU FUEL						3.9X108 BTU (MHV)	
10 ³ scfm	97.5	112.7	210.2	129.3	368.5		

Fig. 4.2. Incineration in a medium-Btu gas-fired boiler.

boiler are heated to ~ 700 to 800°F by heat exchange, the calculated combustion temperature for the tail gases is $\sim 1300^{\circ}\text{F}$. The additional heat required to increase this temperature to 1600°F must be supplied by medium-Btu gas. This amounts to $\sim 4.40 \times 10^8$ Btu of sulfur-free synthesis gas per hr, which costs about $\$3.50/10^6$ Btu. Steam production from the combustion of the tail gases and medium-Btu gas is ~ 600 million Btu/hr, but the value of the steam is only $\$1.27/10^6$ Btu, leaving an energy cost deficit of about $\$7$ million/year.

The cost of the incinerator-boiler system was estimated at $\$6$ million, based on scaled-down gas-fired boiler data⁷ and on estimates obtained from the J. Zink Company.⁸

4.2.3 Catalytic incineration

Fig. 4.3 shows the flowsheet used for estimating capital and operating costs. Catalyst-bed inlet and outlet temperatures are 700°F and 900°F , respectively. In normal operation, the exothermic heat of oxidation of the CO and hydrocarbons is sufficient to supply the heat requirements of the process. An auxiliary heater is required for startup. A venturi ejector is used to recycle hot gases to the catalyst bed to help maintain its operating temperature. The heat contained in the net hot gases leaving the bed is used to preheat the feed gas before the exit gases are discharged to the stack. The discharge temperature of the stack gas is kept above 400°F to prevent downdrafting. The principal utility consumer in the process is the feed-gas blower.

A space velocity of 5000 scf per hr per ft^3 of reactor was used for estimating the required catalyst-bed volume. The space velocity recommended by Air Resources was 15,000 scf/hr/ ft^3 , but we felt that a lower figure was justified in view of the uncertainties in catalyst life and hydrocarbon burnout rates. Catalyst costs were based on data obtained from Air Resources. Heat recovery temperatures were low enough to be within the range of currently available equipment.

The capital cost of catalytic incineration is estimated at $\$14$ million. Operating costs are estimated at $\$2.9$ million/year, most of which is electricity used for driving the inlet gas blower. A credit

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APPROXIMATE COMPONENT FLOWS FOR EQUIPMENT SIZING, LB-MOLES/HOUR:

COMPONENT	(3)	(7)	(10)	(11)	(12)	(13)
H ₂ O		800			2181	5670
SO ₂	0.0	0.0	0.0		6	16
CO ₂	15150 moles/hr	16700	31850		32875	85475
H ₂ S	0.5	2.5	3		0.0	
COS	0.5	2.3	3		0.0	
CO	30	35	65		<200 PPM	
H ₂	35	40	75		0	
CH ₄	85	104	189		0	
C ₂ H ₄	67	82	149		0	
C ₂ H ₆	106	129	235		0	
N ₂				10190	10190	26194
O ₂				2710	800	2080
10 ³ scfm	97.5	112.7	205.2	81.3	290.1	754.3

Fig. 4.3. Incineration in a catalyst bed.

of \$1.8 million/year for steam production reduces the net operating cost to \$1.1 million/year.

Catalytic incineration is still in the developmental stage for the application considered here, although it has been used to a limited extent in industry for the destruction of potential atmospheric contaminants.¹⁵ In the past, catalyst performance has not always been as reliable as desired, probably due to the presence of poisons in the gas streams. Consequently, when the cleanup of contaminants is mandatory, thermal incineration has more frequently been the choice of plant operators. Heavy metals, halides, and sulfur are typical poisons. The platinum group catalysts are permanently poisoned by heavy metals and temporarily by halides and sulfur, and they tend to oxidize sulfur to SO_3 . For the application contemplated here, Engelhard advises that catalyst activity and life cannot be predicted without testing under conditions which approximate those expected in the plant.¹⁶ Catalytic incineration is employed in cases where the market has justified the development costs. Two important applications are in automobile emissions exhaust control and in the destruction of NO_x in nitric acid plants.

