COO-0059-T1
Distribution Category UC-90c

PRE-METHANATION PURIFICATION STUDY: REMOVAL OF LOW CONCENTRATION GASEOUS SULFUR COMPOUNDS (CATALYST POISONS)

FINAL REPORT
FOR THE PERIOD
JULY 1975 - JULY 1977

Edward P. Iaccarino
Martin Lieberman
William F. Taylor

Exxon Research and Engineering Company
Government Research Laboratories
P.O. Box 8
Linden, New Jersey 07036

February 1978

Prepared for the
U.S. Department of Energy
Pittsburgh Energy Technology Center
Under Contract EY-76-C-02-0059

DISCLAIMER

PREFACE

The period of performance of this Contract was 24 months, spanning July 1975 to July 1977. Due to the untimely death of the Principal Investigator, Dr. Edward P. Iaccarino, the final report was unable to be completed until February 1978.

During the course of the implementation of this program, several people made important contributions. The authors wish to acknowledge these contributions as follows: Dr. John W. Harrison, who provided overall management of the program; Dr. Henry Shaw, who initiated the program and participated in the design of the experimental unit; Dr. Gideon M. Varga, who helped in the calibration of analytical equipment and shakedown of the experimental test facility; Mr. Charles D. Kalfadelis, who conducted design calculations and cost estimates; Dr. Ross Madon, who provided valuable consultation on the project; Mr. Eric Vath, who participated in the design and construction of the experimental unit; Dr. Nicholas Kafes, who conducted a theoretical analysis of the Adsorption of Sulfur Compounds from Synthesis Gas under NSF Faculty Research Participation Project Grant No. SER 76-04548; Mr. Jack Fowlks and Mr. William Davis, who were the laboratory technicians for most of the experimentation.

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1. INTRODUCTION

Catalytic methanation is a key process which is becoming increasingly important to our energy plans in the future. In view of the current and projected natural gas requirements, the development of viable large scale methanation systems is of the utmost importance for our future energy plans. However, before catalytic methanation can be used for the commercial production of synthetic natural gas from synthesis gas, the problem of catalyst deactivation must be solved.

Nickel is a superior methanation catalyst. The metal is relatively cheap; it is very active when present in a form having high surface area, and it is the most selective to methane of all materials. Its main drawback is that it is easily poisoned by sulfur compounds, a fault common to all of the more active methanation catalysts (11,12,16).

This deactivation could result in prohibitive operating costs for catalyst replacement (or regeneration) and could make the process economically impractical (20). One approach to this problem is to develop a methanation pre-treatment process which would effectively remove those trace sulfur impurities responsible for the loss in methanation catalytic activity, to very low levels, e.g., less than 0.1 parts per million (PPM) by volume of total sulfur.

In the 72TPD SYNTHANE coal gasification pilot plant located at Bruceton, Pa., two methanation schemes, Hot Gas Recycle (HGR) and Tube Wall Reactor (TWR) are included (10,13). Since most of the experimental process development unit runs with the HGR and TWR reactors produced an effluent gas with a carbon monoxide content above 0.1%, it was recommended that a final "cleanup" methanation reactor be added. The final cleanup methanator for the SYNTHANE plant consists of a small bed of conventional methanation catalyst. It is general practice for bulk H_2S removal from synthesis gas to use a regenerative liquid absorption process. The purification system chosen for bulk removal of the acid gases (CO_2 and H_2S) in the SYNTHANE plant is the Benfield Hot Potassium Carbonate Process. Sulfur compounds expected in the effluent from a Benfield Hot Potassium Carbonate Process empoloyed to test a coal gasification gas stream include H_2S, COS, CS_2, mercaptans and thiophenes. The final sulfur removal scheme for the 72TPD SYNTHANE plant was designed to be two fixed beds of activated carbon that can be regenerated. The fixed bed activated carbon system was designed to operate at 95°F and 1000 psig for the adsorption step.

Exxon Research and Engineering Company, under Contract No. E(36-2)-0059 from the United States Department of Energy (previously Energy Research and Development Administration), has carried out a program to investigate trace sulfur compound removal from synthesis gas prior to methanation. The study was aimed at obtaining experimental data that applies to the SYNTHANE gasification process being developed by the Department of Energy. The program included a literature survey, testing unit construction and operation, data and feasibility analysis, and an engineering and economic analysis of the system chosen. In addition, a theoretical analysis was made of the adsorption of sulfur compounds from synthesis gas under an NSF Faculty Research Participation Project.

The program began as a broad paper study to evaluate candidate trace sulfur removal systems and evolved to a detailed experimental evaluation of a metal impregnated carbon using single and multicomponent blends of the trace sulfur compounds of interest. Several candidate systems were systematically reviewed and eliminated from consideration.

This final report summarizes the work conducted on this contract. The remainder of the report is structured as follows -

Section 2 presents a state-of-the-art review of candidate sulfur guard systems.

Section 3 describes the experimental equipment used in the study.

Section 4 presents the experimental results achieved with the selected sulfur guard system and a discussion of these results.

Section 5 presents a summary of the economic and environmental aspects of the evaluated sulfur guard system.

Section 6 gives the major conclusions of the study.

2. STATE-OF-THE-ART ASSESSMENT

A review of the sulfur removal processes was made with respect to their potential as sulfur guard (trace sulfur removal) systems following a Benfield unit.

Several of these have been classified as unlikely candidates for various reasons. Included in these are dimethyl ether of polyethylene glycol (Selexol), amine solutions, and Stretford type solutions, which all represent alternatives or adjuncts to a Benfield hot carbonate acid-gas removal system. Their applicability is best suited to "bulk" sulfur (plus CO_2) removal with typical product sulfur levels at least one or two orders of magnitude higher than the stringent 0.1 ppm total sulfur required of sulfur guard. Cold methanol (Rectisol) is also an unlikely candidate for a sulfur guard system, per se, since it probably represents a viable solution to the total sulfur removal (acid-gas plus sulfur guard) problem if economics can be justified. Other approaches classified as unlikely are caustic (NaOH) solutions and dolomite or limestone because of the huge loss in capacity for sulfur due to the presence of large quantities of CO_2 relative to sulfur componnds (>100/1) in the entering feed. In addition, thiophene probably would not be removed.

As a result of these considerations, all types of sulfur compound removal processes were reviewed with concentration on the more promising solid adsorbents, with some attention being paid to catalytic conversion systems utilizing the hydrogen in the synthesis gas. The potential of absorption processes, solid adsorbents and catalytic conversion for providing the desired characteristics for the sulfur guard system including discussions held with material suppliers is described in the following paragraphs.

2.1 Absorption Processes

Several absorption processes for removing sulfur compound impurities were reviewed and evaluated for their potential for application in the SYNTHANE coal gasification process. These include -

- Amine Scrubbing
- Benfield Hot Potassium Carbonate Process
- The Linde-Lurgi Rectisol Process
- The IFP Sulfur Removal Process
- Holmes-Stretford Process
- Claus Process
- Selexol Process

As indicated above, with the exception of the Rectisol Process, these processes require an additional trace sulfur componnd removal system to reduce the sulfur compound concentration to the levels required in the present application, i.e. 0.1 parts per million (ppm) by volume of total sulfur.

2.1.1 Amine Scrubbing

A number of processes are available for licensing that use amine scrubbing to sweeten sour gas (5, 18). Basically, acid gases are absorbed in a basic amine solution and the solution is then regenerated to give a gas rich in H_2S and CO_2.

Figure 2.1 is a schematic flow diagram of an amine scrubbing process. Sour gas feed with the composition indicated on the figure, is contacted in a scrubber tower with lean monoethanolamine (MEA) solution. The hydrogen sulfide and carbon dioxide are reduced to 20-200 ppm.

The MEA solution containing the acid gas passes to a hydrocarbon disengaging drum where traces of heavier hydrocarbons are removed to be flared. (These traces of hydrocarbons contain negligible amounts of sulfur.) Lighter hydrocarbons, disengaged from the drum, are sent to a low pressure scrubbing system to remove any traces of sulfur compounds and are then used as fuel.

The H_2S laden MEA solution then passes to a regenerator tower where the acid gases are removed and passed to sulfur recovery. The lean MEA solution may contain sludge which is removed in the amine reclaimer. This sludge contains polluting materials and must be further treated.

2.1.2 Benfield Hot Potassium Carbonate Process

The Benfield Promoted Hot Carbonate absorption process uses two independent but compatible circulating solutions in series to achieve a high purity gaseous effluent combined with high efficiency. As a result of the Benfield Process simplicity and low energy requirements, it received special consideration while evaluating the different processes for pre-methanation purification systems.

This process for acid gas removal involves the contacting of a sour gas stream with a solution K_2CO_3. In addition to H_2S and CO_2, the product of most coal gasification processes will also contain organic sulfur compounds.

Typical trace sulfur components in coal derived gas are as follows (8):

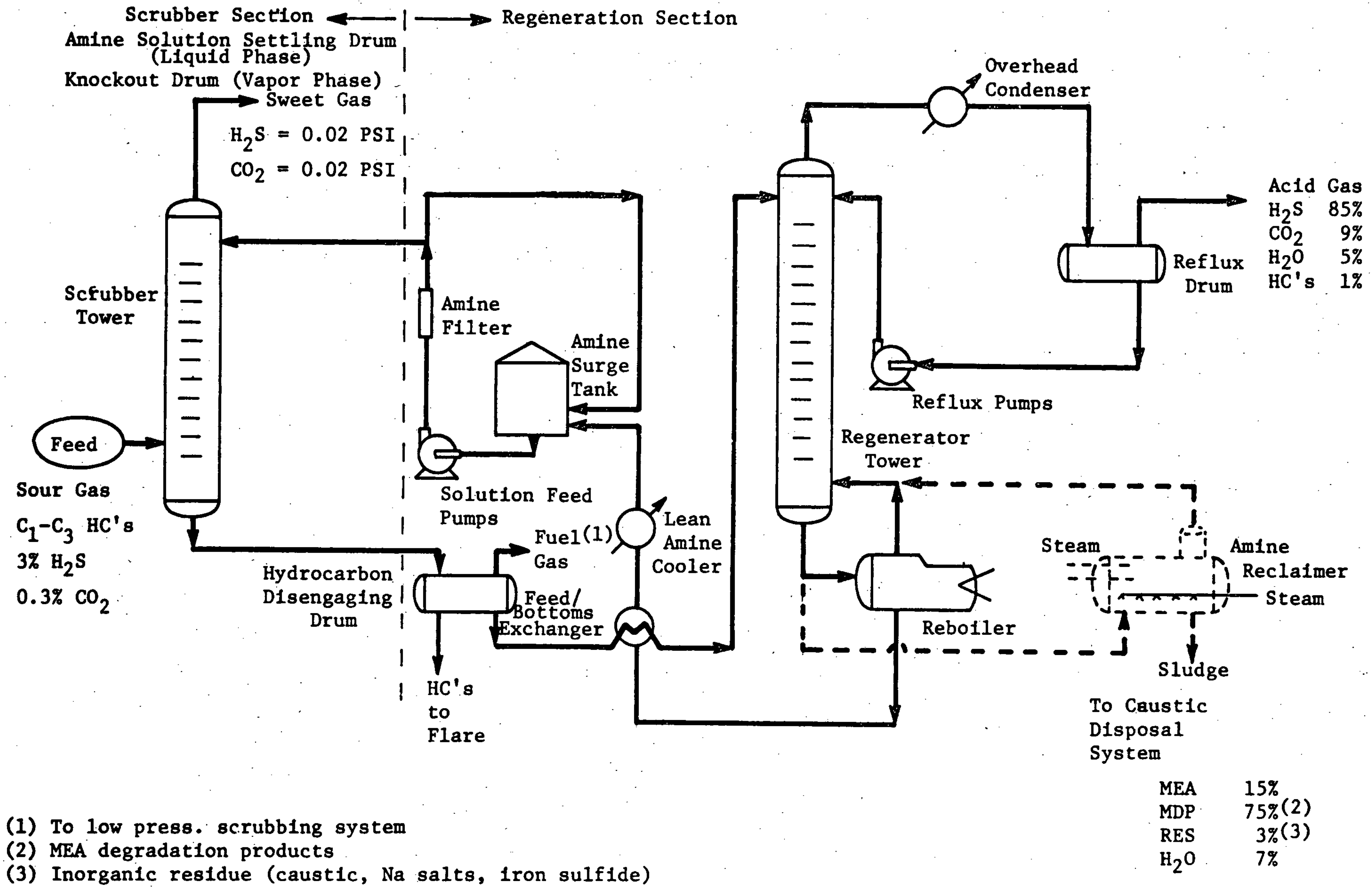
COS	2 to 300 ppm (v/v)
CS_2	0 to 10 ppm (v/v)
Thiophenes	0 to 60 ppm (v/v)
Mercaptans	0 to 60 ppm (v/v)

Analysis of sulfur trace compounds after contacting a bulk removal Hot Potassium carbonate system gave the following approximate removal (2):

Component	Percent Removal
Mercaptans	Over 90%
Carbon Disulfide	75%
Carbonyl Sulfide	75%

FIGURE 2.1

AMINE SCRUBBING



(1) To low press. scrubbing system
(2) MEA degradation products
(3) Inorganic residue (caustic, Na salts, iron sulfide)

Thiophene (C_4H_4S) would not be expected to react chemically with alkaline activated potassium carbonate solution. This expectation has been confirmed in the Benfield Laboratory. However, thiophene removal of about 85% has been reported in a commercial Benfield unit (2,17).

A simplified flow diagram in Figure 2.2 illustrates the carbonate process. The sour gas at elevated pressure (1000-2000 psi) is contacted with recycle, lean K_2CO_3 solution where sulfur compounds are removed to as low as 20 ppm. The pressure on the rich solution is reduced and the acid gases are removed in a regenerator column. The lean K_2CO_3 solution is recycled to the absorber.

The sweet gas (20-100 ppm of sulfur compounds) may be further purified by reaction with Fe_2O_3 or ZnO or by adsorption on activated charcoal or molecular sieves. These trace sulfur compound removal processes are discussed in Section 2.2.

No significant effluent of liquid is purged. Except for small amounts of additives, the solutes are only K_2CO_3 and $KHCO_3$. Heat in the feed gas can be used to supply all or part of the unit's low heat requirements. Unless the CO_2 content is low, it is necessary to treat the acid gas product by means other than a Claus plant.

2.1.3 The Linde-Lurgi Rectisol Process

The Rectisol process, patented and commercialized jointly by Linde and Lurgi, is a technique for removing H_2S, COS and CO_2 from sour gas in such a way that the sulfur containing gases are concentrated sufficiently that they may be processed in a conventional Claus plant. Basically, the Rectisol process involves physical absorption of the acid gases in low temperature methanol and subsequent regeneration of the methanol (24).

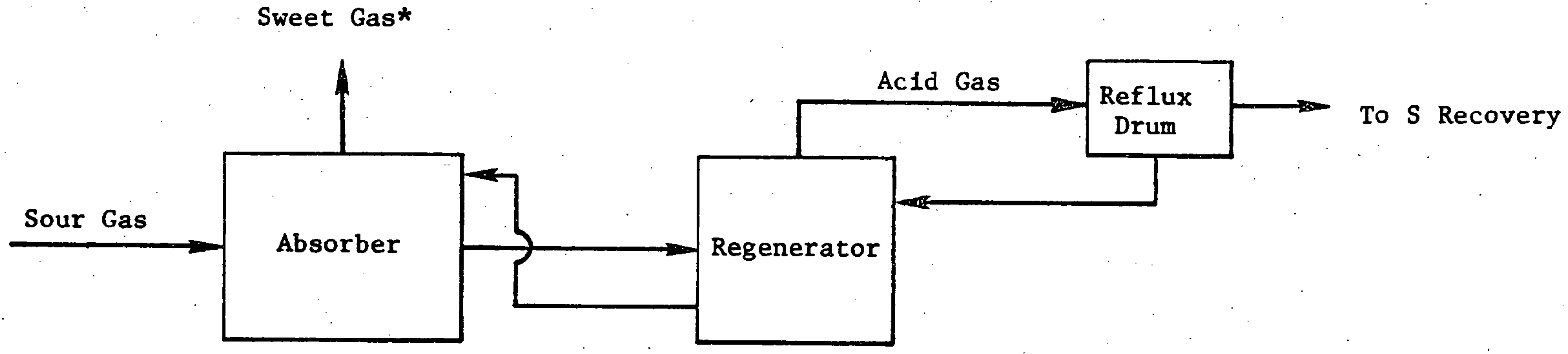
Figure 2.3 shows a two stage Rectisol purification process that produces a high purity synthetic gas and a by-product stream rich in H_2S. The important streams are identified in Table 2.1.

The sour gas enters the first absorber at 441 psia and contacts a stream of low-temperature methanol that has absorbed the equilibrium concentration of carbon dioxide. No CO_2 is removed in this tower and no heat load is imposed. The H_2S in the sweet gas is so low that the gas may be passed to a CO shift converter that utilizes a sulfur-sensitive, low-temperature shift catalyst. After further compression to 725 psia and heat exchange, the gas passes to a second tower where most of the carbon dioxide is removed. The final traces of methanol and CO_2 are removed in an absorber before passing to the nitrogen wash. The carbon dioxide in the methanol from the CO_2 absorber is removed by nitrogen stripping to the point where the methanol-CO_2 solution is in equilibrium with CO_2 in the feed gas. The CO_2 and tail gas contain less than 5 ppm of H_2S.

The methanol from the H_2S absorber still contains too much CO_2 to allow direct use of the gas in a Claus plant. The solution is enriched in H_2S by nitrogen stripping of part of the CO_2. The H_2S plus some of

FIGURE 2.2

BENFIELD HOT K_2CO_3 PROCESS



*The last traces of acid gases may be removed by passing the gas through Fe_2O_3, activated charcoal, molecular sieve or ZnO.

FIGURE 2.3

2 STAGE RECTISOL WASH FOR H_2S AND CO_2-REMOVAL

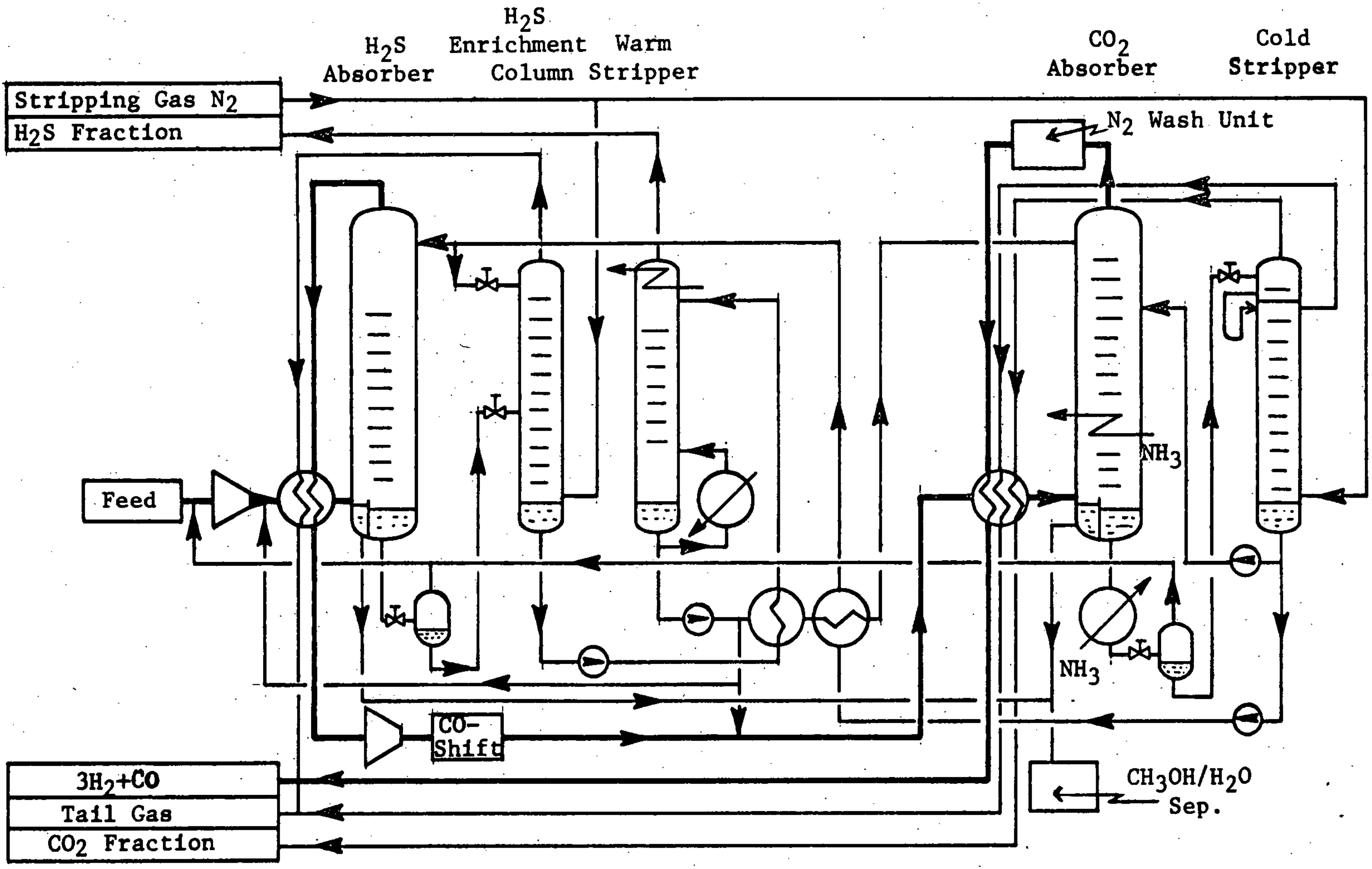


TABLE 2.1

STREAM IDENTIFICATION IN RECTISOL PROCESS (24)

Gas Constituent		Feed Gas to Rectisol I mol %	Feed Gas To Shift mol %	Feed Gas to Rectisol II mol %	Feed Gas to N_2 Wash mol %	CO_2 Fraction mol %	Tail Gas mol %	H_2S Fraction mol %	Stripping Gas
H_2		29.32	30.34	54.21	93.15	0.20	0.44	—	
N_2+A		1.52	1.57	1.03	1.78	--	12.10	2.55	100
CO		56.62	56.61	2.95	4.97	0.12	0.43	--	
CH_4		0.10	0.10	0.07	0.10	--	0.01	--	
CO_2		11.85	11.38	41.74	max 50 ppm	99.68	87.02	71.95	
H_2S		0.59	--	--	--	max 5 ppm	max 5 ppm	25.50	
		100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Total flow	Nm^3/h	105,000	104,818	159,457	91,423	12,060	61,224	2,432	7,500
	lb mol/h	10,324	10,307	15,679	89,895	1,186	6,020	239	737.5
Pressure	atm	31	30	51	49	1.1	1.0	1.5	2.7
	psia	441	427	725	697	15.6	14.2	21.3	38.5

the CO_2 is removed by methanol vapor in a warm stripper. The concentration of H_2S (ca. 25%) is suffieient for sulfur recovery by conventional means.