Air Resources¹⁵ has a commercial catalytic system which has been used to catalytically incinerate hydrocarbons, chlorinated hydrocarbons, and mercaptans in certain types of gases. The catalyst is reported to be resistant to heavy metals and phosphates. The system is currently being tested in the dusty off-gases from both the sintering steps at a steel plant and a lead-melting operation. The formation of SO_3 as a result of sulfur compound destruction appears to be negligible at temperatures below 1000°F . The upper operating temperature for the catalyst is $\sim 1200^\circ\text{F}$.

4.2.4 Incineration — Aqua Claus process

The Aqua Claus process is currently under development. If successful, it will permit reaction of a gas stream containing SO_2 with a H_2S -rich stream in a liquid-phase reactor to produce sulfur.

Although the objectives of this study did not include SO_2 removal, it was felt that it would be useful to indicate how a process such as Aqua Claus might be used in conjunction with catalytic incineration to remove SO_2 from the incinerated gases. In this study, therefore, the Aqua Claus option is an add-on to the incineration option, with the purpose of eliminating all or part of the SO_2 emissions from the incinerator.

The process flow diagram shown in Fig. 4.4 indicates how the Aqua Claus option might be used. The flow plan shown represents a major revision to the standard manner of treatment used in the WESCO plant. The Claus plant and the Stretford plant have been eliminated. Feed streams 3, 4, 5, and 6 come from the Rectisol unit and the H_2S concentrator. All the hydrocarbon-contaminated gases except the concentrated 70% H_2S stream from the Rectisol unit (stream 5) are incinerated to SO_2 . The SO_2 -rich tail gas is reacted with H_2S in the Aqua Claus system, the H_2S being provided by the 70% H_2S stream. The unreacted contaminants in the 70% H_2S stream are returned to the catalytic incinerator. Treatment of the flue gases from the boiler plant is not included in this flow-sheet; it is assumed that flue-gas desulfurization would continue to be used for this stream.

The economics of this method of treatment is not well defined since costs for the Aqua Claus process are not yet available. Indications are that the Aqua Claus plant might cost about as much as a Stretford unit, or perhaps 25% more. A rough cost summation of the route shown in Fig. 4.4 was made by estimating \$20 million for the Aqua Claus unit¹⁷ and \$14 million for catalytic incineration, then subtracting \$15 million for the Stretford unit and \$6 million for the Claus plant, giving a net increase of \$13 million above the base case.

A potential future advantage for the Aqua Claus route is that it offers the possibility of treating the boiler flue gases as well as the other streams shown. If this potential is ever achieved, a substantial reduction in the SO_2 emissions from the overall facility may be possible. In the flowsheet shown, the H_2S -rich stream from the Rectisol unit is not large enough to permit the multigas stream treatment.

APPROXIMATE COMPONENT FLOWS FOR CAPITAL COST ESTIMATION, LB-MOLES/HOUR:

COMPONENT	(3)	(4)	(5)	(6)	(10)	(11)	(12)	(13)	(14)
H ₂ O							1933	1933	
CO ₂	15150	16700	140	1160	33010	140	34389	34389	
H ₂ S	0.5	159	345	2.6	162	6	0	0	
COS	0.5	2.3	0.3	2.2	5	0.3	0	0	
CO	30	35	7		65	7	7	7	
H ₂	35	40	8		75	8	0	0	
CH ₄	85	104	4	38	227	4	0	0	
C ₂ H ₄	67	82	1	32	181	1	0	0	
C ₂ H ₆	106	129	1	51	286	1	0	0	
SO ₂							3	173	
N ₂							11867	11867	11867
O ₂							980	980	3156
10 ³ scfm	97.5	107.7	3.2	8.1	214.3	1.1	309.8	310.9	94.6

Fig. 4.4. Catalytic incineration with Aqua Claus absorber.