2.1.4 IFP's Sulfur Removal Process

Gases exiting from a Claus plant still contain considerable sulfur as H_2S, SO_2, COS, CS_2. To meet environmental standards this gas may have to be treated further to lower the sulfur content. A process developed by the Institut Francais du Petrole (IFP) is designed to accomplish this. Basically, the IFP process continues the reaction of H_2S and SO_2 in the liquid phase with a proprietary catalyst in a proprietary solvent.

As indicated in Figure 2.4, the IFP process is very simple and involves only a few pieces of equipment. Claus unit effluent gas at approximately 260°F is injected into the lower part of the packed column. The tower is designed for low pressure drop. Pressure drop across the system is less than 1 psi. Depending on capacity, one or more packed beds with redistribution are used. Sulfur accumulates in a sump at the bottom of the tower and is continuously drawn off under interface control.

The catalyst solvent is continuously circulated from bottom to top of the tower to maximize gas/liquid contact by counter-current flow. Liquid temperature is maintained at 260-280°F, the heat of reaction being removed by vaporization of condensate injected into the solvent pump-around loop just before entering the top of the column. Circulation is governed by level of the solvent/gas interface at the lower bottom.

No solvent degradation has been found to occur. Although vapor pressure is low at reactor temperatures, some solvent is lost in the overhead and is made up through replacement from a storage tank heated with a steam coil.

Conversions ($H_2S + SO_2$ to S) to be expected in the IFP process will depend on the total $H_2S + SO_2$ concentration in the Claus tail gas as shown (26):

Volume % of $H_2S + SO_2$	% Conversion
0.4 - 0.8	80
0.8 - 1.5	90
1.5	95

Typical operating parameters are shown in Table 2.2.

From an operating point of view, only the ratio of H_2S to SO_2 affects conversion rates. The ratio should be held between 1.9 and 2.1 if conversion is to be maximum. In modern refinery practice, this should present no difficulties, for while feeds to the Claus unit will be subject to wide variations in flow and composition, the use of in-line gas chromatographic and UV spectrophotometric monitors permits automatic regulation of the H_2S/SO_2 ratio in the Claus effluent to ± 5%.

Controlling the ratio in this way not only provides conditions for maximum sulfur recovery in the IFP unit, but maintains recovery in the Claus unit at the highest level also.

FIGURE 2.4

CLAUS UNIT TAIL GAS CLEANING WITH THE IFP PROCESS

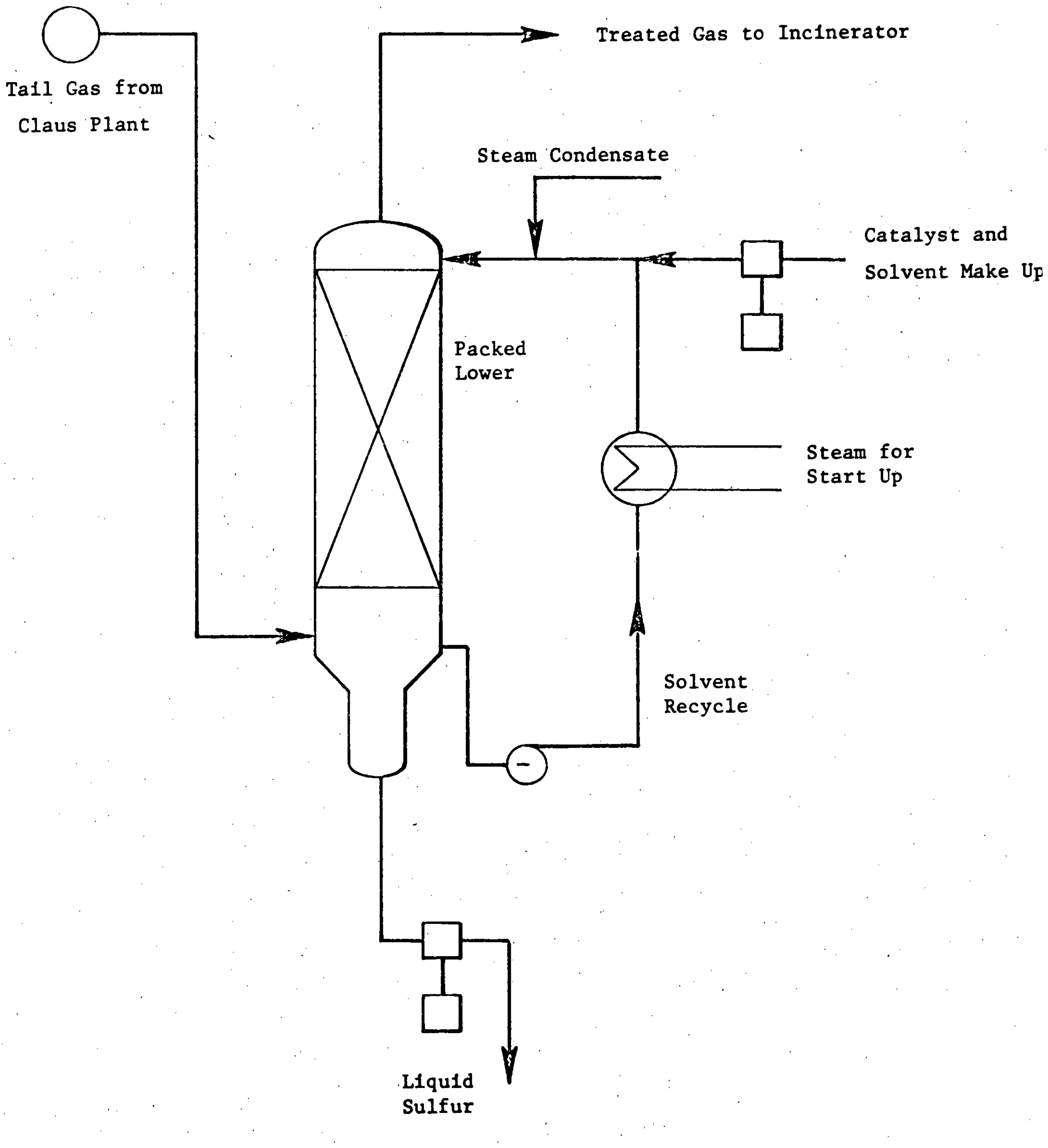


TABLE 2.2

OPERATING PARAMETERS OF IFP PROCESS (26)

			Treating the Tail Gas from a 3 Stage Claus Plant
Tail Gas	Composition Mol.%	H_2S	0.44
		SO_2	0.22
		S	0.37
		H_2O	37.67
		N_2, CO_2, Misc.	61.30
	Conditions	- Temperature °F	260
		- Pressure psig	0.5
	Flow Rate	lb/mol/hr	2367.06
Sulfur Recovery	(on $H_2S + SO_2$ reaction) %		82
		Production lb/hr	420
Treated Gas	to incinerator ppm of $H_2S + SO_2$		1200

The only other variable which can adversely affect sulfur recovery is the concentration of COS and CS_2 in the feed to the IFP unit. While appreciable amounts of these substances are formed in the Claus burner, the first Claus catalytic reactor can reduce the levels well below the 1000-1500 ppm normally encountered in refinery streams. The level will remain essentially constant through the second and third stages, and is unchanged in the IFP unit since the IFP process does not touch COS and CS_2.

To keep COS and CS_2 concentrations at a minimum, it is advisable to run the first Claus converter hotter than usual, and to replace the bauxite with a more sophisticated catalyst. The slightly lower conversion due to running this stage hotter will be compensated for by the higher overall sulfur recovery in the IFP unit.

The sulfur level in the tail gas can be reduced to 200 ppm at considerably greater expense. The more elaborate schemes involve incinerating the Claus tail gas, scrubbing with an ammonia solution and reduction of sulfate ion to SO_2. The SO_2 is mixed with a gas containing H_2S and reacted in the IFP process as described above. Ammonia is recycled. The final gas to the incinerator then contains a maximum of 200 ppm of sulfur and 50 ppm of NH_3.

If the H_2S/SO_2 ratio is held within the range 1.9-2.1, and if the first Claus reactor is run to keep down COS and CS_2, the overall sulfur recovery for the combined Claus/IFP system can be in excess of 99.2%, equivalent to stack SO_2 emissions of about 1500 ppm. The only source of pollution is the stack gas.

2.1.5 Holmes-Stretford Process

The Holmes-Stretford Process is a method of removing hydrogen sulfide from gases and converting them directly to elemental sulfur. This highly developed chemical process is a key to economical desulfurization of gas streams from coke ovens, SNG plants, refineries and new coal gasification processes. Figure 2.5 gives a flow diagram for this process.

The gas to be purified is countercurrently scrubbed in a scrubber with an alkaline solution containing a vanadium salt along with anthraquinone disulfonic acid (ADA). The hydrogen sulfide is just dissolved in the circulating liquor and then oxidized to free sulfur by reducing the vanadium from its pentavalent form to its quadrivalent state.

$$2H_2S + 2Na_2CO_3 \longrightarrow 2NaHS + 2NaHCO_3$$

$$2NaHS + 4NaVO_3 + H_2O \longrightarrow Na_2V_4O_9 + 4NaOH + 2S$$

The H_2S is converted to elemental sulfur by the vanadic salt which itself is reduced to the vanadium form, from pentavalent to quadrivalent. To make the cycle reversible, anthraquinonic disulfonic acid is employed as an oxidant to restore the quadrivalent vanadium back to the pentavalent state. During this reaction, the ADA is reduced to semiquinone.

$$Na_2V_4O_9 + 2NaOH + H_2O + 2ADA \longrightarrow 4NaVO_3 + 2ADA \text{ (reduced form)}$$

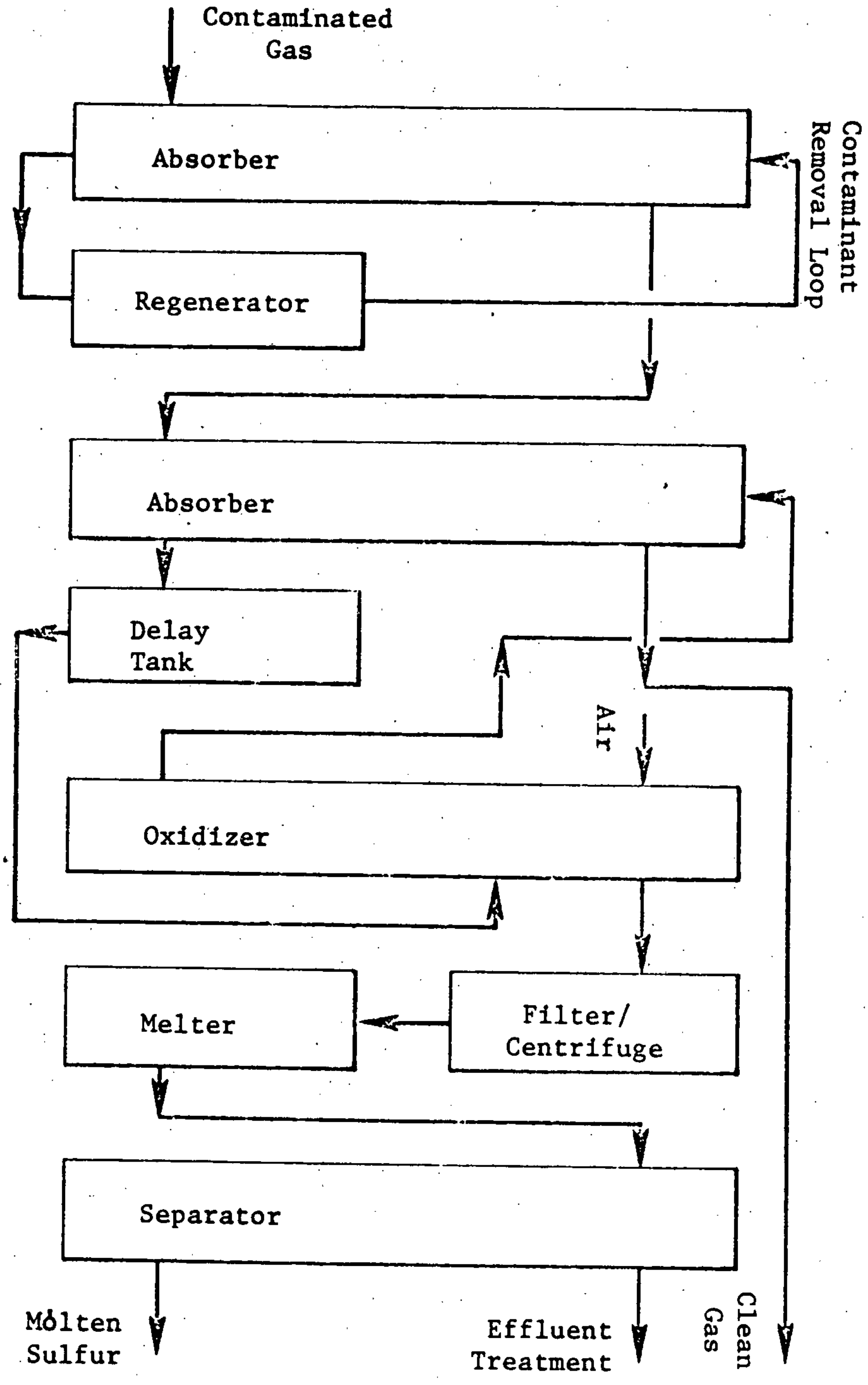


FIGURE 2.5

HOLMES-STRETFORD PROCESS

The ADA is subsequently reoxidized with air in separate oxidizer vessels back to the original ADA configuration.

$$2\text{ADA (reduced form)} + O_2 \longrightarrow 2\text{ADA} + 2H_2O$$

Due to the formation of by-product salts such as sodium sulfate and sodium thiocyanite, it is necessary to purge liquor from the process system. The Holmes Stretford Process includes a new technique for the treatment of this liquor resulting in zero effluent discharge. Purity of the sulfur will be of the order of 99.5% depending on the contaminants of the feed gas. Potential contaminants include unsaturated hydrocarbons, tar fog, free carbon and oil mist.

The effluent stream from the Stretford process containing sodium thiosulfate and sodium thiocyanate (in some cases) must be treated prior to discharge. Holmes has developed and piloted four alternate methods to handle effluents from this process:

- Evaporation or spray drying
- Biological degradation
- Oxidative combustion
- Reductive incineration

The reductive incineration process results in a zero effluent discharge because all the products from this step are recycled.

The Holmes-Stretford Process is capable of handling gas flow rates of 0.1 to 190 million SCFD, the inlet concentrations of H_2S in the coal gas is reduced from 0.03 to 95% V/V in the inlet gas stream to 1.0 to 500 ppm V/V in the outlet gas stream.

2.1.6 Claus Process

Recovery of sulfur from hydrogen sulfide streams is usually effected by the Claus process. The process involves burning a portion of the hydrogen sulfide to produce a gas stream with an H_2S/SO_2 ratio of 2. The hydrogen sulfide and sulfur dioxide are then converted to elemental sulfur in one or more reactors containing activated alumina or bauxite as catalyst. The reactions involved are:

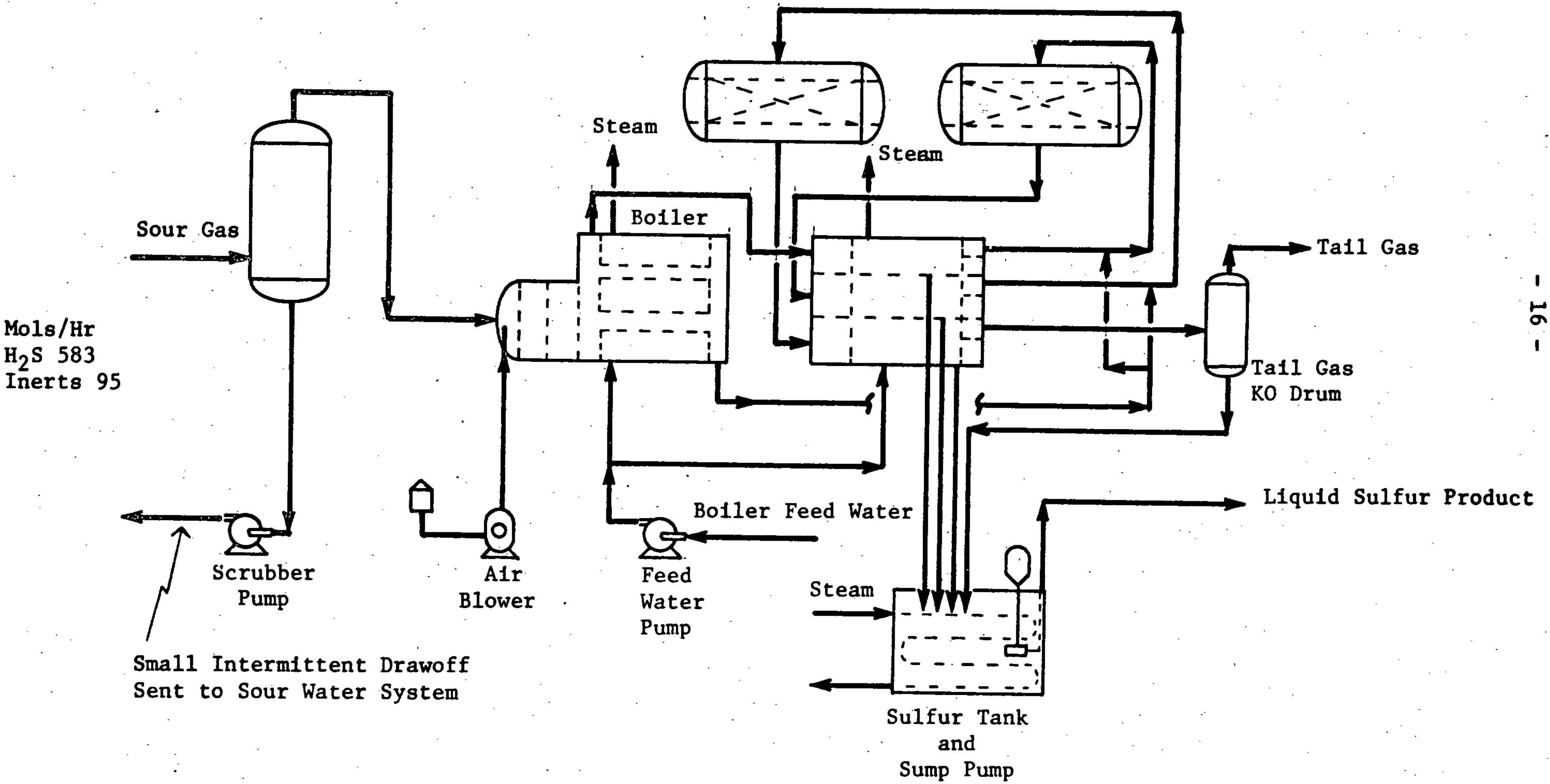
$$(1)\quad 2H_2S + O_2 \longrightarrow 2S + 2H_2O$$
$$(2)\quad 2H_2S + 3O_2 \longrightarrow 2SO_2 + 2H_2O$$
$$(3)\quad 2H_2S + SO_2 \longrightarrow 3S + 2H_2O$$

Claus plants can be operated in a number of configurations. A typical configuration is presented in Figure 2.6.

Figure 2.6 is an example of a Claus plant with two converters. Often three converters are used and, if the concentration of H_2S is 15-25 mole percent, only one-third of the acid gas passes through the burner in

FIGURE 2.6

TYPICAL CLAUS PLANT



order to maintain a flame. The H_2S rich gas is usually the product of an absorption process used to clean up a gas stream.

The feed gas passes through a knockout drum to remove sour water and then enters a furnace where it is mixed with sufficient air to burn any hydrocarbons plus one-third of the H_2S. The oxidation takes place at temperatures greater than 1800°F. Heat is recovered from the hot gas stream in a waste heat boiler. Part of the stream passes through a condenser where it is cooled to about 400°F by producing steam. Sulfur is thereby condensed and passed to a heated sulfur tank in the liquid state.

After the first condenser, the cooled gas is mixed with sufficient hot gas from the waste heat boiler to raise the temperature to that required for conversion (greater than 450°F). The gas then enters the primary converter where sulfur is produced by reaction 3. The sulfur produced in the first converter is condensed in a second condenser and the gas from this condenser is again re-heated by mixing with hot gas from the waste heat boiler. The heated gas passes through a second catalyst bed, a third condenser and to a knock-out drum where the last sulfur is removed.

The tail gas still contains appreciable quantities of sulfur (0.5% or more). A third converter will reduce the sulfur content but the effluent will still be too high in sulfur content to allow direct venting. In the past, the tail gas has been incinerated and vented through a stack.

2.1.7 Selexol Process

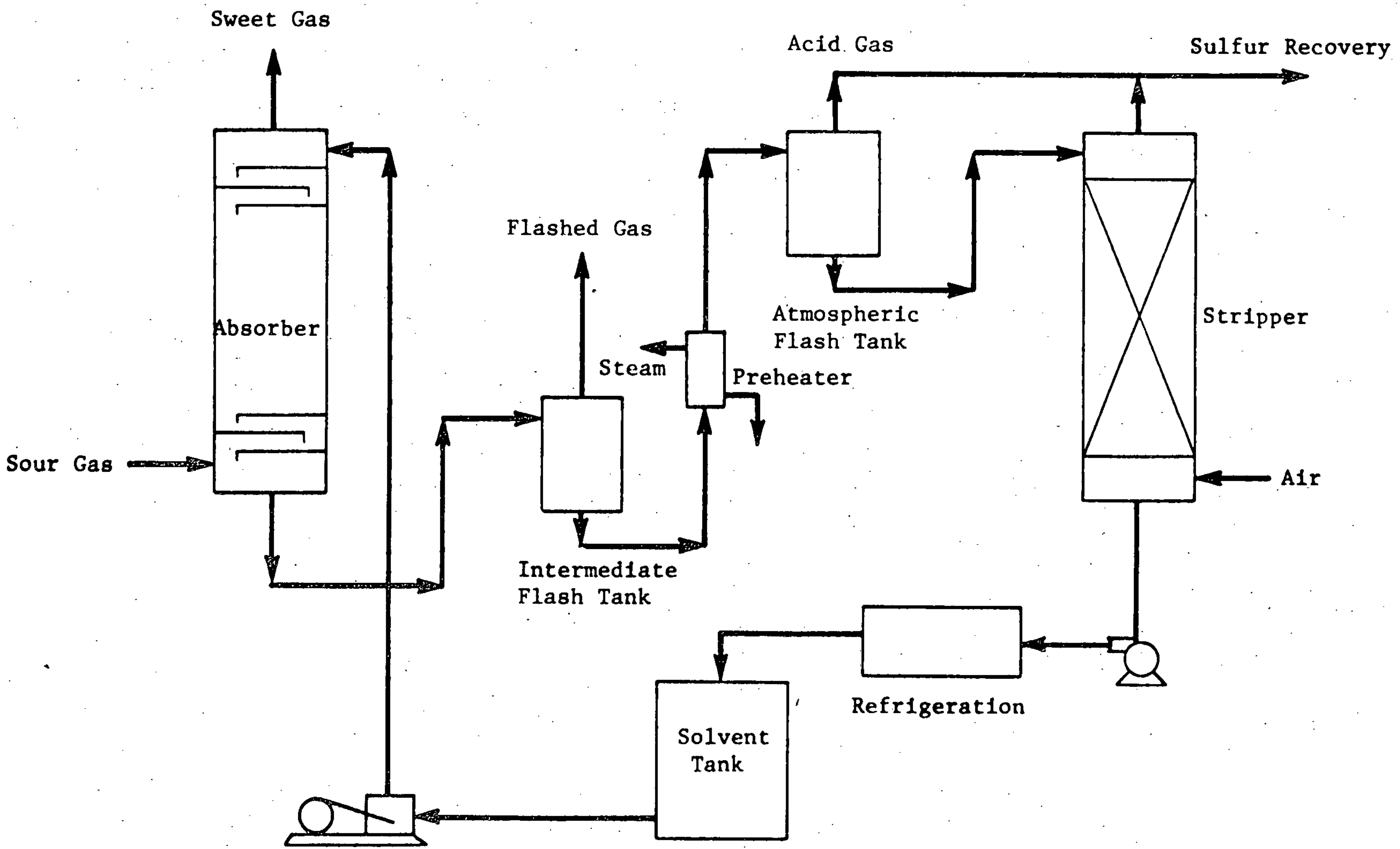
The Selexol Process, at first used to extract CO_2 from synthesis gas, has now been adapted to the treatment of natural gas. It offers a direct economical means for removal of acid gases to produce sweet dry gas. Process solvent consists of the dimethyl ether of polyethylene glycol (DMPEG). It displays high physical absorption capacity for the acid gases, including hydrogen sulfide, carbon dioxide, carbonyl sulfide and mercaptans (25).

"Sour" gas is admitted at the bottom of the absorber, Selexol's solvent is sprayed from the top of the absorber. The sour gas contacts the Selexol solvent countercurrently in the absorber. The Selexol's solvent absorbs the acid gases out of the sour gas. The sweet gases thus obtained exit from the top of the absorber. The acid gas rich solvent, at first, is flashed in an intermediate flash tank where some of the acid gases are flashed off. The intermediate Selexol solvent is preheated and then sent to an atmosphere flash tank where acid gases are further flashed. The hot solvent is sprayed from the top of a stripper. Air is blown in from the bottom of this stripper. This air strips all the sulfur constituents from the Selexol's solvent. The sulfur compounds along with acid gases are treated in a sulfur recovery unit. The lean Selexol's solvent is pumped out from the bottom of the stripper and cooled in a refrigeration unit and stored in the solvent storage tank for recirculation to the absorber.

Process performance is illustrated by data obtained from the (pilot-plant) unit shown in Figure 2.7 with 580 psig feed gas containing 25 vol. % H_2S and 10% CO_2, presented in the table below (25).

FIGURE 2.7

SELEXOL PLANT



Feed Gas (Vol. %)	
H_2S	25
CO_2	10
COS	0.110
CH_3SH	0.020
Pressure, psig	500

	Solvent Removal	Complete Removal
Solvent loading (scf acid gas/ gallon solvent)	10.40	4.50
Sweet gas (Vol. %)		
H_2S	0.0001	0.0001
COS + CH_3SH	0.00015	0.00015
CO_2	7.5	0.3
Acid gas (Vol. % hydrocarbon)	<2.0	<2.0

2.2 Trace Sulfur Compound Cleanup Processes

With the exception of the Rectisol process, none of the processes described in 2.1 can reduce sulfur compound levels to that required for protection of the methanation nickel catalyst in the SYNTHANE Process. Another (trace sulfur compound) removal system used in series with one of the above processes is required to obtain levels of the order of 0.1 ppmv sulfur impurities. Candidate processes that have the potential to accomplish this include -

- Dry Box Process
- Seaboard Process
- Caustic Soda Scrubbing
- Cyclic Use of Calcined Dolomite
- Molecular Sieves
- Catalytic Conversion
- Zinc Oxide
- Iron Oxide
- Activated Carbon
- Metal Impregnated Activated Carbon

Each of these processes/systems is briefly discussed below.

2.2.1 Dry Box Process

Of perhaps greatest economic importance is the "dry-box" process for removing hydrogen sulfide from coke-oven gases and other industrial gases. In this process, hydrated iron oxide is coated on shavings or other supporting material spread on trays in rectangular boxes. The gas, to which sufficient air has been added to provide an oxygen concentration of 0.6-1.0%, is passed over the iron oxide. The hydrogen sulfide reacts to form ferric sulfide, which, in turn, is reoxidized by the added oxygen to the original iron oxide and sulfur. After some use, it is necessary to remove the iron oxide and allow it to become thoroughly revivified in the air before returning it to the boxes for further use. The iron oxide is finally discarded when the total sulfur content reaches 50 to 60%. When used for final cleanup, the oxide may be discarded with a sulfur content as low as 30%. The advantages of the dry-box process are the completeness of removal of hydrogen sulfide and the simplicity of the process. The dry-box process is one of the most selective methods of removing hydrogen sulfide in the presence of carbon dioxide. A process related to the dry-box process has been used in several plants in Germany. In this process, gas to which the stoichiometric amount of oxygen and 330-500 ppm of ammonia have been added, is passed over activated carbon. The hydrogen sulfide is thereby converted into sulfur, which can then be recovered by extraction with ammonium sulfide solution. The hydrogen sulfide content of the treated gas is reduced to about 1 ppm.

2.2.2 The Seaboard Process

This process was developed by Koppers Company in 1920. Large volumes of air are employed to strip the hydrogen sulfide from the absorbent. The hydrogen sulfide is not usually recoverable from this process. The air used in the reactivation operation tends to oxidize some of the hydrogen sulfide to thiosulfate; hence, it is necessary to discard some of the absorbent periodically and add fresh solution to maintain the desired composition (3.0-3.5% Na_2CO_3). Somewhat related to the Seaboard process for recovering hydrogen sulfide as elementary sulfur are the ferrox process and the nickel process. In the ferrox process, a suspension of iron oxide is used as catalyst and in the nickel process, nickel sulfate is generally employed.

2.2.3 Gas Cleaning Using Caustic Soda Solution

Where complete removal of relatively small quantities of hydrogen sulfide is necessary, it is the practice to use sodium hydroxide solutions. This is normally a batch operation, the solution being replaced when most of the sodium hydroxide has been converted into sodium sulfide. Gas-liquid contacting devices employed to effect this reaction include packed towers, jet scrubbing devices, and simple bubbling of the gas through the solutions. In some cases the removal of hydrogen sulfide is carried out in two stages, the gas being first contacted with a solution of sodium sulfide, which is converted to the hydrosulfide, concentrated, and sold. The gas is then contacted with a solution of sodium hydroxide, which completely removes the remaining traces of hydrogen sulfide from the gas, the solution being converted to sodium sulfide, which is later converted to sodium hydrosulfide.

Calcium hydroxide is a less expensive base, but its insolubility and that of calcium sulfide cause processing difficulties. It is therefore less frquently used than sodium hydroxide.

Where hydrogen sulfide must be removed from acid gases such as carbon dioxide, alkaline absorbents cannot be used. In these cases, oxidizing agents such as potassium permanganate solution or a buffered solution of sodium dichromate and zinc sulfate are used.

2.2.4 Cyclic Use of Calcined Dolomite to Desulfurize Fuels Undergoing Gasification

Clean power systems are being developed in which coal or oil would be either gasified or pyrolyzed at high pressure in fuel treating processes. In such processes, sulfur in the fuel would be converted to H_2S, which would be captured by either fully calcined or half-calcined dolomite.

$$[CaO + MgO] + H_2S = CaS + MgO + H_2O \qquad (1)$$

$$[CaCO_3 + MgO] + H_2S = [CaS + MgO] + H_2O + CO_2 \qquad (2)$$

Reaction (2) can be conducted in reverse to regenerate half calcined dolomite and to obtain H_2S at a concentration sufficient for conversion to elemental sulfur in a Claus system:

$$[CaS + MgO] + H_2O + CO_2 = [CaCO_3 + MgO] + H_2S \qquad (3)$$

Equilibrium for reaction (2) or (3) is a strong function of temperature, the regeneration being favored at low temperature. The primary interest is in the application of the reactions in systems where the solid is used cyclically.

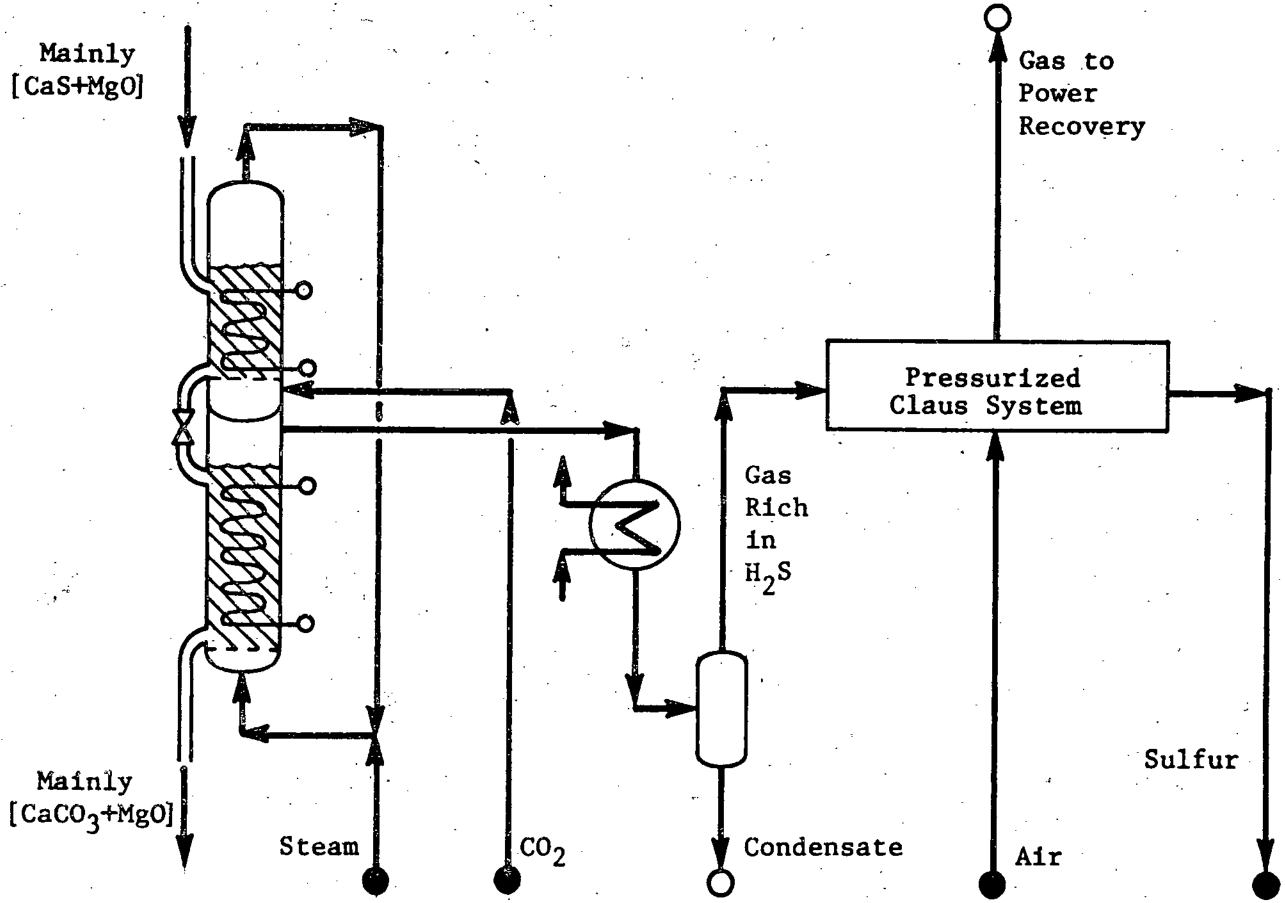
Figure 2.8 shows equipment suitable for sulfur recovery when desulfurization is accomplished by means of reaction (1) so that the solid charged to the sulfur desorber contains CaO. The sulfur desorber in the figure houses two fluidized beds: a lower bed for conducting reaction (3) and an upper bed in which CaO is converted to $CaCO_3$ in the absence of steam. Provision of the upper bed allows one to use a higher stream partial pressure in reaction (3) than would otherwise be possible, for one does not have to worry about the formation of $Ca(OH)_2$. Both beds of the figure might operate at 1100°F.

2.2.5 Gas Sweetening Using Molecular Sieve Method

Numerous crystalline aluminosilicates have been synthesized. Their structural properties have been presented as follows (4):

FIGURE 2.8

CYCLIC USE OF CALCINED DOLOMITE SULFUR DESORBER AND SULFUR RECOVERY



Type	Chemical Formula	Crystalline Structure
4A	$0.96 \pm .04 Na_2O \cdot Al_2O_3$ $1.92 \pm .09 SiO_2 \cdot nH_2O$	cubic a = 12.32 Å
5A	Similar to 4A, 75% Na ion replaced by Ca ion	cubic a = 13.32 Å
13X	$0.83 \pm 0.05 Na_2O \cdot Al_2O_3$ $2.48 \pm .03 SiO_2 \cdot nH_2O$	cubic a = 24.95 Å

Trace sulfur cleanup involves the use of the type 13X. These molecular sieves have a pore diameter of 8.9 Å. Hydrogen sulfide and mercaptans have molecular dimensions small enough to enter these pores. This particular application of removing sulfur compounds is an example of selective adsorption. The more polar sulfur compounds are more strongly adsorbed than the hydrocarbons. The CO_2 influences the amount of H_2S adsorbed, reducing it by 5-10 percent at high CO_2 concentrations. In some streams, water is present. The water is removed very quickly at the inlet end of the adsorber. The weight of adsorbent in this water adsorption zone must be added to the bed requirements for the sulfur removal. In the removal of sulfur compounds, it is necessary to stop the adsorption when the sulfur compounds first appear in the effluent. The next step is removal of the entrained liquid in the bed and depressurization to 60-120 psig. The desorption step consists of passing hot purge gas at 60-120 psig in the same direction as the sour gas feed. Regeneration is performed at 400-500°F. The lower temperatures remove the H_2S and the higher temperatures the mercaptans. The gas requirement is 20-25 mol for 100 lb of molecular sieve. It is desirable that the purge gas be dry, sweet and contain no oxygen. The oxygen would react with the H_2S to form sulfur which would be deposited in the absorber and poison the adsorbent. The cooling is accomplished by introducing liquid feed or product at the bed top. This cooling liquid should contain less than 1 grain of sulfur per 100 cu. ft. A cooling flow of 4 gallons per minute per square ft. of bed cross-section has been found adequate.

Among the potentially limiting handicaps associated with molecular sieves mentioned is that dealing with its ability to handle COS. Not only are questions of limited sorption kinetics and capacity involved, but also the fact that sieves have been reported to promote the reaction between CO_2 and H_2S to form COS and H_2O. A quantitative indication of the extent of this problem was recently reported by Cines, et al. (3). These workers used various molecular sieves (manufacturers not specified) to treat natural gas containing only H_2S as sulfur at 33 ppm levels. Approximate operating conditions were 50 atm pressure, ambient temperature, space velocity of 5000 hr^{-1}, and 2.2% CO_2 in feed. With Type 13X sieves (10 Å pore size, Na form), they found that at H_2S breakthru (1 ppm in effluent), 88% of the H_2S that had apparently been adsorbed by the sieve had actually been eluted by their column as COS. Considerably lower conversions (5-17%, defined as above) were found with Type 5A sieves (5 Å pore size, Ca form) but these are generally considered to offer limited capacity for larger organic sulfur molecules. It is possible that reduced space velocity would lessen this effect by allowing increased COS sorption. Use of 5A followed by 13X sieves might have potential under some circumstances. In any event, the problem represented a serious limitation with respect to the present application. Sieve manufacturers are apparently working on methods to reduce COS formation tendency (see, e.g., Turnock, et al. (21)).