4.2.5 Absorption (hot carbonate process)

Figure 4.5 shows how hot carbonate absorption might be used to treat the CO₂-rich streams. Hot carbonate solution absorbs both H₂S and CO₂. Most of the CO and hydrocarbons are not absorbed and are recycled to the Rectisol unit (stream 14). The small amounts of CO and hydrocarbons that are absorbed are released by flashing the solution at a lower pressure and are then recycled to the absorber. Eventually, due to readjustment of concentrations in the absorber, this material discharges with stream 14. Another adjustment of concentrations takes place in the Rectisol unit through the buildup of recycled CO and hydrocarbons, resulting in the discharge of these components with the treated product gas stream (stream 9 in Fig. 3.1).

Aqueous inorganic chemical absorption systems pick up relatively little of the hydrocarbons or CO entering with the CO₂. However, sufficient amounts of CO and hydrocarbons are dissolved in the water for a two-stage flash recycling ~15% of the absorbed CO₂ to be required in order to decontaminate the liquor going to the stripper.

Hydrogen sulfide reacts with the hot carbonate along with the CO₂. The rate at which H₂S dissolves in a catalyst-free carbonate solution is many times greater than that of the CO₂. The lower portion of the absorber system shows a section where H₂S is absorbed in the aqueous carbonate. This liquor flows to an independent stripper. The H₂S-rich overhead from the stripper is routed back to the Stretford plant.

The COS is relatively insoluble; however, when it dissolves, it slowly hydrolyzes to H₂S. As a result, the liquor leaving the bottom of the CO₂ absorber will contain a large fraction of the H₂S that was formed from the COS. Since little of the H₂S formed from COS is lost in the flash, the CO₂ stream (stream 12) cannot be completely decontaminated. A few ppm of sulfur will always be encountered. Standards proposed by EPA specify whether the sulfur should be completely removed or oxidized to SO₂. A possible solution is to reduce the H₂S content of the CO₂ stream to ~0.1 ppm by reaction with ZnO at a temperature in the range of 300 to 500°F. By using heat exchange, the auxiliary fuel requirements can be kept to very low levels.

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APPROXIMATE COMPONENT FLOWS FOR EQUIPMENT SIZING, LB-MOLES/HOUR:

COMPONENT	(3)	(7)	(10)	(12)	(13)	(14)	(16)	
H ₂ O		800	800	2000		2		
CO ₂	15150	16700	31850	31250	300	300	600	STREAM 12 MAY STILL NEED ZnO TREATMENT FOR H ₂ S ELIMINATION
H ₂ S	0.5	2.5	3	0.1	2.9	0	2.9	
COS	0.5	2.3	3	0.1		2.9	2.9	
CO	30	35	65			65	65	
H ₂	35	40	75			75	75	
CH ₄	85	104	189			189	189	
C ₂ H ₄	67	82	149	1.5		147.5	147.5	
C ₂ H ₆	106	129	235	1.0		234	234	
10 ³ scfm	97.5	112.7	210.2	209.5	1.9	6.4	8.3	

Fig. 4.5. Hot carbonate absorption of acid gas.

Another approach, which would be more economical, is to use selective catalytic incineration of the H_2S and COS . This has the advantage of meeting the requirement that all sulfur releases be in the form of SO_2 .

Capital cost estimates for the process route shown in Fig. 4.5 were developed from estimates of major item costs and by scaling literature values.¹⁷ A price of \$25 million was estimated for a single train without selective H_2S absorption or hydrocarbon flashing. The additional H_2S absorption section and the flash vessels were estimated to increase the cost by ~30%. The ZnO chemical absorption system was estimated at about \$5 million, giving a total plant cost of about \$38 million.

Operating costs for this route are very high due to the large amounts of utilities consumed in the absorption and regeneration steps. In view of the large capital and operating costs, the economics of this route is very unfavorable.