2.2.6 Catalytic Conversion

Satterfield, et al. (22) have recently published some results on hydrodesulfurization of thiophene over molybdenum-based catalysts. For example, using a Ni/Mo catalyst in a once-thru tubular reactor with 1% thiophene in pure hydrogen at 11 atm total pressure and a space velocity of ca. 7500 hrs^{-1}, essentially complete conversion (>99%) of thiophene was achieved at ca. 300°C. The authors also noted the fractional conversion of thiophene in pure H_2 increased with decrease in thiophene partial pressure and claimed conversion rate was nearly zero order with respect to initial thiophene partial pressure. This latter result was actually based on runs using a Co/Mo catalyst at thiophene partial pressures ranging from ca. 30-150 mm Hg, but the authors implied a similar trend was expected with Ni/Mo. If, indeed, this trend is extrapolative down to lower thiophene partial pressures and total system pressure is not greatly influential (the 45 ppm thiophene level at 70 atm total pressure planned for investigation in our program represents a partial pressure of 2.4 mm Hg), the above results are encouraging. However, the authors indicate that, based on past work, H_2S in feed gas does inhibit the reaction.

A consultation was held with Prof. C. N. Satterfield to discuss catalytic hydrodesulfurization matters specific to our program. As indicated, Satterfield and others have recently published some information on thiophene conversion over molybdenum-based catalysts. Over the range of conditions used in that study, they found conversion rate was nearly zero order with respect to initial thiophene partial pressure (per cent conversion being inversely proportional to concentration). Professor Satterfield did feel, however, that at the very low thiophene partial pressures to be used in our work, the conversion rate would likely be first order in thiophene concentration. He bases this mainly on earlier work published by Satterfield and Roberts (23) where they studied the hydrogenolysis kinetics of thiophene over Co/Mo catalyst in a differential reactor, at 1 atm pressure, and found that rate was correlated by a Langmuir-Hinshelwood type of kinetic expression. If one uses the model and appropriate rate and adsorption constants derived by them, both of the above discussed behavior trends manifest themselves when appropriate values of thiophene partial pressure are used.

It is stressed that their model was based on experimentation performed at 1 atm pressure, and accordingly, the effects of extrapolation to the 70 atm range planned in our program are not known. With this in mind, the model does predict the magnitude of the inhibition effect due to H_2S. This turns out to be essentially unimportant at low H_2S levels.

With regard to the important question of catalyst poisoning effects due to the high (15%) CO levels in synthesis gas, Professor Satterfield indicated that he did not have any first hand knowledge.

Neither was he aware of information to quantitatively predict the extent of methanation over presulfided Ni/Mo or Co/Mo catalysts in our range of interest.

Regarding other poisons in coal-derived synthesis gas, he did point out that aromatics (especially three ring aromatics), olefins, diolefins, etc., will compete for catalyst sites thereby reducing HDS activity. This should not be much of a problem for an HDS sulfur guard catalyst downstream of a Benfield unit since the feed at that point, in theory, should be essentially free of such materials. A more likely area for concern would be in connection with the upstream Co/Mo catalyst planned for water-gas shifting (one-half the total gas stream) in the SYNTHANE process train. Although specifically designed to carry out the shift reaction, this unit has also been envisioned to effect a large conversion of organic sulfur contained in the feed to H_2S. Thus, system upsets in the oil scrubbing system upstream of the shift reactor could be a problem.

It is possible that catalytic conversion of organic sulfur to H_2S would be required as part of an overall sulfur guard system. The major difficulty here involves selecting a candidate that can achieve relatively high conversion (via hydrogenation or hydrolysis) of the very low level organic sulfur compounds, while allowing little or no methanation or shifting to occur in the bulk gas stream. A major problem with methanation and, to a lesser extent, shifting involves the fact that both are exothermic reactions and more costly processing schemes than simple once-through fixed bed reactors would be required to remove generated heat and avoid runaway reaction.

An important consideration regarding catalytic conversion involves position of the reactor within the overall processing train. For example, placement before the acid-gas removal step would be desirable in order to take advantage of the H_2S removal capacity of that system which would not be affected at all by the incremental increase in loading. Furthermore, the gas is hot and would require no additional heating. However, high concentrations of H_2S and CO_2 would unfavorably influence hydrogenation or hydrolysis equilibrium, and other impurities retained in the gas at this point might affect catalyst performance and life. Placement directly before a ZnO reactor (and possibly downstream of activated carbon) might prove feasible as long as total sulfur loading to the conversion reactor was sufficiently low not to impose an uneconomically high H_2S loading on non-regenerable ZnO.

Another variation might be placement downstream of acid-gas treatment but upstream of activated carbon and zinc oxide. This would require an additional heating and cooling step, however. Finally, placement within the acid-gas treatment step might be possible, for example, with a system such as the Benfield "Hi Pure" system which uses a DEA scrubber for additional gas cleanup to supplement the primary hot-carbonate scrubber. Placement of the conversion step could be between both scrubbers. This would have the advantage of working with a relatively clean gas stream that was low in CO_2 and H_2S, as well as allowing the incremental H_2S to be sent directly to the DEA scrubber without having to overburden downstream sulfur guard units such as activated carbon and/or zinc oxide. At least one disadvantage would, of course, be the incorporation of an additional heating and cooling step. Problems of physical incompatability with "Hi Pure" might also be restrictive.

2.2.7 Zinc Oxide

Zinc oxide was another active material considered for this application (1). It is probably unsurpassed in its potential to achieve ultra-low levels of sulfur, in the form of H_2S, in treated gas streams. The reaction between ZnO and H_2S to form ZnS and H_2O is so strongly favored thermodynamically that equilibrium levels of 1 ppb or less H_2S are predicted over the normal operating temperature range (350-400°C) for gas streams containing 0.1% H_2O. Under practical operating conditions, H_2S levels of <0.1 ppm are claimed by suppliers. High temperature operation is required for two reasons. First of all, although low temperatures thermodynamically favor formation of ZnS, the absorption capacity of the material drops rapidly when operation falls below ca 350°C. (Absorption capacity varies greatly according to processing conditions, but capacities of approximately 20 wt % sulfur are typically claimed by suppliers for commercial operation before exiting H_2S levels exceed 0.1 ppm.)

Another reason for high temperature operation of ZnO is that other sulfur compounds must be thermally decomposed to H_2S before any significant removal is noted. Removal of such compounds as methyl mercaptan and carbon disulfide is not generally considered as presenting great difficulty. Carbonyl sulfide removal is more controversial with success apparently dependent on the specifics of the operation. The major limitation of ZnO, as expected, involves thiophene which is thermally quite stable. Thermal decomposition data on thiophene, specific to our needs, have not yet been found, but preliminary indication is that very little decomposition occurs at temperatures approaching 500°C. Because the formation of ZnS is so strongly favored, even at high temperature, regeneration of ZnO is generally considered to be uneconomical and is not practiced. As a result, sulfur loadings to ZnO must be minimized in order to achieve economic operation. Various ZnO absorption catalysts are commercially available (e.g. Girdler's G-72, Katalco's 32-4, Topsoe's HTZ)*.

2.2.8 Iron Oxide

In general, in order to avoid iron carbonyl formation, iron oxide catalyst is usually run at temperatures >200°C. Temperatures in the range of 350-400°C, similar to those often used for zinc oxide, are sometimes used. This is done presumably for the same reasons as for zinc oxide; namely to increase sorbent capacity and help promote decomposition of the so-called "reactive sulfur compounds" (mercaptans, CS_2, COS (?)). Above 175°C, in the presence of H_2, Fe_3O_4 is considered the active sorbent/catalyst because the following reaction is favored

$$3\ Fe_2O_3 + H_2 \rightarrow 2\ Fe_3O_4 + H_2O$$

Thus, the H_2S desulfurization reaction is

$$Fe_3O_4 + H_2 + 3H_2S \rightleftarrows 3\ FeS + 4\ H_2O$$

while for zinc oxide it is

$$ZnO + H_2S \rightleftarrows ZnS + H_2O$$

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*Specification of tradenames in this report does not constitute endorsement by the U.S. Department of Energy.

Using thermodynamic equilibrium data provided by Imperial Chemical Industries, the following approximate equilibrium H_2S levels are predicted (19):

Temp (°C)		Equil. H_2S (ppm) Over Metal Oxide*			
		Fe_3O_4		ZnO	
	H_2O =	0.17%	1.7%	0.17%	1.7%
200		0.03	0.5	1×10^{-5}	1×10^{-4}
250		0.05	1.1	9×10^{-5}	9×10^{-4}
300		0.07	1.5	3×10^{-4}	3×10^{-3}
370		0.13	2.7	2×10^{-3}	2×10^{-2}
400		0.15	3.2	3×10^{-3}	3×10^{-2}

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*Gas contains 45% H_2.

As indicated, for streams containing 0.17% H_2O (comparable to the 0.1-0.2% in simulated SYNTHANE syntheses gas feed), even at temperatures of 400°C, equilibrium H_2S levels over zinc oxide are approximately 50x lower than over iron oxide. (Much larger differences are predicted at lower temperatures.) It should be pointed out that under actual commercial run conditions, dynamic equilibrium values would, no doubt, be higher than the above figures. However, <0.1 ppm H_2S levels using zinc oxide are often claimed by suppliers, depending on processing conditions.

2.2.9 Activated Carbon

Fixed beds of activated carbons have historically been used for removing odorous compounds from gaseous streams. Specially treated activated carbons have been formulated by catalyst manufacturers for the removal of sulfur compounds, including hydrogen sulfide, carbonyl sulfide and mercaptans from hydrocarbon streams. A typical activated sorbent is coconut shell char containing 5% (wt) copper made by Girdler (G-32 J). The physical properties of G-32 J are (9):

Surface Area	900 m^2/g
Pore Volume	0.6 cm^3/g
Bulk Density	0.56 to 0.61 g/cm^3
Particle Size	4 x 8 mesh granules 8 x 30 mesh granules

Activated carbon has a desulfurization capacity of about 2×10^5 ft^3 of natural gas per pound of sorbent in reducing sulfur mole fraction from about 30 ppm (v/v) to 0.2 ppm (v/v). High molecular weight hydrocarbons can severely reduce adsorption capacity and must be removed prior to entering the bed. Alternatively, they must be removed during regeneration or the duty cycle may be reduced to 10% that of a fresh bed.

The useful life of activated carbon sorbents has been found to be about 2 years in most applications. The sorbent is generally regenerated with superheated steam at 400 to 500°F near atmospheric pressure. Usually this requires 12 to 25 pounds of steam per hour per cubic foot of carbon. After steaming, the carbon bed should be purged with inert or process gas prior to putting it back on stream. Carbon beds are generally operated at ambient temperatures. Oxygen or air must be excluded from these beds since activated carbon can act as oxidation catalysts, thus destroying the bed due to excessive temperature rise.

2.2.10 Metal (CuO/Cr_2O_3) Impregnated Activated Carbon

Pittsburgh Carbon 7-2 (Katalco FCA) is the adsorbent that was planned for the SYNTHANE 72 TPD unit. Pittsburgh Carbon is the original supplier of both Katalco 7-1 (unimpregnated) and 7-2 carbons (their designation being BPL and FCA, respectively). Girdler's G-32W grade of metal-impregnated activated carbon is also supplied by Pittsburgh Carbon and is apparently equivalent to FCA. The metallic impregnants are copper and chromium. The copper, apparently present as the oxide, provides for bulk H_2S desulfurization by forming the corresponding metal sulfide. The role of the chromium species is less certain but it may promote conversion of some organic sulfur to H_2S. The precise nature and composition of impregnants is confidential although non-proprietary information published by Girdler describing their G-32W material indicates approximately 6 wt % copper and 3.4 wt % chromium (as metals). Both BPL and FCA (7-1 and 7-2) are produced from identical coal-based carbon sources with the only major difference, besides metal impregnation, being in surface area. According to Pittsburgh Carbon, the impregnation process lowers the original BPL surface area of ca 1050 m^2/g to approximately 750 m^2/g for FCA. Accordingly, some loss in absolute adsorptive capacity of the carbon portion of the material is likely for FCA relative to BPL.

Regarding the expected performance of activated carbon, Pittsburgh Carbon agreed with other catalyst suppliers consulted (CCI, Katalco, Girdler) that COS represented the most difficult sulfur compound to adsorb. However, in general disagreement with the others, Pittsburgh Carbon was quite optimistic with respect to the ability of activated carbon to handle most of the thiophene. None of the above firms supplied specific information to support their predictions. It is likely that some of this apparent contradiction may be due to the fact that performance is no doubt highly dependent on the numerous specifics of the operation, not the least of which includes the fact that adsorption of specific species is often dependent on the nature and concentration of other adsorbates present in the gas stream.

[illegible]alytic and Chemicals, Inc., Louisville, Kentucky, was quite emphatic [illegible] their belief that activated carbon (plain or impregnated grades) would not be suitable for the spectrum of sulfur compounds (hydrogen sulfide, methyl mercaptan, carbonyl sulfide, carbon disulfide, and thiophene) at the expected levels (10-80 ppm) requiring removal down to 0.1 ppm sulfur. It was felt that only in the case of methyl mercaptan (maximum levels of ca 20 ppm predicted) would system loading capacity and removal efficiency possibly prove activated carbon to be a viable approach to sulfur guard. They indicated that capacities for H_2S, CS_2, and C_4H_4S were considerably lower (1/2-1/3 or less of that for CH_3SH) so that target removal efficiencies could not be economically achieved. Finally, and perhaps most importantly, it has been their experience that activated carbon has little or no value as a system for removing carbonyl sulfide (which, at ca 80 ppm maximum predicted levels could represent the most prevalent sulfur compound feed to a premethanator sulfur guard system). This is despite the fact that adsorption isotherm data in the literature for COS on activated carbon indicate very high equilibrium adsorption (8).

Regarding the expected performance of activated carbon, representatives of Katalco offered reservations similar to those advanced in discussions with CCI. The most important of these involves the probability of reduced capacity for thiophene compared to methyl mercaptan, and poor performance with respect to removal of carbonyl sulfide. If the limitation regarding COS proves real, it may not represent a crucial limitation. This is despite the fact that COS may represent the predominant sulfur compound exiting a hot carbonate scrubber if one assumes a minimal COS removal efficiency of 75% as has been reported in some commercial installations (7). This is because special designs of the Benfield system (e.g. their "Hi-Pure" process which employs a dual scrubbing system consisting of hot potassium carbonate followed by diethanolamine) are claimed by the manufacturer to be able to approach 99% removal efficiency and achieve <10 ppm COS levels without great difficulty (7).

3. DESCRIPTION OF EXPERIMENTAL UNIT

An experimental unit was constructed in order to make experimental measurements of trace sulfur removal at the actual conditions expected for the SYNTHANE pilot plant process stream. The unit was designed to operate at high pressure, with a completely simulated synthesis gas and to have the capability to handle up to all five of the trace sulfur compounds of interest. The sulfur purification system was to operate at 1000 psig with a synthesis gas composition prior to final sulfur removal of the following approximate composition:

	Mole %
H_2	45.0
CO	15.0
CO_2	1.0
CH_4	35.0
C_2H_6	1.0
N_2	2.85
H_2O	0.15
Sulfur compounds	as indicated below
Total	100.0

The following sulfur compounds and the range of their respective concentrations were to be investigated:

Hydrogen sulfide	15 - 25 ppm (v/v)
Mercaptans	15 - 25 ppm (v/v)
Thiophenes	35 - 45 ppm (v/v)
Carbon disulfide	8 - 12 ppm (v/v)
Carbonyl sulfide	70 - 80 ppm (v/v)

It was desired that the synthesis gas be purified prior to methanation down to a total sulfur content of less than 0.1 ppm (v/v). This objective of removing sulfur down to a final content of less than 0.1 ppm (v/v) was of prime importance.

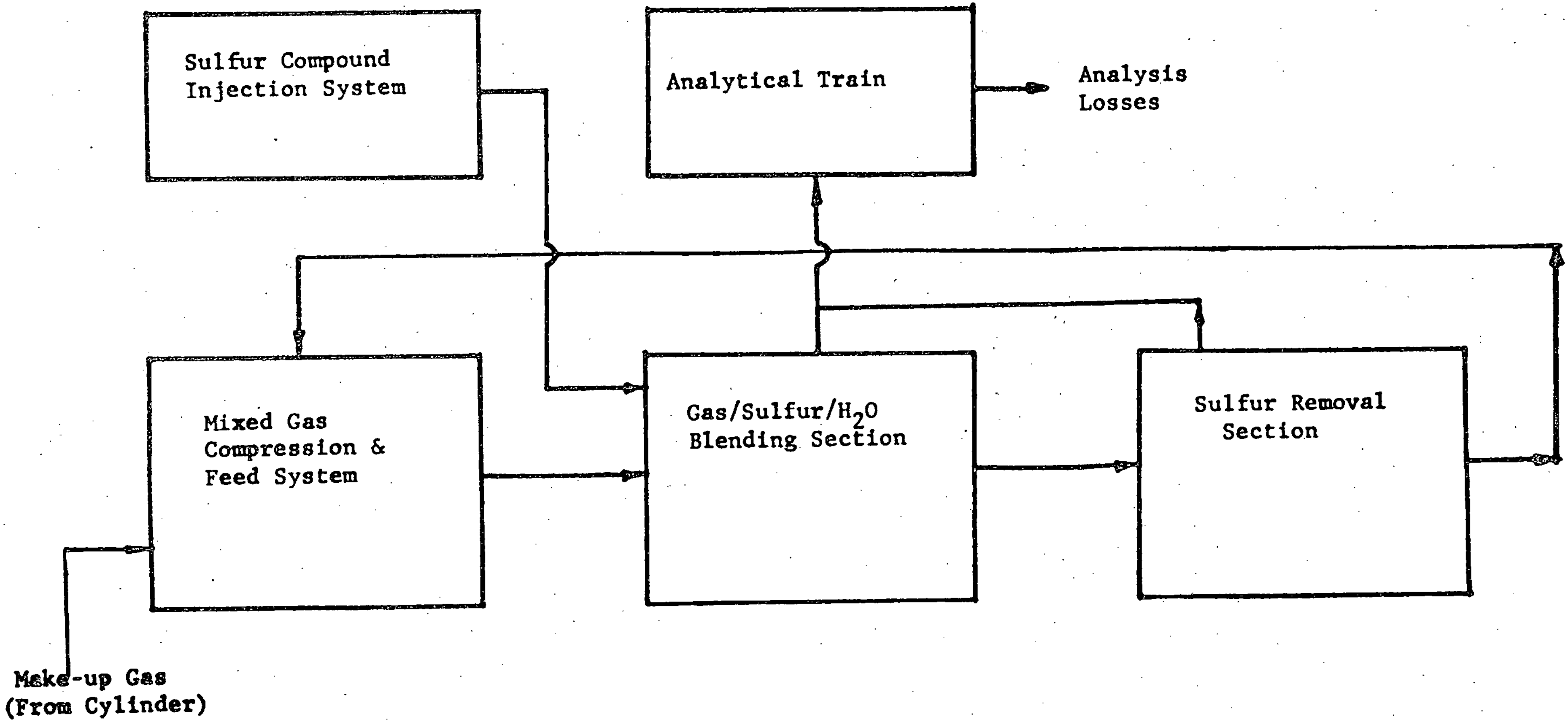
The test unit consists of five basic subsystems:

1. Mixed Gas Compression and Feed System
2. Sulfur Compound Injection System
3. Gas/Sulfur/Water Blending Section
4. Sulfur Removal Section
5. Analytical Train

A simplified block diagram illustrating subsystem interaction is shown in Figure 3.1. A brief description of each subsystem follows:

FIGURE 3.1

TEST UNIT BLOCK DIAGRAM



3.1 Mixed Gas Compression and Feed System

Pre-blended synthesis gas (ca 45% H_2, 15% CO, 1% CO_2, 3% N_2, 35% CH_4, and C_2H_6), free of sulfur compounds and water, was purchased from suppliers in conventional compressed gas cylinders. This gas enters the suction side of the gas compressor at ca 2.7 MPa (400 psig). Gas exits the compressor at ca 10.3 MPa (1500 psig) where a certain fraction, dependent on system demand, is sent forward while the remainder is by-passed back into the compressor. Maximum compressor output is 250 SCFH. (As a point of reference, four 0.53 cm I.D. x 30 cm long reactors operating in parallel at a space velocity of 50,000 SCF/hr/SCF bed (equivalent to a space velocity of approximately 700 hr^{-1} at 1000 psig) requires a total of 48 SCFH.) An accumulator is also provided to dampen compressor pulses while a blow-by tank is used to monitor mechanical condition of the compressor.