4.2.6 Absorption (cold water)

A technique employed by industry for removing relatively small amounts of acid gases from gas streams such as natural gas is high-pressure absorption of the gas contaminants in water by countercurrent contact in packed towers.¹⁸ Application of this principle to the decontamination of the effluent streams requires the absorption of nearly all the CO_2 , H_2S , C_2H_4 , and C_2H_6 . However, the solubilities of the gases are quite low even at high pressures. These low solubilities, coupled with the very large amount of CO_2 , present two disadvantages for this method of effluent decontamination: (1) the need for very large and expensive equipment, and (2) high electric power costs for recirculating the water.

The advantages of the water absorption system over other aqueous systems for flue-gas decontamination are: a simple plant design, very inexpensive absorbent, and no heat exchanger requirements.

Two pressure reduction flash stages are used to lower the hydrocarbon concentration (C_2H_4 and C_2H_6) of the CO_2 -rich water solution from the absorption tower. The flashed hydrocarbons, along with a portion of the CO_2 , are recompressed and recycled to the absorber inlet.

Approximately 20% of the gas stream is recycled to reduce the nonmethane hydrocarbon content of the CO₂ effluent gas stream to <100 ppm (maximum EPA limits). Power recovery turbines are used at each of the pressure reduction flash stages to recover part of the power that is required for pumping the absorber water. It is estimated that 45 to 50% of the pumping power may be recovered.

The CO₂-rich water stream is stripped of CO₂ and H₂S by flashing to atmospheric pressure. The desorption is supplemented by air stripping to adequately lower the gas concentration of the water before it is recycled. Another disadvantage of the water absorption system is that the CO₂ effluent stream from the stripping tower contains H₂S and will require desulfurization or conversion to SO₂.

Due to their low solubilities, only traces of COS, CO, H₂, and CH₄ are absorbed by the water. These gases combined with the nonmethane hydrocarbon gases from the flash stages and some CO₂ leave the top of the absorption tower and are recycled to the Rectisol system or used as fuel. Based on the higher heats of combustion for the gas components of recycle stream, the heating value is ~3700 Btu/lb.

Corrosion may be a problem due to the high concentration of CO₂ in water. Assessment in terms of corrosion rate must be determined. However, corrosion inhibitors can be effectively used along with stainless steel in potentially susceptible areas, and interior coatings can be employed for the contact towers.

Capital costs for the water absorption process were developed from the major equipment items based on in-house cost data. The estimated overall cost was \$66 million.

4.2.7 Removal of CO by cuprous ammonium carbonate solution

The absorption of CO by cuprous ammonium solutions¹⁹ has been extensively used in the purification of ammonium synthesis gas. The absorption process is capable of lowering the CO content of the synthesis gas to <10 ppm when carried out at high pressure in a countercurrent contactor. This process would be employed in addition to another effluent purification process which does not remove CO, such as a molecular sieve system.

The generally accepted absorption reaction for the cuprous ammonium salt solution is shown below:

The carbonate system was selected over the formate or acetate solution for this preliminary evaluation because the operating costs are less and the effluent stream to be treated has a high CO_2 content. Operating data for carbonate systems indicate that a satisfactory $(\text{CO}_3)^{2-}$ equilibrium can be maintained by the absorption of CO_2 from the gas being treated and the evolution of an equal quantity during regeneration.

A simplified flow diagram for the absorption of CO from the effluent gas stream 11 is presented in Fig. 4.6. The system encompasses the CO absorber, regenerator, NH_3 recovery unit, residual CO oxidizer, and regenerated absorption solution cooler.

The feed gas to the absorber must be sulfur-free because sulfur compounds (H_2S , COS, etc.) are deleterious to the ionic equilibrium of the system. The copper sulfide precipitate that would form in the presence of sulfur would eventually plug the absorber unit. In evaluating this process for treatment of the effluent gas stream 11 it is assumed that: (1) the large amount of CO_2 will not upset the system equilibrium or prevent the absorption of CO, (2) the side reactions between CO_2 and the ammonium ions in the absorption solution forming ammonium bicarbonate and carbonate will not prevent regeneration of the absorption solution to the original ionic species, and (3) the absorption of CO_2 into the cuprous ammonium solution can be extrapolated from normal operating pressures of ~1700 psia to the desired pressure of 300 psia. These assumptions will have to be resolved before the process can be employed for removal of CO from the effluent stream.