3.2 Sulfur Compound Injection System

The original approach used for injection of sulfur compounds involved volumetric displacement from a syringe-like apparatus containing each of the compounds (H_2S, COS, CS_2, methyl mercaptan, and/or thiophene) as liquids under pressure. The piston is threaded so that it advances 2.54 cm in 16 revolutions. The piston, in turn, is driven by a synchronous motor connected to the piston through a series of precision gears with a gear reduction ratio of 3000/1. The motor has a maximum output of 72 RPM which can be stepped down in 100 equal increments. Operation at full speed results in a piston linear displacement of 0.23 cm/hr. Actual volume displacement would be determined by the surface area of the piston face. (As a point of reference, a piston of 2.54 cm diameter operating at the above maximum setting would result in an 80 ppm level of COS for a gas flow of 250 SCFH.) After leaving the syringe, the sulfur compound is transported through a 0.2 cm I.D. tube where it is combined with the sulfur-free synthesis gas in a blending tee. Contained within the entire tube is a wire which serves to reduce the transport tube volume. In addition, the wire extends beyond the outlet of the tube into the blending tee and serves as the final conduit by which the sulfur compound contacts the flowing gas stream. The net result is that drop formation at the tube outlet is avoided due to the wire's providing sufficient surface area for rapid evaporation of the liquid feed.

The system described above was used for the first few single component adsorption test runs. However, because of problems in maintaining the feed concentrations at the desired levels (particularly for low concentrating feeds) a different gasifing system was designed and installed. This alternative approach to feeding of sulfur compounds, consisted of introduction, at ca 6.8 MPa (1000 psi), of sulfur compound(s) in suitable carrier gas into the main synthesis gas stream. This approach, which required purchasing sulfur-containing gas from suppliers, in addition to the current sulfur-free synthesis gas, had associated with it certain penalties. For example, the carrier gas could not be of the same composition as the synthesis gas. In this regard, it was the policy of one of our gas suppliers (Matheson) to not fill any cylinders containing CO and any sulfur compounds above 6.8 MPa (1000 psi) because of their experience with system instability problems and long-term cylinder corrosion possibilities. (The above pressure also represents our effective cylinder exhaustion pressure.) In addition, they could not guarantee the stability of <1% H_2S gas mixtures unless they were prepared in ultra-pure inert carriers such as H_2 or N_2 or blends, thereof. Furthermore, because of incompatibility problems between COS and H_2S, they could not guarantee stability of mixtures containing both of these gases.

Accordingly, the approach taken regarding purchase of sulfur containing gases was to purchase single sulfur compounds (except H_2S) or 4-component mixtures in CO-free simulated synthesis gas (CO balance made up with N_2), while H_2S was purchased in a 45/55 H_2/N_2 gas. (All were in Teflon-lined cylinders.) These gases, in turn, were metered into the sulfur-free bulk simulated synthesis gas stream in much the same way planned for the liquid microinjection pump.

3.3 Gas/Sulfur/Water Blending Section

After exiting the compressor, synthesis gas enters a temperature-controlled (air bath) insulated box where sulfur compounds are introduced (see above) and water may be added. Addition of water is done by bubbling gas through a saturator whose temperature can be controlled from approximately room temperature up to ca 95°C. Accordingly, for a gas stream at approximately 6.8 MPa (1000 psig), water content could be adjusted from 0.1% to 1%. The option to omit water introduction was also provided. The well-mixed synthesis gas is then sent to a manifolding line where it is split into a maximum of four streams for feeding to reactors at 6.8 MPa (1000 psig). A small slip stream at 100 kPa (15 psig) could also be diverted for analysis.

3.4 Sulfur Removal Section

The sulfur removal section consisted of an air-heated insulated box whose temperature could be controlled from just above ambient to ca 425°C. The reactor arrangement consisted of four parallel reactor tubes of 0.53 cm I.D. and 30 cm length containing test material and equipped with thermocouples to monitor bed temperature. Gas flow may be directed to any number of reactors with flow rate to each capable of independent monitoring and control. Other reactor geometrics and arrangements could be easily accommodated. For example, the compressor output capacity would allow for a single 2.43 cm I.D. x 30 cm long reactor operating at a space velocity of 50,000 SCF/hr/SCF bed. It would also be possible, by minor piping modifications, to increase reactor bed length and monitor gas composition at various points within a bed by arranging the four reactors in series. Thus, a wide range of experimental schemes can be addressed. After exiting each reactor, a small side stream of treated gas could be sent for analysis while the bulk of sulfur-free treated gas is depressurized back to ca 2.7 MPa (400 psig) and dehydrated by cooling and passage through a Linde 3A molecular sieve. In the recycle mode after water removal, each stream is recombined and sent back to the compressor where any sampling losses are continuously made up with cylinder-stored synthesis gas.

3.5 Analytical Train

The analytical train consisted of three gas chromatographs, two of which are F & M Model 720's (thermal conductivity detectors) while the third is a Perkin-Elmer Model 3920 equipped with flame ionization detection for hydrocarbons and flame photometric detection for sulfur compounds. The flame photometric detector is capable of detecting <1 nanogram of sulfur. Thus, in order to detect sulfur levels on the order of 0.1 ppm, gas samples on the order of 10 ml (at standard conditions) were required.

3.6 Unit Shakedown Experience

During the course of our experimental program, several unanticipated equipment difficulties were encountered which considerably delayed the start of experimental work. A synopsis of the major equipment problems encountered is presented in Appendix A. These dealt primarily with the compressor problem, analytical problems and the sulfur delivery system.

Solution of the compressor problem required rebuilding of idle compressors after the original unit proved inadequate. Regarding the analytical problems, considerable effort was expended in adapting state-of-the-art techniques where information and experience pertinent to project needs were quite limited, to provide the necessary means to monitor a spectrum of different sulfur compounds in actual synthesis gas over several orders of magnitude in concentration range. The originally conceived sulfur delivery system (sulfur pump) resulted in a large development effort that proved to be beyond state-of-the-art with respect to our requirements. After considerable evaluation of alternative approaches, a new delivery system was installed and its performance proved very favorable. As a result of this effort, a single versatile experimental unit was developed that reproduces the operating conditions expected in the SYNTHANE process and whose data can be used to address many of the questions and possible solution routes that might arise with respect to our objective of recommending a sulfur guard system for the SYNTHANE process.

4. EXPERIMENTAL RESULTS

After careful evaluation of the candidate sulfur guard systems described in Section 2, and giving consideration to the limited time on the program, the experimental effort concentrated on the metal impregnated activated carbon sorbent.

This section discusses the results of single and multicomponent adsorption of trace sulfur compound gases on metal-impregnated (copper and chromium oxides) activated carbon sorbent. This material, designated Katalco 7-2, is the same material planned for eventual use in the 72 TPD SYNTHANE pilot plant unit.

4.1 Selection of Sulfur Compound Feed Concentrations

An important consideration in this study involved the selection of sulfur compound feed concentrations to be addressed in our experimental program. The difficulty in selection of appropriate levels stemmed mainly from the fact that the original sulfur compound levels in the SYNTHANE gasifier effluent are strongly dependent on coal used (variation of one or two orders of magnitude are not uncommon based on the limited data available). In addition, several questions remained regarding the expected performance of the hot potassium carbonate (Benfield) system preceeding sulfur guard. After reviewing the situation, it was decided that the original concentration range would define the upper limit of concentrations addressed (i.e. H_2S $\sim$25 ppm, CH_3SH $\sim$25 ppm, CS_2 $\sim$12 ppm, COS $\sim$80 ppm, C_4H_4S $\sim$45 ppm), and thus would provide the most severe test of the adsorbents capacity to breakthrough.

The rationale for selection of the above concentrations as upper limits was based essentially on reviewing recent results for SYNTHANE gasifier effluent concentration (6), selecting those concentrations derived from the worst coal listed (Illinois No. 6), and assuming Benfield performance based on the recent paper of Parrish and Neilson (17). Other factors that entered included the fact that shifting one-half of the gas prior to acid-gas treatment should reduce the organic sulfur by one-half, while some upset in the hot carbonate scrubber might occur. More specifically, for methyl mercaptan, assuming a maximum gasifier effluent of 60 ppm, one-half of the gas shifted, and a minimum 70% Benfield removal efficiency, results in an approximate 10 ppm level as feed to sulfur guard. For carbon disulfide at 10 ppm maximum gasifier effluent, one-half shifting, and 70% minimum removal via Benfield, the result is an approximate 2 ppm level. For carbonyl sulfide at 300 ppm maximum gasifier effluent, half shifting, and 75% minimal removal (as high as 99% apparently has been achieved commercially), the result is ca 40 ppm. For thiophenes at 60 ppm maximum gasifier effluent, half shifting, and no removal by Benfield, a level of 30 ppm is obtained. Other factors, such as removal by some of the unit operations preceeding the Benfield (e.g. the oil scrubber) would probably reduce all of the above even further.

Accordingly, the upper concentration limits listed for the above four organic sulfur compounds are quite conservative even if Benfield performance periodically drops below minimum expected levels. The H_2S level of 25 ppm was deemed reasonable based on claims by Benfield that levels of <10 ppm can be routinely achieved with certain versions of their process. However, this particular impurity must be addressed with more caution since its level in gasifier effluent may be orders of magnitude higher (5,000-15,000 ppm) than the others, and upsets in the Benfield could result in extremely high discharge levels. Special precautionary measures probably would have to be incorporated into a plant design (e.g. routing gas to a furnace, etc.) to handle a major system upset involving large H_2S breakthrough.

In most of the experimental runs, a superficial velocity of 1.36 cm/sec was used. This value was a design value which may not be optimum for the system investigated.

4.2 Single Component Adsorption Studies

Separate adsorption breakthrough studies were conducted with each of the sulfur compound gases of interest in this study. This section describes the tests made with carrier gas (nitrogen or simulated synthesis gas) using only one sulfur compound component at a time. Subsequent studies which were carried out with multiple sulfur compounds are described in Section 4.3.

4.2.1 Hydrogen Sulfide in Nitrogen

Very preliminary experimental testing using metal-impregnated (copper and chromium oxides) activated carbon was conducted using H_2S in nitrogen. This material designated Katalco 7-2 was planned for eventual use in the 72 TPD pilot plant. Although supplied by Katalco, it is actually manufactured by Pittsburgh Chemical and designated as their FCA type. In-house analysis indicated this material contained, as metals, 8.00% Cu, 2.73% Cr, and 0.32% Fe. The runs were made to provide a preliminary, ball-park estimate of the maximum activity of the impregnated carbon since published data on this material was not in the open literature.

As previously described, a once-through operation mode using sulfur-containing carrier gas was adopted. The sulfur-containing gas employed in this run consisted of 110 ppm H_2S and 53 ppm H_2S, both in pure nitrogen. Because of supply restrictions, shallow beds ($\leq$ 15 cm) were used. Low superficial velocities ($\leq$ 0.64 cm/sec) were also used to contain the mass transfer zone within the bed.

Three tubes were charged with carbon bed depths of 6.4, 7.5, and 15.0 cm, respectively, and 110 ppm H_2S in N_2 at superficial velocities (at run conditions) of 0.64, 0.32, and 0.64 cm/sec, respectively, used as initial feed. (The superficial velocity design value of the pilot unit for the SYNTHANE Process is 1.38 cm/sec, while the 110 ppm H_2S level is greater than the $\sim$25 ppm H_2S maximum levels anticipated.) After nearly 8 hours of run time, the utilizable 110 ppm H_2S cylinder gas was exhausted and switching over to 53 ppm H_2S in N_2 was required to continue the runs. No breakthrough occurred after running for a cumulative time of 31 hours at which time feed gas again was depleted. Accordingly, neither the 7.5 or 15 cm beds produced required capacity data and, thus, detailed discussion will be confined only to the run containing 6.4 cm of carbon. (These runs did serve to support the relatively high capacity levels found in the one good run.) Namely, if one assumes that capacity does not vary with H_2S feed concentration over the range used and uses the capacity levels found in the one good run, together with various assumptions regarding breakthrough curve shape, breakthrough times of $\sim$35 hours are predicted.

Regarding the one run which provided capacity data, breakthrough occurred <10 minutes after 53 ppm H_2S feeding commenced. The transient history of the run is shown in Figure 4.1, with specific details given in Table 4.1. Prior to breakthrough in this run (as well as during the entire length of the two aborted runs) no detectable H_2S (<0.1 ppm) in the effluent was found. Because of the change in feed concentration just prior to breakthrough, the effluent levels plotted in Figure 4.1 are as % of H_2S in feed to the reactor which was continuously dropping toward 53 ppm because of upstream mixing time lags. The feed level to the reactor was, in turn, determined by monitoring the feed concentration to the fourth reactor which contained no carbon.

As indicated in Table 4.1, the H_2S capacity at breakthrough was found to be 5.7 wt % of the carbon charge, or 189,000 standard volumes of gas treated per volume of carbon used. Approximate maximum capacities of 6.7 wt % and 222,000 vols. gas/vol carbon were also calculated using highly idealized models of adsorption which visualize the bed at breakthrough as consisting of a fully saturated zone and a zone of completely unusued bed (see, e.g., Lukchis (14)). Such numbers in theory, represent capacities which could be approached in very long beds where the mass transfer zone is assumed to be independent of bed length and, thus, would represent a very small fraction of the total bed length.

Even though the system of H_2S in pure N_2 would be expected to give very high adsorption capacities, the levels found were higher than expected. For example, if it is assumed that all of the Cu is utilized to form the sulfide, given the 8% Cu level found, 4% maximum H_2S loading capacity would be possible from this removal mechanism. It is not possible to account for the balance by assuming physical adsorption on the carbon and using the equilibrium adsorption isotherm data published by Grant et al (8) for H_2S on Pittsburgh BPL carbon (equivalent to unimpregnated Katalco 7-2). For the H_2S partial pressures used in the experiment, the above reference indicates <0.1 wt % H_2S pickup. It is possible that the above cited data is not applicable, or other effects, including total system pressure, were responsible.

4.2.2 Hydrogen Sulfide in Dry Synthesis Gas

Experimentation using Katalco 7-2 (equivalent to Pittsburgh FCA) metal-impregnated (Cu and Cr oxides) continued using H_2S in dry synthesis gas. Other analytical results showed this carbon to have S = 0.69%, C = 72.7%, H = 0.78%, N = 1.51%, ash (@788°C) = 18.8%, and surface area (BET) = 727 m^2/g. This material was the same as planned for use in the 72 TPD pilot plant.

One of the four reactor tubes was left empty, while the remaining three were charged with 1.6, 1.6, and 3.2 gms of carbon, respectively, which represented bed depths of approximately 6.4, 6.4, and 12.7 cm, respectively. Superficial velocities of 0.66, 1.33, and 1.33 cm/sec (the latter being comparable to the 1.38 cm/sec 75 TPD PDU design value), respectively, were used. Dry simulated synthesis gas was used as the carrier gas, with H_2S being injected via the sulfur pump.

TABLE 4.1

REMOVAL OF H_2S IN PURE N_2 USING METAL-IMPREGNATED ACTIVATED CARBON

Carbon:

Katalco 7-2 (12-30 mesh)
Impregnants (as metals) = 8.0% Cu; 2.7% Cr
Packing Density = 0.53 g/ml (33 lb/ft^3)
Bed Depth = 6.37 cm
Bed Diameter = 0.775 cm
Charge = 3.0 ml = 1.59 g

Feed Gas:

110 ppmv H_2S in pure N_2 ($t \leq 8$ hrs)
53 ppmv H_2S in pure N_2 ($t > 8$ hrs)

Run Conditions:

Pressure = 6.9 MPa (1000 psi)
Temperature = 27°C
Vol. Feed Rate = 19.7 std. ml/sec (2.5 SCFH)
Superficial Velocity (actual) = 0.64 cm/sec
Space Velocity (STP) = 23,600 hr^{-1}

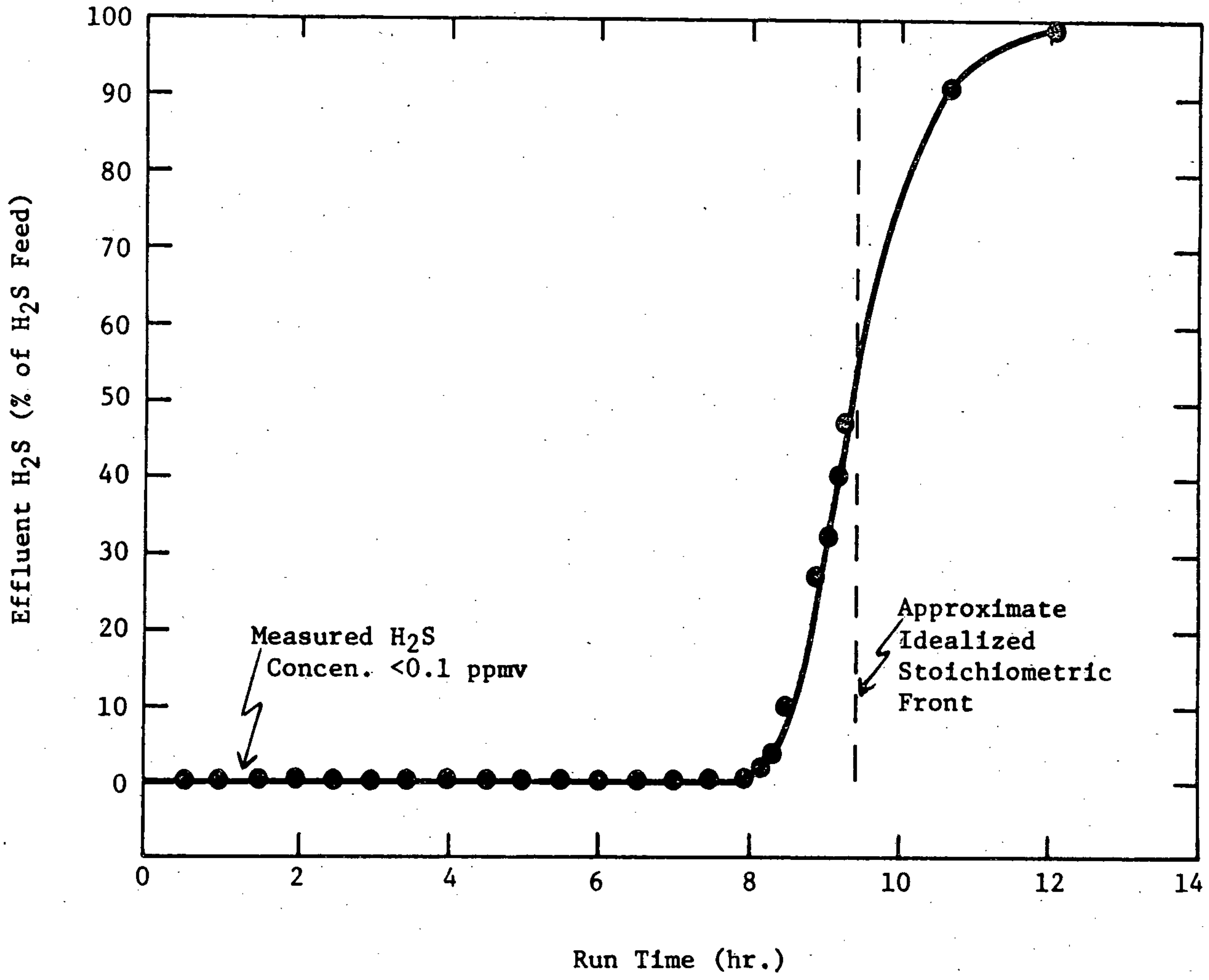
Results:

Time to Breakthrough = 8.0 hrs
Effluent H_2S Before Breakthrough = < 0.1 ppmv
H_2S Capacity @ Breakthrough = 5.7 wgt % of Carbon
Approx. Max. H_2S Capacity* = 6.7 wgt % of Carbon
Vol Gas (STP)/Vol Carbon @ Breakthrough = 189,000
Approx. Max. Vol Gas (STP)/Vol Carbon* = 222,000

* Calculated by assuming idealized stoichiometric front (vertical breakthrough curve) occurs at 50% of feed concentration, or from Fig.4.1at ca. t = 9.4 hrs. Accordingly, the 6.37 cm bed at breakthrough is idealized as consisting of 5.42 cm (6.37 x 8.0/9.4) of fully saturated carbon and 0.95 cm of completely unused bed. Maximum capacities and volumes calculated thus represent (using such an idealized model) levels which could be approached in very long beds.

FIGURE 4.1

REMOVAL OF H_2S IN PURE N_2 USING
METAL-IMPREGNATED ACTIVATED CARBON
Reactor 1, Run 1, 4231-6
(See Table 4.1 for Run Details)



Because of performance problems with the sulfur pump, the run was characterized at various times by widely differing H_2S concentrations in carrier gas. However, there did exist one period of approximately 3 hours duration where the effluent concentration from the empty reactor remained between 250-300 ppm H_2S. (This level represents approximately one order of magnitude higher than desired in feed.) After calculating the amounts of H_2S fed to the reactors during the entire run, it turned out that approximately 80% of the toal H_2S fed up to the breakthrough point of each reactor occurred during this period. Furthermore, breakthrough for each charged reactor occurred during this somewhat stable interval. Accordingly, this interval served as a basis upon which the entire run was quantified. The average effluent concentration from the empty reactor (275 ppm) during this period was used as the equivalent feed concentration. Coupling this with the value of total H_2S fed to each reactor up to their breakthrough points, an equivalent time to breakthrough for each reactor was calculated in order to put the entire run on a better comparative basis. Breakthrough curves, themselves, were determined by direct comparison of the effluent levels from each charged reactor to the actual effluent value from the empty reactor existing during breakthrough. For the case of reactors 2 and 4, the empty reactor effluent H_2S level remained essentially in the 255-270 ppm range during their respective breakthroughs, while this level began to fall (eventually to the $\sim$150 ppm range) shortly after the last (reactor 1) breakthrough curve began to develop.

Although the aforementioned $\sim$3 hour interval was generally classified as one of relative stability, there did exist an inexplicable pecularity; namely, the H_2S feed concentration measured considerably upstream of the reactors averaged about 20% less than the effluent level from the empty reactor during the majority of the 3-hour interval. One can only speculate that wall desorption phenomena may have been occurring. In any event, the effluent from the empty reactor was considered to be a less biased estimate of the actual feed to the charged reactors.

A summary of run conditions and results are given in Table 4.2, while the transient effluent history from the three charged reactors using an equivalent run time axis is shown in Figure 4.2. Prior to breakthrough in all runs, no detectable H_2S (<0.1 ppm) was found. This was also found for the run using 110 ppm H_2S in N_2 carrier gas. This was encouraging in view of the very high levels of H_2S ($\sim$275 ppm) and very short bed residence times of $\sim$2 or 4 seconds (calculated using 40% as the bed void fraction).

Calculated bed H_2S capacities to breakthrough of 5.7, 6.9, and 8.6 wt % of carbon were found. These results appeared high, especially the 8.6% level. It is also possible that the other metal oxides present (2.7% Cr, 0.32% Fe, as metals) may also tie up some sulfur. Regarding the chromate specifically (often speculated as performing a catalytic role in conversion of some organic sulfur to H_2S), there does exist some data which may indicate that under some conditions it may serve as an oxidation source for the partial in-situ regeneration of CuS back to CuO, thus increasing the capacity of FCA for H_2S via formation of some elemental sulfur (9). Finally, analysis of the spent carbon from reactors 2 and 4 indicated, after deduction of initial sulfur, levels of 6.1 and 5.0% sulfur, respectively. Little of this would be expected to be due to physically adsorbed H_2S which should have been largely desorbed. In view of all of the above, the general finding of H_2S capacity levels above 4%, under the run conditions followed, appeared reasonable.

TABLE 4.2

REMOVAL OF H_2S IN DRY SIMULATED SYNTHESIS GAS USING METAL-IMPREGNATED ACTIVATED CARBON (RUN 2, 4231-24)

Carbon:	Katalco 7-2 (12-30 mesh); 0.53 g/ml Impregnants (as metals) = 8.0% Cu; 2.7% Cr
Feed Gas:	~275 ppm H_2S[1] in Dry Simulated Synthesis Gas (H_2 = 45%; CO = 15%; CH_4 = 35%; CO_2 = 1%; C_2H_6 = 1%, N_2 = 3%)
Pressure:	6.9 MPa (1000 psig)
Temperature:	32°C

Bed Diameter = 0.775 cm

	Reactor 1	Reactor 2	Reactor 4
Carbon charged (gms)	1.59	1.59	3.18
Bed Depth (cm)	6.35	6.35	12.70
Vol. Feed Rate (std. ml/sec)	20.4	40.7	40.7
Superficial Velocity, actual (cm/sec)	0.66	1.33	1.33
Space Velocity, STP (hrs^{-1})	24,400	48,900	24,400
Time to Breakthrough (hrs)[2]	3.72	2.33	3.08
Effluent H_2S before Breakthrough (ppm)	< .1	< .1	< .1
H_2S Capacity @ Breakthrough (wgt %)	6.9	8.6	5.7
Approx. Max. H_2S Capacity (wgt %)[3]	7.7	10.6	6.0
Vol. Gas (STP)/Vol. Carbon @ Breakthrough	91,000	114,000	75,000
Approx. Max. Vol. Gas (STP)/Vol. Carbon[3]	101,000	140,000	80,000

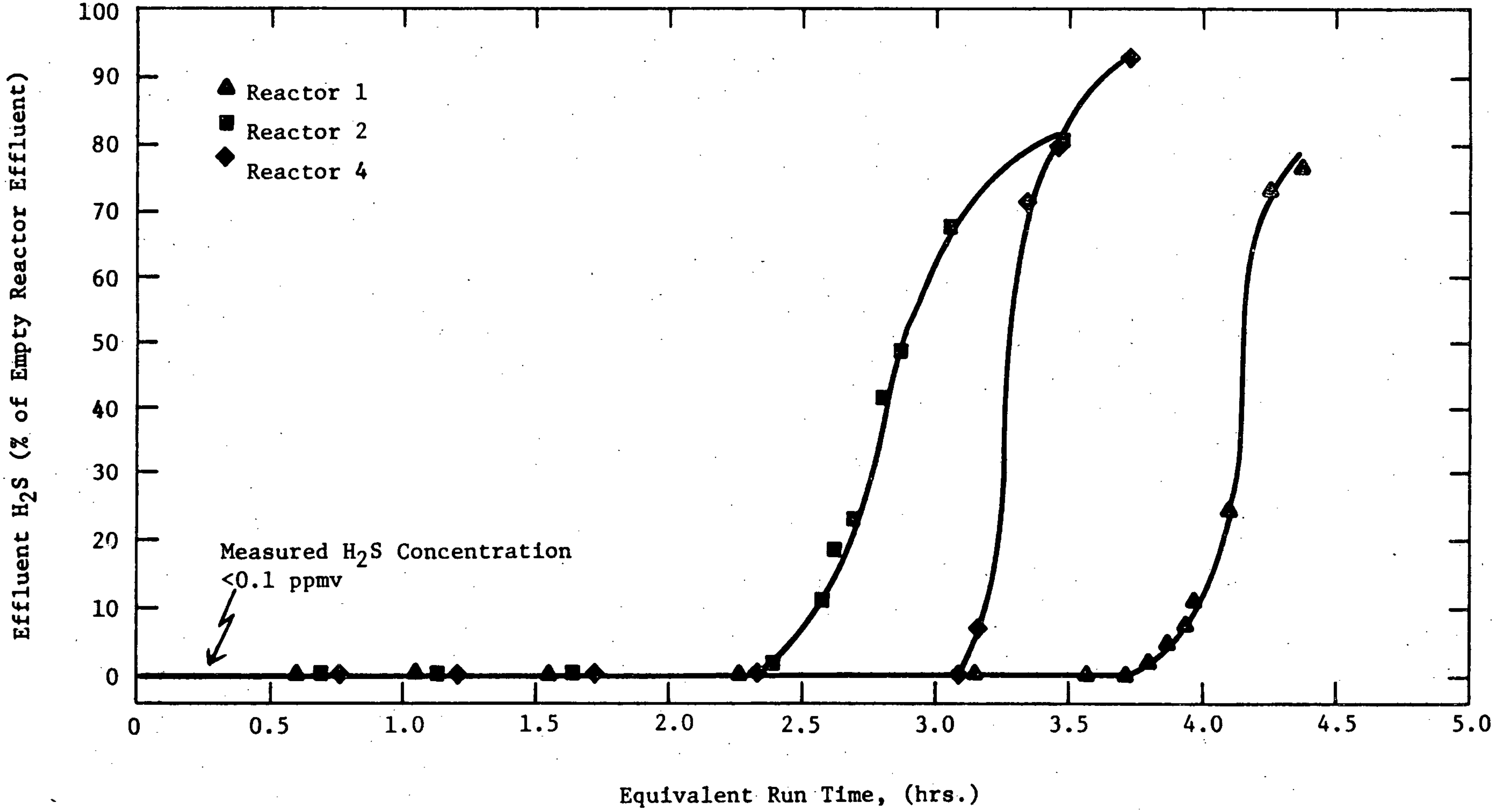
1. Represents effluent concentration (± 25 ppm) from empty reactor during most meaningful period of run (see discussion in text).

2. Based on 275 ppm average feed level, and cumulative total H_2S feed to each reactor to breakthrough point.

3. Calculated by assuming idealized stoichiometric front (vertical breakthrough curve) occurs at 50% of feed concentration.

FIGURE 4.2

REMOVAL OF H_2S IN DRY SIMULATED SYNTHESIS GAS
VIA METAL-IMPREGNATED ACTIVATED CARBON
Run 2, 4231-24 (See Table 4.2 for Run Details)



An estimate of the natural variability in these types of adsorption measurements can be made by examining the results shown in Table 4.2. For example, comparing reactor 1 and 2 results, where the bed depth remained constant, a doubling of superficial velocity resulted in a 25% increase in capacity. This could be explainable if the system were mass transfer limited, but capacity in reactor 4 at the same high superficial velocity as reactor 2, displayed a drop in capacity. Similarly, comparing the capacity results of reactor 2 and 4, where superficial velocities were the same, but the bed depth in reactor 4 was doubled, showed a 17% drop in capacity for the deeper bed.

4.2.3 Carbonyl Sulfide in Synthesis Gas

Experimentation using impregnated (Cu and Cr oxides) carbon was conducted with COS representing the sulfur compound feed. Based on the literature, it was considered likely that COS represented the most difficult of the five sulfur compounds (H_2S, COS, CS_2, CH_3SH, and thiophene) for the metal-impregnated carbon to remove.

The sulfur pump was used as the means of sulfur compound introduction, during this set of experiments.

Initial experimentation consisted of three beds, two of which contained 1.59 g each of metal-impregnated carbon (Katalco 7-2, equivalent to Pittsburgh FCA) while the third contained 1.59 g of unimpregnated carbon (Katalco 7-1, equivalent to Pittsburgh BPL). Bed depths of 6.5, 6.5, and 7.6 cm, respectively, and superficial velocities of ∿1.3, 2.6, and 1.3 cm/sec, respectively, were used. Very high COS levels (∿300-400 ppm) were fed. In all cases, breakthrough of COS occurred prior to taking the first effluent samples (ca one-half hour after initiating COS feed). Thus, the possibility of containment of COS by the two varieties of carbon at the superficial velocities used could not be established. Furthermore, with the exception of the reactor containing the metal-impregnated carbon at a 1.3 cm/sec superficial velocity, breakthrough of the other two reactors was essentially complete, with the initially measured effluent levels comparable to feed levels. Regarding the other reactor, effluent levels remained in the 20-50 ppm range for approximately an additional half-hour, and then rapidly climbed to concentrations comparable to the others.

It was obvious that deeper beds and, in general, less severe conditions would be required to gain useful information regarding COS removal. One useful and interesting observation did apparently manifest itself from this run, however. This was the observation that at comparable conditions, the metal-impregnated carbon was apparently superior to the unimpregnated material with respect to COS containment and removal.

Additional experimentation was next conducted using deeper beds, at a superficial velocity of 1.36 cm/sec (comparable to the SYNTHANE 72 TPD pilot plant design value of 1.38), and with metal-impregnated carbon, exclusively. One of the reactors was left uncharged, while the others contained beds of 12, 24, and 49 cm depth. Simulated synthesis gas, approximately saturated with H_2O, was used as the carrier gas.

Sulfur-pump performance problems associated with fluctuating levels in feed were present. However, an approximate average empty reactor effluent concentration of 150 ppm COS characterized much of the run during which time the large majority of sulfur was fed to the charged reactors. Using 150 ppm COS as an equivalent feed concentration, and coupling this with the actual values of total COS fed to each reactor (determined by using actual COS effluent levels from the empty reactor) up to their breakthrough points, an equivalent time to breakthrough for each reactor was calculated in order to put the entire run on a comparative basis. Breakthrough curves themselves were determined by direct comparison of the effluent levels from each charged reactor to the actual effluent values from the empty reactor measured during breakthroughs.

Run conditions and results are summarized in Table 4.3, while the transient effluent concentration from each reactor (calculated as % of effluent from the empty reactor) using an equivalent run time axis is shown in Figures 4.3 and 4.4. (An expanded ordinate for reactors 2 and 4 data is also presented in order to better quantify the initial phases of their respective breakthroughs.) Actual breakthrough points for reactors 2 and 4 were selected as midway between the respective two points of sulfur non-detectability and detectability. For reactor 1, such a large increase in concentration occurred between these two points that the last (and only) point of non-detectability was selected as the breakthrough point.

Prior to breakthrough in all reactors, no detectable (<0.1-0.2 ppm) COS was found, although this period was very brief for both the 12 and 24 cm beds. Indicative of this are the calculated bed capacities at breakthrough of ∿0.55 wt % of carbon for both of these cases, compared to the 1.75% calculated for the 49 cm bed. Such a dramatic increase beyond a certain bed length is common for adsorbents where the adsorbate is not strongly adsorbed. The considerable length of time required for a breakthrough curve to develop relative to the time for breakthrough to occur, as shown in Figures 4.3 and 4.4, is also characteristic of such systems.

It logically follows that considerable unused bed capacity exists for the three cases run. An approximation of the maximum COS capacity obtainable in very long beds was made by assuming an idealized vertical breakthrough occurs at the point where effluent concentration equals 50% of the feed concentration following the method of Lukchis (14). When such an approximate technique was used for the current data, maximum adsorptive capacities ranging from 2.5-4.0 wt %, as listed in Table 4.3, resulted. It is interesting to note that this essentially equilibrium capacity range is similar to the equilibrium adsorption isotherm data for COS on BPL unimpregnated carbon (see Grant, et al (8)). For 150 ppm COS at 6.9 MPa (1000 psig), which is equivalent to a COS partial pressure of 1.0 kPa (0.15 psia), their results indicate a 3.5% equilibrium capacity. Such agreement may be fortuitous. If it is not, it may indicate that the presence of non-sulfur adsorbates present in the simulated synthesis gas, as well as total system pressure, have little influence on equilibrium COS adsorption. It is likely, however, that the presence of other sulfur compounds that are more strongly adsorbed than COS and more apt to be competing for the same adsorptive sites, would reduce COS adsorptive capacity considerably. Such determinations are discussed later when

TABLE 4.3

REMOVAL OF COS IN SIMULATED SYNTHESIS GAS USING METAL-IMPREGNATED ACTIVATED CARBON (RUN 5, 4231-64)

Carbon:	Katalco 7-2 (12-30 mesh); 0.55 g/ml Impregnants (as metals) = 8.0% Cu; 2.7% Cr
Feed Gas:	∿ 150 ppmv COS[1] in Simulated Synthesis Gas (H_2 = 45%; CO = 15%; CH_4 = 35%; CO_2 = 1%; C_2H_6 = 1%; N_2 = 3%; H_2O = 0.07%)
Pressure:	6.9 MPa (1000 psig)
Temperature:	33°C
Bed Diameter:	0.775 cm

	Reactor 1	Reactor 2	Reactor 4
Carbon Charged (gm)	3.18	6.36	12.72
Bed Depth (cm)	12.2	24.4	48.6
Vol. Feed Rate (std. ml/sec)	41.7	41.7	41.7
Superficial Velocity, actual (cm/sec)	1.36	1.36	1.36
Space Velocity, STP (hrs $^{-1}$)	25,880	12,940	6,470
Time to Breakthrough (hrs)[2]	0.30	0.59	3.84
Effluent COS Before Breakthrough (ppm)	<.1-.2	<.1-.2	<.1-.2
COS Capacity @ Breakthrough (wgt %)	0.55	0.54	1.75
Approx. Max. COS Capacity (wgt %)[3]	3.6	2.5	4.0
Vol. Gas (STP)/Vol. Carbon @ Breakthrough	7,800	7,600	24,800
Approx. Max. Vol. Gas (STP)/Vol. Carbon[3]	51,300	35,300	57,100

[1] Represents approximate average effluent concentration from empty reactor during majority of run time (see discussion in text).

[2] Based on 150 ppm average feed level, and cumulative total COS fed to each reactor up to breakthrough (see text for additional discussion).

[3] Calculated by assuming idealized stoichiometric front (vertical breakthrough curve) occurs at point where effluent equals 50% of empty reactor effluent.

FIGURE 4.3

REMOVAL OF COS IN SIMULATED SYNTHESIS GAS
VIA METAL-IMPREGNATED ACTIVATED CARBON
Run 5,4231-64 (See Table 4.3 for Run Details)