The overhead vapor from the regenerator will contain 7 to 8% CO in CO_2 and can be recycled as additional raw gas feed to the shift conversion unit.

Carbon steel is generally considered satisfactory for cuprous ammonium salt solutions, but the presence of CO_2 will result in corrosion conditions in the vapor sections of the system. Stainless steel is recommended for the corrosive areas.

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STREAM (11) MUST BE FREE OF H_2S AND COS . THIS PROCESS WILL BE AN ALTERNATE ADD-ON TO ADSORPTION ON MOLECULAR SIEVES TO REMOVE THE CO
 APPROXIMATE COMPONENT FLOWS FOR CAPITAL COST ESTIMATION, LB-MOLES/HOUR:

COMPONENT	(11)	(12)	(13)
H_2O			
CO_2	31850	800	31050
H_2S	0	0	0
COS	0	0	0
CO	65	65	0
H_2	75		75
CH_4	189		189
C_2H_4	1.5		1.5
C_2H_6	1		1
10^3 scfm	202.7	5.4	197.3

Fig. 4.6. Cuproammonium complexing of CO .

The capital cost for the auxiliary process to remove CO from the partially decontaminated effluent stream was estimated at \$20 million. An additional \$5 million would be needed for a hot ZnO process to remove the traces of sulfur compounds from the feed gas stream, giving a total estimated capital cost of \$25 million. This estimate was determined from major equipment items and in-house cost data.

4.2.8 Adsorption

An unsuccessful search was made for an adsorbent capable of removing CO and nonmethane hydrocarbons from a CO₂-rich gas. Also, adsorbents with sufficient selectivity to separate CO₂, C₂H₄, and C₂H₆ do not appear to exist. The two best candidates are activated carbon and molecular sieves, which are about equally effective on a capacity basis. However, if the pore size of the sieve exactly matches the molecular size of the species being adsorbed, the adsorption capacity may be increased several fold.

In the application envisaged here, it was assumed that adsorption would be used to remove the nonmethane hydrocarbons and that a separate supplemental add-on process such as cuprous ammonium absorption would be used to remove the CO. However, the economics of this route is unfavorable, basically because the adsorption capacities for C₂H₄ and C₂H₆ are poor, even at temperatures as low as -50°F. Lower temperatures are not possible due to the liquefaction of CO₂. Operation at 100°F (to eliminate the cost of refrigeration) would require working pressures in the range of 1000 to 2000 psig in order to obtain working capacities equivalent to those at 100 psig and -50°F. A rough estimate based on activated carbon indicated a capacity of 0.3 lb of C₂H₆ per 100 lb of carbon.²⁰

To determine whether the development of improved adsorbents has any economic promise in this application, an adsorbent was hypothesized which has a capacity of 1.5 lb of C₂H₆ per 100 lb of adsorbent. A scheme using this material in a fixed-bed cyclic process at 100 psia and -50°F is shown in Fig. 4.7. The diagram does not show the very complex manifolding system that is required in actual operation. No attempt was made to include the unsteady-state heating and cooling effects which take place as the beds are cycled from adsorption to regeneration to cooling. Heat exchangers were sized on a steady-state basis.

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MANIFOLDS FOR SWITCHING BEDS ARE NOT SHOWN
 APPROXIMATE COMPONENT FLOWS FOR EQUIPMENT SIZING, LB-MOLES/HOUR:

COMPONENT	(3)	(7)	(10)	(11)	(12)
H ₂ O		800	800	0	0
CO ₂	15150	16700	31850	5000	26050
H ₂ S	0.5	2.5	3	0	3
COS	0.5	2.3	3	0	3
CO	30	35	65	65	0
H ₂	35	40	75	75	0
CH ₄	85	104	189	184	5
C ₂ H ₄	67	82	149	1.5	148.5
C ₂ H ₆	106	129	235	1.5	233.5
10 ³ scfm	97.5	112.7	210.2	33.6	171.6

Fig. 4.7. Absorption at low temperatures.

Based on a cost of \$50 million for major equipment items, which is probably a low estimate, and an energy cost roughly equal to the value of the impure synthesis gas recovered, \$8 million per year, even a very selective adsorbent process would be extremely expensive. An additional capital cost of \$20 million for an add-on system such as cuprous ammonium carbonate to remove CO from the vent-gas stream would have to be coupled to the above cost to complete the decontamination.

4.2.9 Cryogenic separation (liquefaction-distillation)

A simplified flowsheet of a proposed low-temperature liquefaction-distillation process is presented in Fig. 4.8 for separating and recovering the hydrocarbons and CO air pollutants present in the Lurgi process tail gas. In this scheme, the contaminated feed gas is compressed and cooled to liquefy nearly all the CO_2 , H_2S , C_2H_4 , C_2H_6 , and possibly some CH_4 . The liquid phase is separated from the noncondensables (H_2 , CO , and residual CH_4) and fractionated in the first distillation tower for separation of the CH_4 , C_2H_4 , and a small amount of CO_2 . In the second distillation tower, the underflow is enriched in C_2H_6 and contains the H_2S and COS, whereas the overhead distillate is essentially all CO_2 and will comply with EPA air quality standards when subsequently vented to the atmosphere.

The streams enriched in C_2H_4 and C_2H_6 from the distillation towers are combined with the noncondensable gases and recycled to the Rectisol unit.

In the C_2H_4 - CO_2 - C_2H_6 system, the vapor pressure of the CO_2 at the separation temperatures and pressures falls between that of the two organics; consequently, two distillation towers are required. In the absence of vapor-equilibrium data* for the multicomponent system, assumptions were necessary in order to define the preliminary engineering requirements. It was assumed that: (1) essentially complete separation

* Subsequent to the preparation of this manuscript papers on relative vapor equilibrium data were presented at the 70th Annual A.I.Ch.E. Meeting, Nov. 15, 1977. One paper reviewed a six-component simulated sour gas system at subambient temperatures.

APPROXIMATE COMPONENT FLOWS FOR EQUIPMENT SIZING, LB-MOLES/HOUR:

COMPONENT	(3)	(7)	(10)	(12)	(13)	(14)	(15)	(16)
H ₂ O		800		0	0	3	0	0
CO ₂	15150	16700	31850	1000	3000	24050	3000	7000
H ₂ S	0.5	2.5	3	0	0	0	3	3
COS	0.5	2.3	3	0	0	0	3	3
CO	30	35	65	30	35	0	0	65
H ₂	35	40	75	(50) ^a	(25)	0	0	75
CH ₄	85	104	189	(20)	(179)	0	0	189
C ₂ H ₄	67	82	149	0	147.5	1.5	0	147.5
C ₂ H ₆	106	129	235	0	0	1.5	233.5	233.5
10 ³ scfm	97.5	112.7	210.2	6.9	21.3	151.5	20.4	48.6

^aparenthesis indicate an unmeasured value.

Fig. 4.8. Carbon dioxide liquefaction - distillation process.

of C_2H_4 would be effected in the first tower, (2) the $C_2H_6^+$ concentration in the CO_2 overhead from the second tower would be within the maximum EPA limits, (3) only traces of H_2S and COS would be present in the overhead from the second tower, and (4) component separation factors were extrapolated from vapor-equilibrium data for binary systems.²¹⁻²³

Because of the lack of data, the sizing of the distillation columns is subject to considerable uncertainty. This uncertainty is magnified in the case of the $C_2H_6-CO_2$ column because of the unusually large heating and cooling requirements. The key economic factors for the cryogenic separation system are the large capital and operating costs of the distillation towers and the refrigeration plant.

The low processing temperatures and the nonaqueous solutions should minimize the corrosion problems. It was therefore assumed that carbon steel would be adequate as a material of construction. The temperatures are not sufficiently low to require the use of stainless steel except perhaps in areas of high vapor velocity.