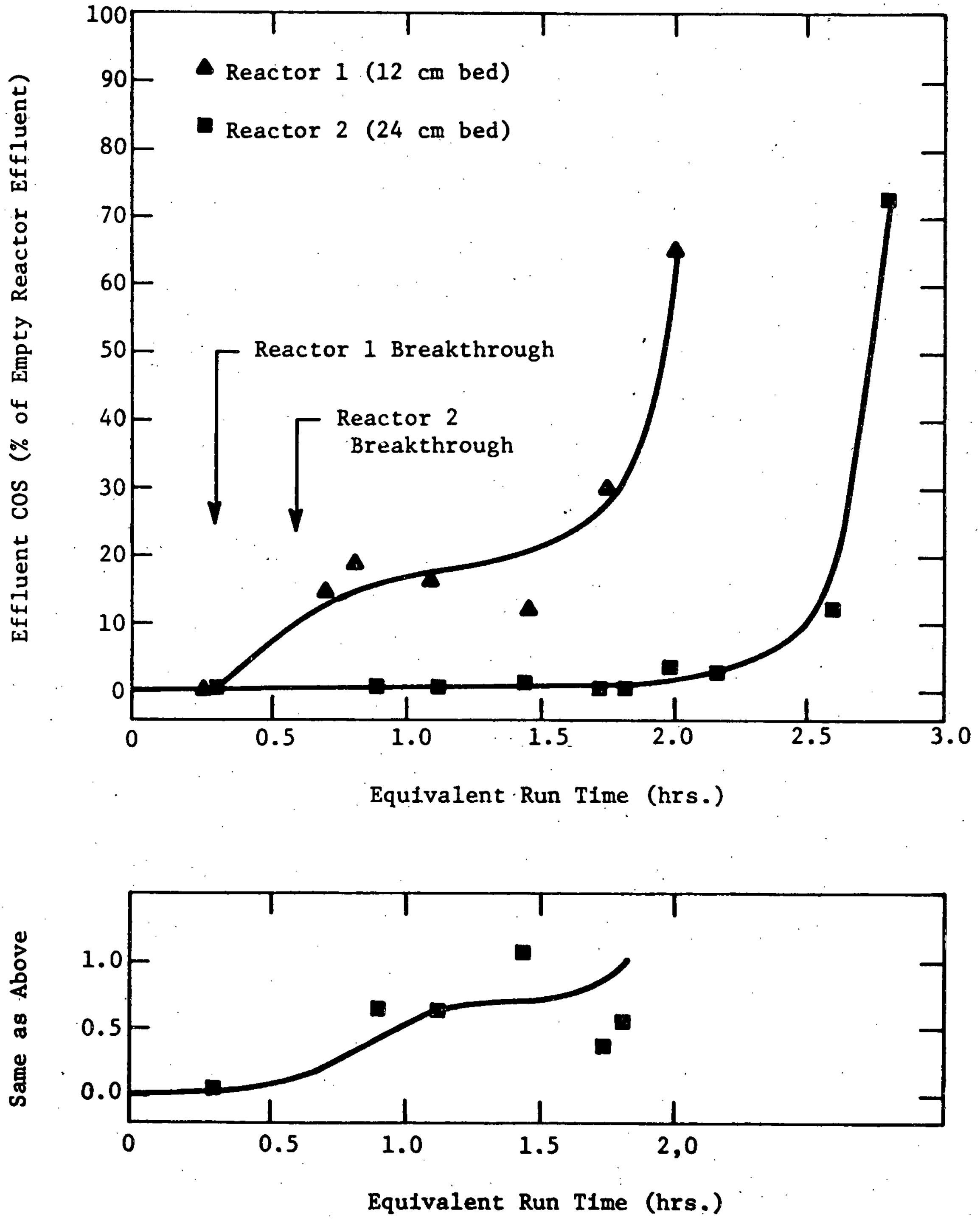
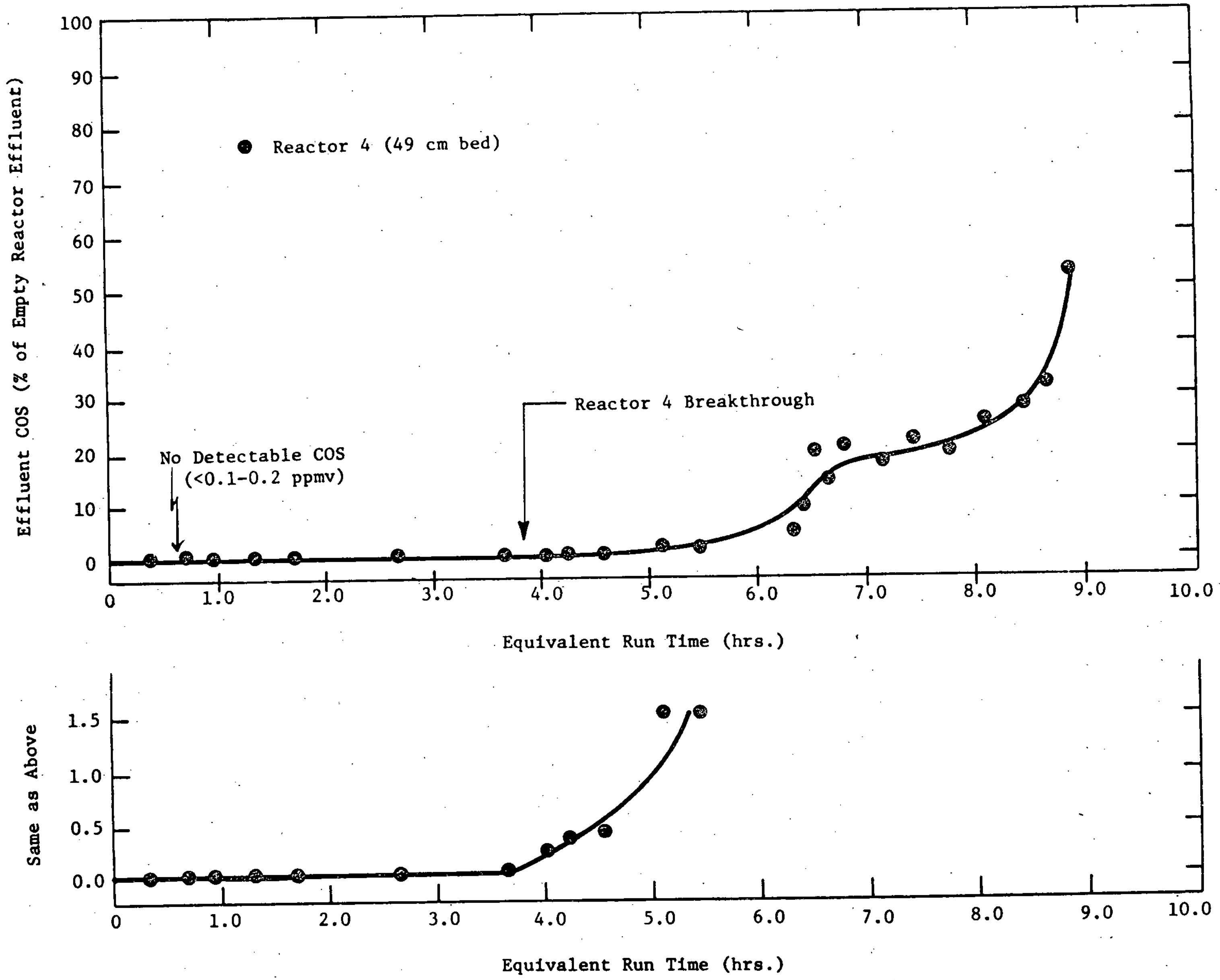


FIGURE 4.4

REMOVAL OF COS IN SIMULATED SYNTHESIS GAS VIA METAL-IMPREGNATED ACTIVATED CARBON
Run 5, 4231-64 (See Table 4.3 for Run Details)



multicomponent sulfur compound feeds are presented. However, the results obtained in this run indicated that the impregnated carbon is capable of removing COS down to target levels when it is present as the sole sulfur species in simulated synthesis gas processed at a superficial velocity and total system pressure comparable to that planned for the 72 TPD pilot plant.

4.2.4 Thiophene in Synthesis Gas

Experimentation using metal-impregnated (Cu and Cr oxides) activated carbon continued with thiophene (C_4H_4S) in simulated synthesis gas representing the sulfur compound fed. Thiophene contained in CO-free simulated synthesis gas (CO balance made up with N_2) was introduced via the sulfur feed system into water saturated sulfur-free simulated synthesis gas at a blend ratio of ∿1/9.

Three parallel beds were charged with impregnated carbon (Katalco 7-2 which is equivalent to Pittsburgh FCA) at levels of 0.8, 1.6, and 3.2 g, resulting in bed depths of 3.2, 6.4, and 12.8 cm, respectively. A superficial velocity of 1.37 cm/sec (equivalent to the current 72 TPD pilot plant design value) at 6.9 MPa (1000 psig) was maintained in all reactors. The remaining reactor was left uncharged to facilitate start-up and achievement of desired feed levels and occasionally monitor downstream thiophene levels during the run. After the desired feed concentration was reached, flow to the charged reactors was begun, while flow to the empty reactor was greatly reduced to conserve gas supplies. Run conditions and results are summarized in Table 4.4 while transient histories of thiophene effluent levels are shown in Figure 4.5.

Before discussing the results further, it is appropriate to point out that the run involving the deepest bed (reactor 4) was characterized by what is believed to be a "false breakthrough" in that detectable thiophene levels in the sampling line were noted before actual breakthrough occurred. Completion of experimentation with this particular reactor involved overnight shutdown of the unit. Prior to shutdown, no detectable (<0.1 ppm) thiophene in reactor 4 was noted. During the shutdown period, the reactor lost ∿1 MPa in pressure and it is possible some minor desorption from the carbon bed occurred. When the reactor was brought back to pressure and feed gas at the desired thiophene concentration sent to the reactor, the first sample taken (at ∿6.5 hours in Figure 4.5) contained ∿0.4 ppm C_4H_4S. If the breakthrough had been real, subsequent increases in effluent levels would have been expected, but instead none was noted. Instead, levels in the ∿0.1-0.3 ppm range were found during the next 3.5 hours, and were considered due to trace residual quantities that were not purged from lines leading from the reactor to the sampling port. Accordingly, breakthrough for reactor 4 was judged to take place when effluent levels first surpassed 0.4 ppm, which occurred after ∿10 hours of total run time. Instrument lag time was too short to be considered a factor in the results.

With the exception of that mentioned above, no detectable thiophene (<0.1 ppm) was found in the effluent of any of the reactors prior to breakthrough. Thiophene capacity levels at breakthrough for the 3.2 cm and 12.8 cm beds were calculated to be 6.5 and 8.6 wt% of carbon charged. The higher level found for the deeper bed was expected as unused bed capacity, at the same superficial velocity, should represent a smaller fraction of the total bed than would be the case for the shallow bed. Surprisingly, the lowest breakthrough capacity level was found for the 6.4 cm bed. However, it was

TABLE 4.4

REMOVAL OF THIOPHENE IN SIMULATED SYNTHESIS GAS USING METAL-IMPREGNATED ACTIVATED CARBON (RUN 7, 4231-82)

Carbon: Katalco 7-2 (12-30 mesh); 0.53 g/ml
Impregnants (as metals) = 8.0% Cu; 2.7% Cr

Feed Gas: ∿ 53 ppmv C_4H_4S ① in Simulated Synthesis Gas (H_2 ∿ 45%; CO ∿ 13.5%; CH_4 ∿ 35%; CO_2 ∿ 1%; C_2H_6 ∿ 1%; N_2 ∿ 4.5%; H_2O ∿ 0.08-0.09%) ②

Pressure: 6.9 MPa (1000 psig)

Temperature: 32.7 ± 0.5°C

Bed Diameter: 0.775 cm

	Reactor 1	Reactor 2	Reactor 4 ③
Carbon Charged (g)	0.80	1.60	3.20
Bed Recovered (g)	0.91	1.58	3.79
Bed Depth (cm)	3.2	6.4	12.8
Vol. Feed Rate (std. ml/sec)	41.7	41.7	41.7
Superficial Velocity, actual (cm/sec)	1.36	1.36	1.36
Space Velocity, STP (hrs^{-1})	99,400	49,700	24,900
Time to Breakthrough (hrs)	1.83	2.88	9.93
Effluent C_4H_4S Before Breakthrough (ppm)	<0.1	<0.1	<0.1
C_4H_4S Capacity @ Breakthrough (wgt % of Carbon)	6.50	5.18	8.65
Approx. Max. C_4H_4S Capacity (wgt % of Carbon) ④	11.4	7.8	10.4
Vol. Gas (STP)/Vol. Carbon @ Breakthrough	182,000	143,000	247,000
Approx. Max. Vol. Gas (STP)/Vol. Carbon ④	319,000	212,000	298,000

1. Represents time-averaged feed concentration prior to breakthrough. Individual averaged feed levels for reactors 1, 2 and 4 were 53.2, 53.9, and 52.2 ppmv, respectively.

2. CO and N_2 levels are slightly lower and higher (1.5% absolute), respectively, than usual synthesis gas levels due to dilution by CO-free (N_2 supplemented) thiophene carrier gas.

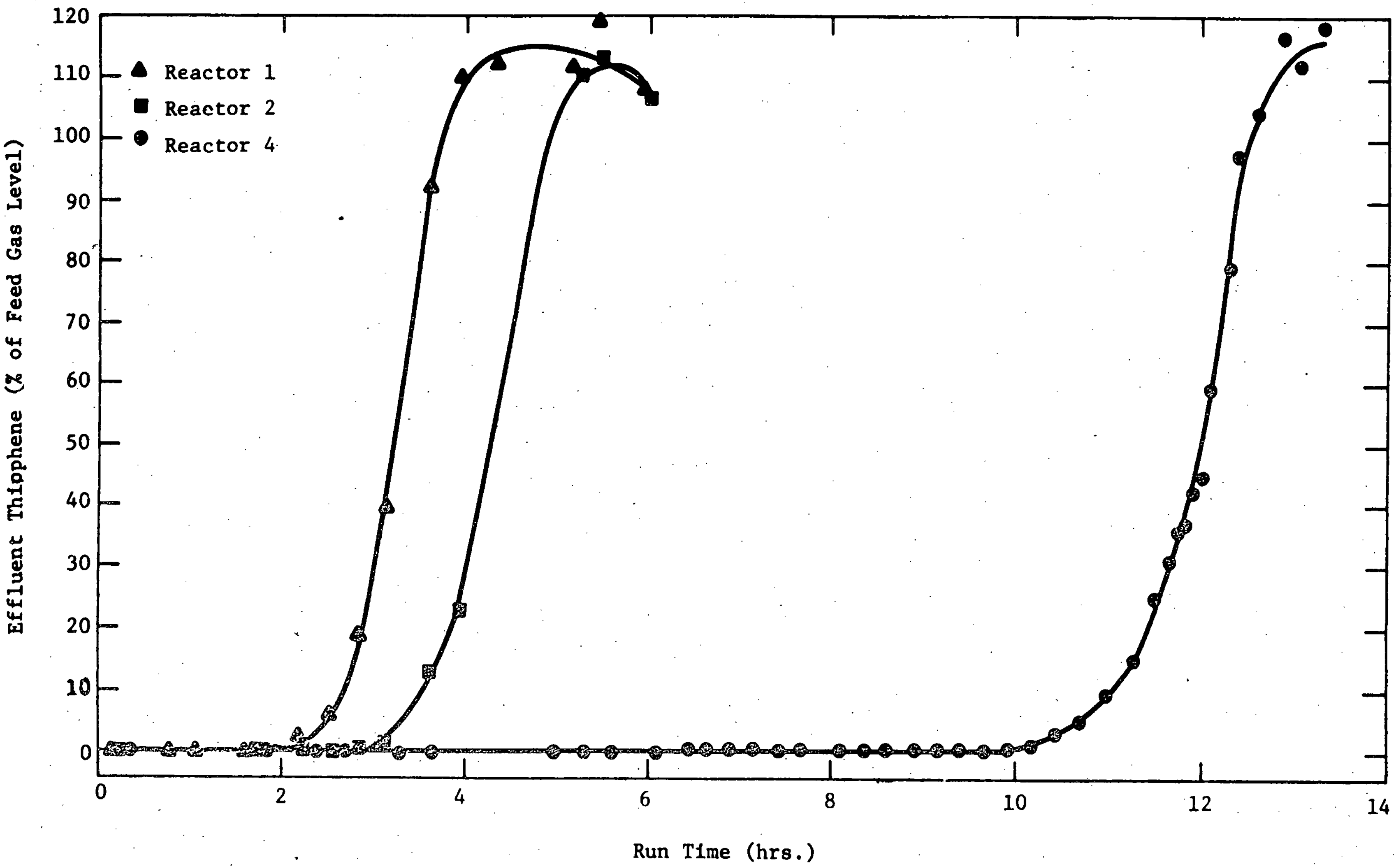
3. Results ignore "false breakthrough" as discussed in text.

4. Calculated by assuming idealized stoichiometric front (vertical breakthrough curve) occurs at point where thiophene effluent equals 50% of feed concentration. Factor applied to breakthrough results is ratio of run time to 50% point/run time to breakthrough.

FIGURE 4.5

REMOVAL OF THIOPHENE IN SIMULATED SYNTHESIS GAS VIA METAL-IMPREGNATED ACTIVATED CARBON

Run 7,4231-82 (See Table 4.4 for Run Details)



noted that while the weight of recovered bed from reactors 1 and 4 ranged from 10-20 wt % higher than that charged, that from reactor 2 was actually slightly less than its original charge. It is possible that a weighing error may have occurred in charging reactor 2 or a loss of material took place during the run.

Bed capacities were put on a common basis by estimating the dynamic equilibrium capacity of a fully saturated bed by using the technique which involves adjusting the breakthrough capacity by the ratio of the total run time for effluent to reach 50% of feed level to the time to reach breakthrough. When this idealized approximate technique was used, maximum adsorptive capacities (in theory, approachable in long beds) of 11.4% and 10.4% were calculated for the beds used in reactors 1 and 4, respectively, as given in Table 4.4

Regarding the breakthrough curves, as shown in Figure 4.5, two additional comments are in order. First of all, with regard to reactor 2, less than a desired number of data points was obtained during the development of the curve. This was due to the fact that a gas chromatograph problem occurred during this period which lasted approximately 50 minutes during which time no valid data were obtained. When the problem was corrected, the breakthrough for reactor 2 was essentially complete. Another phenomenon, noted for all three curves, was the fact that effluent breakthrough levels eventually reached a point where they exceeded levels of thiophene in the feed gas. For the two reactors (1 and 2) which were monitored past their breakthrough maxima, the trend back to equal feed and effluent levels was manifest. Such a phenomena is not unusual, however, when multiple adsorbates are present in a feed. Accordingly, the observation probably can be explained in terms of some displacement of a small portion of adsorbed thiophene by other species in the synthesis gas mix. Some system transient effects, related to location of sampling ports and fluctuations in feed concentration may also be involved.

In general, the experimental results indicate that the impregnated carbon is capable of removing expected maximum thiophene concentrations down to target levels when it is present as the only sulfur species in simulated synthesis gas processed at a pressure and superficial velocity equal to that planned for the 72 TPD pilot plant. Furthermore, adsorption capacity is reasonably high relative to COS.

4.2.5 Hydrogen Sulfide (Low Concentrations) in Synthesis Gas

Experimentation using impregnated (Cu and Cr oxides) activated carbon for removal of low concentrations of H_2S in simulated synthesis gas was carried out. The gas blending sulfur delivery system was used for this work.

Initial charges consisted of three parallel beds of impregnated carbon (Katalco 7-2, equivalent to Pittsburgh FCA) containing 0.8, 1.59, and 1.59 g, respectively, of material. Respective superficial velocities (at operating conditions) through each were 1.37 (equivalent to the 72 TPD pilot plant design value), 1.37, and 2.74 cm/sec. The remaining reactor was left uncharged to monitor downstream H_2S levels. Because H_2S, for introduction into simulated synthesis gas, was contained in a 55%/45% N_2/H_2 carrier gas and blending ratios were higher than planned, the ultimate composition of feed gas with respect to its other constituents varied somewhat from established target levels. With the exception of H_2, maintained at its ∿45% desired level, the remaining gross components were reduced by <u>ca</u> 20% (relative) levels while an N_2 level of <u>ca</u> 10% (absolute) higher was calculated. The entire feed gas blend also contained water, introduced via the saturator, at levels close to saturation at the conditions run.

After running the three reactors for ∿14 hours cumulative time over two days (with intermittent shutdown and system lock in) and having noted no detectable H_2S breakthrough, coupled with our limited supply of rapidly diminishing H_2S for maintaining necessary levels, it was decided to discontinue the feed to reactor 2 which would be expected to be the last to breakthrough. In addition, flow to the empty reactor was reduced to ∿10% of its original level. (Previous experimentation using 275 ppm average H_2S levels in dry simulated synthesis gas had yielded H_2S capacity levels to breakthrough in the 7% range.) Since physical adsorption of H_2S on carbon should be minimal vs. the believed major removal mechanism of conversion of CuO to CuS, it was expected that roughly comparable levels would also be eventually found, assuming conversion approached stoichiometric levels. A rough estimate of H_2S fed to the 14-hour point indicated such a total feed level was near and the decision was made to insure sufficient supply of H_2S at target pressure levels to obtain breakthrough curves on the two remaining charged reactors.

Surprisingly, after an additional 13 hours of cumulative run time (27 hours of total run time), still no breakthrough of either the 0.8 g (3.2 cm depth) bed operating at a superficial velocity of 1.37 cm/sec, or the 1.59 g bed running at 2.74 cm/sec was noted. It was then decided to discontinue feeding the deeper bed, as pressure in the H_2S cylinder had reached a point where maintenance of ∿1000 psig in the reactor was no longer possible. It then became necessary to reduce reactor pressure in the one remaining charged reactor to continue the run until breakthrough was achieved (and beyond), which eventually did take place after a total cumulative run time of ∿41 hours.

A summary of run conditions and results for this one reactor are given in Table 4.5, while the transient history of effluent levels (as % of feed), as well as pressure and superficial velocity maintained, is shown in Figure 4.6. As indicated in Table 4.5, H_2S capacity to breakthrough, calculated by summing total feed to reactor 1 during the entire period, amounted to 19.7 wt % of carbon charged. The run was continued for an additional ∿24 hours (total run time of ∿65 hours) to obtain information relative to breakthrough. Including the additional net H_2S removed during this period, the total H_2S removed up to termination amounted to 31.9 wt % of original carbon charged (equivalent to 22.1 wt % of bed recovered).