The capital cost for the cryogenic separation process was estimated to be \$99 million. This estimate was developed from major equipment items and in-house costing data. A more detailed engineering evaluation of the process would undoubtedly reveal more efficient arrangements for heat exchange systems and possibly reduce the reflux ratio in the $C_2H_6-CO_2$ separation tower. However, it is clear that both the capital and operating costs of the system would still be very expensive.

4.2.10 Permeable membrane separation

Permeable membranes for separating the common gases are still in the early developmental stage. Packages of membranes having surface areas of <100 square feet have been tested; however, the scale of the system for the present application is ~8 million square feet.

Two types of membranes may be considered in this context. One is a 1- μ -thick silicone rubber polymer cast on a microporous backing. The other is a solution of activated potassium carbonate held within the pores of a membrane such as a 1-mil-thick polysulfone ultrafiltration type.^{9,10} These composites are supported on wire screens.

To obtain more economical diffusion rates, it would be desirable to use extremely thin membrane barriers (e.g., silicone rubber film of 0.1 μ or polysulfone film of 0.1 mil) on a porous support film. Techniques for preparing such films are still being sought.

A possible application of membrane separation is shown in Fig. 4.9. The flowsheet shows only the removal of CO and hydrocarbons from a CO₂-rich stream. The product streams from the membrane separation are a CO₂ stream containing very small amounts of hydrocarbons and CO (stream 13) and a smaller recycle CO₂-rich stream containing ~95% of the hydrocarbons and CO.

In the application considered in this report, separation of H₂S and CO₂ is also required, since the feed streams are contaminated with H₂S. Any H₂S in the feed will be found in stream 13. Membrane separation of the H₂S and CO₂ will require a relatively small amount of membrane surface area per stage but a large number of stages. Because of its complexity, this separation is not shown in Fig. 4.9. However, its cost was included in the overall cost estimate for this option.

Based on a future large-scale, well-developed industry, projected membrane costs were estimated at \$5/ft².^{9,10} The overall process cost on this basis was \$75 million.

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COMPONENT	⑪	⑫	⑬
CO ₂ MOLES/HOUR	31850	2000	29050
H ₂ S	0	0	0
CO ₂	0	0	0
CO	65	60	5
H ₂	75	71	4
CH ₄	189	179	10
C ₂ H ₄	1.5	0	1.5
C ₂ H ₆	1	0	1
10 ³ scfm	202.7	14.6	188.2

Fig. 4.9. Permselective membrane removal of CO.

5. APPENDIX

Basic EPA philosophy requires the maximum economically achievable desulfurization of the boiler flue gas. Sulfur dioxide removal efficiencies for boilers burning 2 to 5% sulfur coal are between 85 and 95% for lime scrubbers.²⁴ Assuming that 95% removal can be guaranteed, the Best Available Technology Economically Achievable standard for SO₂ emissions would be ~250 ppmv. Based on the results of wet scrubbing with fly ash,²⁵ lime scrubbing of the flue gas from a boiler burning 0.8% sulfur coal may be able to reduce the SO₂ to <100 ppmv (i.e., + 90% efficiency).

The sulfur concentration of the Lurgi SNG plant tail gases after reaction with the air necessary to convert the hydrocarbons to CO₂ and the sulfur compounds to SO₂ is on the order of 150 ppmv of SO_x. If these tail gases are introduced into a boiler employing 2 to 5% sulfur coal, an increase in total sulfur emissions from the overall plant to the atmosphere will result. The gases will leave at 250 ppmv of SO₂ rather than 150 if burned with a clean fuel.

In the case of the low-sulfur coal-fired boiler, a net reduction of SO₂ emissions to the atmosphere is possible since all gases would leave at <100 ppmv of SO₂. The major uncertainty is whether lime scrubbing would be considered to have a proven ability for continuous operation at <150 ppmv of SO₂ in the gaseous effluent.

In line with the basic EPA philosophy, incineration, which is independent of the boiler system, must employ sulfur-free fuel.

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