Such levels are many times higher than one would predict assuming the main H_2S removal mechanism is via irreversible conversion to CuS (H_2S physical adsorption assumed of very minor significance at the low partial pressure run) given the 8.0 wt % Cu level in the carbon used. Total sulfur

TABLE 4.5

REMOVAL OF H_2S IN SIMULATED SYNTHESIS GAS USING METAL-IMPREGNATED ACTIVATED CARBON (RUN 6, 4231-76)

Carbon: Katalco 7-2 (12-30 mesh); 0.53 g/ml
Impregnants (as metals) = 8.0% Cu; 2.7% Cr

Feed Gas: ∿21.7 ppm H_2S[1] in Simulated Synthesis Gas
(H_2 ∿ 45%; CO ∿ 12%; CH_4 ∿ 28.1%; CO_2 ∿ 0.8%;
C_2H_6 ∿ 0.8%; N_2 ∿ 13.3%; H_2O ∿0.05-0.1%)[2]

Initial Pressure[3]: 6.9 MPa (1000 psig)

Temperature: 32.5 ± 1°C

Bed Diameter: 0.775 cm

	Reactor 1
Carbon Charged (gm)	0.800
Bed Recovered (gm)	1.157
Bed Depth (cm)	3.2
Vol. Feed Rate (std. ml/sec)	41.7
Initial Superficial Velocity[3], actual (cm/sec)	1.37
Space Velocity, STP (hrs^{-1})	99,400
Time to Breakthrough (hrs)	40.7
Total Run Time (hrs)	64.8
Effluent H_2S Before Breakthrough (ppm)	<0.1-0.2
H_2S Removed at Breakthrough (wgt % of C)	19.7
H_2S Removed at End of Run (wgt % of C)	31.9
Vol. Gas Fed (STP)/Vol. Carbon @ Breakthrough	4×10^6

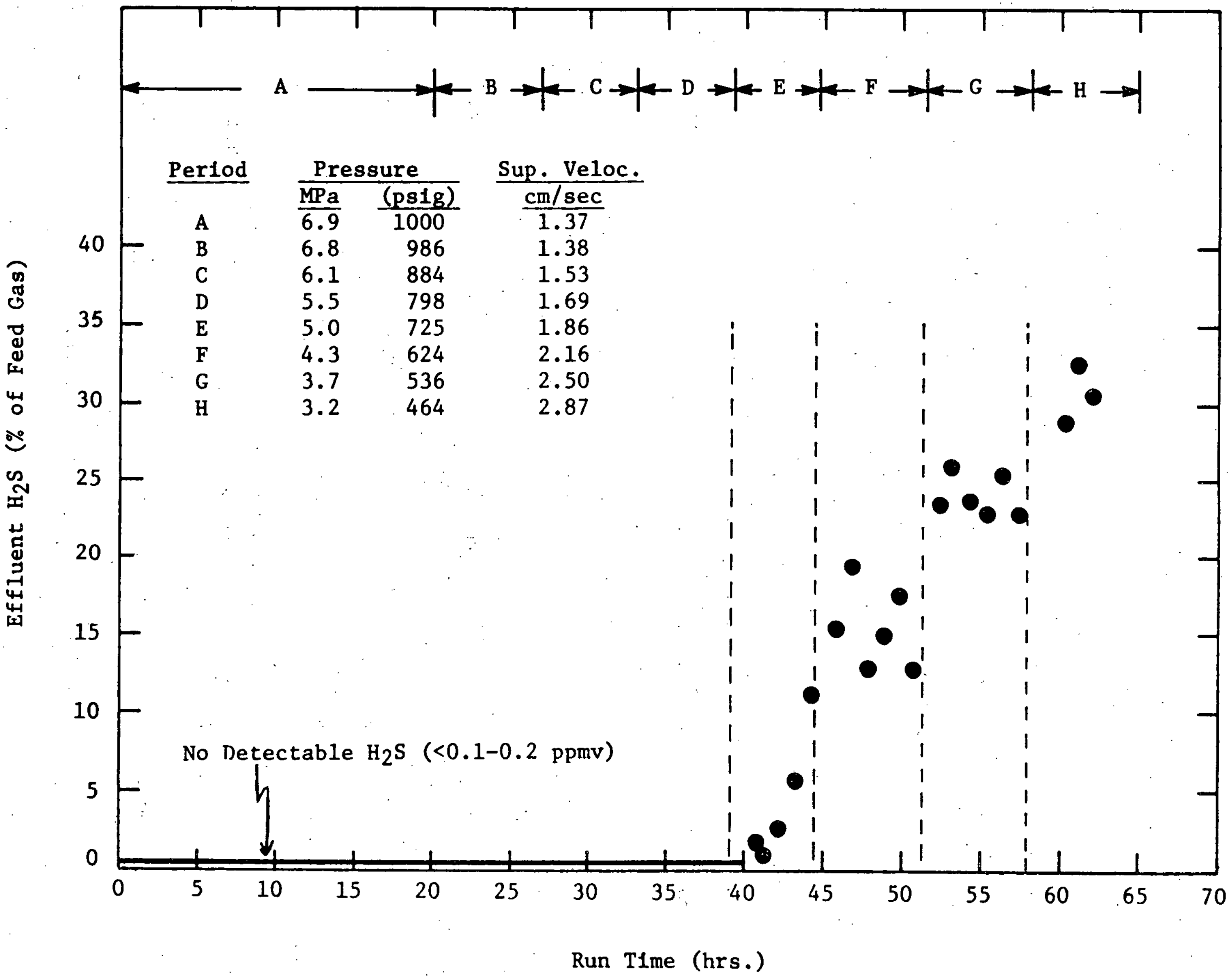
[1] Represents time-averaged feed concentration during entire run. Average concentration before breakthrough was 17.7 ppm; during remainder of run it was 28.5 ppm.

[2] Synthesis gas composition differs in some respects to that used previously due to dilution by H_2/N_2 H_2S carrier gas.

[3] See Figure 4.6 and discussion in text for additional information.

FIGURE 4.6

REMOVAL OF H_2S IN SIMULATED SYNTHESIS GAS VIA METAL-IMPREGNATED ACTIVATED CARBON
Run 6, 4231-76 (See Table 4.5 for Run Details)



Period	Pressure MPa	Pressure (psig)	Sup. Veloc. cm/sec
A	6.9	1000	1.37
B	6.8	986	1.38
C	6.1	884	1.53
D	5.5	798	1.69
E	5.0	725	1.86
F	4.3	624	2.16
G	3.7	536	2.50
H	3.2	464	2.87

analysis of the recovered bed was run to ascertain the validity of the high removal levels found. Initial testing, using a technique (Dietert analysis) considered valid for solids containing sulfur up to ∿7%, indicated much higher levels were present. Parr bomb testing was then done and yielded a sulfur content of the sample of 29.2 wt %. After deducting for sulfur present in the original virgin impregnated carbon (0.69 %) and converting to an equivalent H_2S basis, the result was 30.5 wt % of bed recovered, compared to the 22.1 wt % figure cited in the previous paragraph. Despite some discrepancy in agreement, the result of the sulfur analysis offers substantial support that the high removal noted is valid.

Additional evidence of high removal involved the deeper carbon bed (1.59 g, 6.4 cm) which was on stream for a cumulative time of 27 hours at the higher superficial velocity of 2.74 cm/sec before premature run termination. Using the approximate H_2S feed gas levels over this period yielded an H_2S pickup of 11.8 wt % of original carbon charged (11.1 wt % of the 1.69 g of material recovered). Total sulfur analysis by Parr bomb indicated, after making corrections for original sulfur and converting to an equivalent H_2S basis, an H_2S pickup of 14.3 wt % of recovered material compared to the calculated 11.1% level.

The reason for such high apparent H_2S removal is not clear. It is possible that in situ regeneration of CuS back to CuO and elemental sulfur promoted by possible oxygen contamination in sulfur-free synthesis gas, or the presence of the chromium oxide impregnant may be involved. Regarding the former, O_2 levels in the various gases originally charged to the unlined synthesis gas cylinders are sufficiently low that levels of well below 50 ppm would be expected in originally filled cylinders. Furthermore, given the high reducing conditions, very high H_2 partial pressure, and metal surfaces, it would be reasonable to assume its existence as molecular oxygen (as opposed to conversion to H_2O) would be short-lived.

Regardless of the specific mechanism(s), the evidence to date supports the fact that under the conditions addressed in our experimental program, mechanisms more complex than purely physical adsorption or irreversible conversion of H_2S to CuS were taking place. It is possible that, given the complexity of the feed system, the nature of the metal-impregnated carbon involved, and the run conditions present, catalytic conversion reactions involving H_2S (possibly to elemental sulfur or some other highly sorbed sulfur species?) were occurring.

In addition, it was observed that the color of recovered bed from the long duration run was not the typical pure black coloration observed after earlier reported runs involving COS in wet simulated synthesis gas or H_2S (at feed concentrations greater than an order of magnitude above this run). In contrast, the particle surface had an original dark green contrast which has tended to become dark blue with time as it was contained in its sampling bottle. In addition, the material from the bed run for a 27-hour cumulative time also displayed particles with similar coloration, as well as some that had a rust brown appearance possibly indicative of elemental sulfur or copper formation.

Returning to the earlier discussion regarding potential involvement of kinetic and catalytic phenomena, another interesting observation dealt with the form taken by the breakthrough curve. For illustration purposes, in Figure 4.6 are plotted only a fraction of the total number of data points taken. (In addition, those points taken upon daily resumption of the run, when transient effects are most pronounced, were not included.) Discounting the first period (E) when breakthrough was first manifest and effluent levels reached ∿10% during the first 4 hours of breakthrough prior to temporary shutdown, the remaining three periods (F, G, and H) were generally characterized by periods where the effluent levels (as % of H_2S concentration in feed gas) remained at relatively similar levels within each period. (The fluctuations within a given period, as shown in Figure 4.6, were not reasonable if, among other things, one realizes that, for a feed level of 20 ppm H_2S, for example, a difference of only 1 ppm in measured effluent resulted in a 5% absolute change in effluent levels as plotted.) Each of these periods was characterized by a reduction in reactor pressure (at the same volumetric flow condition) and, thus, an increase in superficial velocity, or decrease in bed residence time, (as well as a change in concentrations and/or partial pressures of feed gas constituents, and possibly increased fouling of the bed itself). It becomes nearly an impossible task to attempt to predict the influence of each of these on this highly complex system. However, viewing the approximate step-like effluent levels noted, a highly simplistic analysis in terms of response only to residence time change leads to the observation that the step-like appearance in the breakthrough curve is qualitatively correlated with a change in this parameter, which lends some support to the involvement of kinetic and catalytic phenomena.

4.2.6 Methyl Mercaptan in Synthesis Gas

Experimentation directed at evaluation of metal-impregnated (Cu and Cr oxides) activated carbon for removal of methyl mercaptan (CH_3SH) was conducted. Initially, three parallel beds were charged with 0.8, 1.6, and 3.2 gm of impregnated carbon (Katalco 7-2, equivalent to Pittsburgh FCA) representing bed depths ranging from 3.2 to 12.8 cm. Methyl mercaptan, in CO-free simulated synthesis gas (CO balance made up with N_2) was blended into sulfur-free simulated synthesis gas in the usual manner to provide feed gas to the reactors at 6.9 MPa (1000 psig). A superficial velocity of 1.36 cm/sec (equivalent to the current 72 TPD pilot plant design value) was maintained in each reactor.

Shortly after mercaptan-containing gas feed to the reactors was begun some problems were experienced. First of all, the primary pressure regulation system used in the sulfur-compound armored rotameter feed system was not functioning properly and prevented maintenance of a constant flow of mercaptan-rich gas for blending with mercaptan-free bulk feed gas. This problem was overcome by by-passing the primary pressure control system and using the pressure regulator on the gas cylinder itself to maintain desired feed pressure for this system. Concurrently, gas chromatograph problems developed which initially led to the erroneous belief that breakthrough of CH_3SH had occurred in the shallow bed reactor. Diagnosis and correction of the problem indicated this was not the case. Because of the uncontrolled nature that characterized the first 2-3 hours of the run, it was decided to discontinue feed to both the shallow and deep bed reactors, and keep only the intermediate bed reactor (Reactor 2) on-stream for the remainder of the day. This would minimize consumption of the mercaptan-rich gas used to prepare the reactor feed gas, and, depending on whether breakthrough did or did not occur during the day, would dictate the strategy regarding resumption of the run involving the other reactors.

Breakthrough did not occur, and a rough estimation of the CH_3SH fed indicated it to be ∿3.5 wt % of carbon charged. This figure, coincidentally, is approximately equal to the CH_3SH adsorption capacity expected (based on the isotherm equilibrium data of Grant, et al (8)) for unimpregnated Pittsburgh BPL carbon (essentially unimpregnated FCA) if allowed to equilibrate with pure CH_3SH at a total pressure equal to the average mercaptan partial pressure used in the run. Because great dissimilarities existed between our system and such an idealized system, utilization of such available data to predict performance in our system is speculative, at best.

Since breakthrough had not occurred, it was decided to resume the run the following day by continuing to feed Reactor 2, which had been locked in overnight, and initiating flow to a freshly charged shallow (3.2 cm) bed (Reactor 1). This approach was followed since we had established that the 6.4 cm bed removed CH_3SH to a level below detectable limits (∿0.2-0.3 ppm) while allowing appreciable run time to accumulate. Furthermore, CH_3SH capacity level was not known, and, given the limited supply of mercaptan-rich gas, a more conservative consumption rate was believed warranted.

Approximately 12 additional hours of run time were logged during the day before overnight shutdown and reactor lock-in was done. No breakthrough for either reactor occurred. Methyl mercaptan removal levels had now reached approximately 13% of carbon charged for Reactor 1 and ∿10% for Reactor 2. Both reactors were put on stream the next day. After ∿8 hours of run time, Reactor 2 was shut down. A rough calculation indicated removal levels of ∿23% of carbon charged for Reactor 1 and 15% for Reactor 2, without any indication of mercaptan breakthrough. These facts, coupled with our diminishing supply of high pressure mercaptan, dictated such an action.

Feed to Reactor 1 was continued for an additional 5 hours that day, followed by an additional 26.5 hours over the two following days for a cumulative total run time of 51.2 hours. Beginning at approximately 33 hours, reduction in reactor pressure below 6.9 MPa (1000 psig) was instituted because pressure in the mercaptan cylinder had dropped to a point where maintenance of original reactor pressure was not possible. A total of three step reductions in reactor pressure were done with the final one, carried out after ∿44 hours of run time, resulting in a reactor pressure of 5.2 MPa (∿750 psig) over the last ∿7 hours of the run. During all but the final 3 hours of the run, the volumetric feed (STP) to the reactor was held constant. Thus, resultant superficial velocity increased when the above pressure reductions were instituted.

Various considerations dictated that termination of the run be made. As a result, it was decided to markedly increase the loading to the system in an attempt to cause mercaptan breakthrough to occur. This consisted of more than doubling the volumetric feed to the reactor which was equivalent to a superficial velocity roughly triple the initial run value. In addition, the CH_3SH concentration in feed gas, which averaged ∿32 ppm for the entire run, was also increased such that when the detectable mercaptan in reactor effluent was finally noted after ~50 hours of total run time, the feed level had reached 48 ppm, while at the termination of the run, one hour later, it was ~56 ppm. During the brief one hour period over which detectable breakthrough effluent was monitored, no abrupt increase in effluent levels was noted (an increase of from 0.4 ppm to 1.0 ppm occurred).

A summary of run conditions and results for the run involving Reactor 1 is given in Table 4.6. As shown, the CH_3SH capacity to breakthrough, calculated by summing the total feed to Reactor 1 during the appropriate period, amounted to 63.5 wt % of original carbon charged. When the amount removed during breakthrough is also included, the figure increases to 67.5 wt % of carbon charged.

Such enormous pickup was surprising. It was speculated that various reaction mechanisms were operational that might be converting the mercaptan to other species such as H_2S or elemental sulfur. In Section 4.2.2, dealing with removal of H_2S via the same metal-impregnated carbon, very high H_2S removal levels were also noted. In that particular case, total sulfur analysis of the recovered bed actually indicated a somewhat higher sulfur pickup than that which had been calculated using feed gas rates and concentrations.

With this in mind, total sulfur analysis was done on the recovered bed from Reactor 1. It was recognized that the result should be lower than the originally calculated value because most of any sulfur in the form of sorbed CH_3SH would have been desorbed from the carbon at atmospheric pressure. The level found, however, was considerably lower than expected. A level of only 9.54% S was found, which, after deducting for original sulfur present in fresh impregnated carbon (0.69%), converting to an equivalent CH_3SH basis as well as a carbon charged basis, amounted to an equivalent CH_3SH pickup of only 16.0 wt % of carbon charged. (Subsequent sample analyses also confirmed the original sulfur analysis.) Thus, only 25% of the CH_3SH calculated as having been removed was accounted for.

It is possible that under the experimental conditions used, sufficiently high sorption (physical and possibly chemical) of CH_3SH may have occurred, followed by subsequent desorption after system depressurizing, to account for the results. Unfortunately, no monitoring of effluent was done when the experimental unit was depressurized prior to discharging the reactors. The possibility of conversion of CH_3SH to non-adsorbed sulfur species is unlikely as these would have appeared as large extraneous peaks in the g.c. chromatograms. Such were not noted.

One additional item is worth noting. This involves the bed recovered from Reactor 2 whose operation was prematurely terminated. As indicated earlier, a CH_3SH pickup of 15.0 wt % of carbon charged was calculated for the period during which the reactor was fed. Total sulfur analysis of the recovered bed (again confirmed by additional analysis) indicated a level of 9.38% sulfur, which, when the same equivalency exercise was applied as mentioned earlier, resulted in a CH_3SH pickup of 15.4 wt % of carbon charged. Thus, agreement was remarkably close. In addition, this result is essentially identical to the 16.0% figure obtained with Reactor 1. Whether or not this

TABLE 4.6

REMOVAL OF METHYL MERCAPTAN IN SIMULATED SYNTHESIS GAS USING METAL-IMPREGNATED ACTIVATED CARBON (RUN 8, 4231-86)

Carbon: Katalco 7-2 (12-30 mesh); 0.53 g/ml
Impregnants (as metals) = 8.0% Cu; 2.7% Cr

Feed Gas: ∿ 31.7 ppmv CH_3SH① in Simulated Synthesis Gas (H_2 ∿ 45%; CO ∿ 12.1%; CH_4 ∿ 35%; CO_2 ∿ 1%; C_2H_6 ∿ 1%; N_2 ∿ 5.9%; H_2O ∿ 0.06 - 0.09%)②

	Reactor 1
Carbon Charged (gm)	0.800
Bed Recovered (gm)	0.952
Bed Diameter (cm)	0.775
Bed Depth (cm)	3.2
Temperature (°C, ± 0.3)	32.6
Initial Pressure[3] (MPa)	6.9
Initial Vol. Feed Rate③ (std. ml/sec)	41.7
Initial Superficial Velocity③, actual (cm/sec)	1.36
Initial Space Velocity③, STP (hrs^{-1})	99,500
Time to Breakthrough (hrs)	50.3
Total Run Time (hrs)	51.2
Effluent CH_3SH Before Breakthrough (ppm)	<0.2 - 0.3
CH_3SH Removed at Breakthrough (wgt % of C)④	63.5
CH_3SH Removed at End of Run (wgt % of C)	67.5
Vol. Gas Fed (STP)/Vol. Carbon @ Breakthrough	5.25×10^6

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1. Represents time-averaged feed concentration prior to breakthrough.

2. CO and N_2 levels are slightly lower and higher (2.9% absolute), respectively, than target synthesis gas levels due to dilution by CO-free, N_2- supplemented, CH_3SH carrier gas.

3. Changes during run were as follows:

Time Interval hrs.	Pressure MPa (psig)	Gas Feed std. ml/sec	Superfic. Vel. cm/sec	Space Vel. hrs^{-1}
0 -32.6	6.9 (1000)	41.7	1.36	99,500
32.6-37.9	6.4 (928)	"	1.46	"
37.9-43.8	5.7 (826)	"	1.64	"
43.8-48.4	5.2 (754)	"	1.79	"
48.4-49.2	" "	92.8	3.99	221,000
49.2-51.2	" "	98.3	4.22	235,000

4. See discussion in text.

result might be indicative of a sulfur removal mechanism which is limited, at ∿16% pickup, and irreversible with respect to desorption of the sulfur species when pressure is reduced to atmospheric, is not known. Had Reactor 2 been operated longer, additional evidence of this possibility may have accrued.

The results indicate that the impregnated carbon is quite effective in reducing maximum methyl mercaptan concentrations expected down to target levels when present as the sole sulfur species in simulated synthesis gas processed at conditions consistent with those planned for the 72 TPD pilot plant. Furthermore, the capacity data obtained indicates CH_3SH to be the most strongly adsorbed of the sulfur species examined (H_2S, COS, thiophene, and CH_3SH) as single component contaminants. Accordingly, one would not expect methyl mercaptan to strongly impact on the design of a carbon adsorption system.

4.2.7 Carbon Disulfide in Synthesis Gas

Experimentation using metal-impregnated (Cu and Cr oxides) activated carbon for removal of CS_2 in simulated synthesis gas was carried out. CS_2, contained in CO-free simulated synthesis gas (CO balance made up with N_2) was fed via the armored rotameter sulfur feed system into water-saturated, sulfur-free simulated synthesis gas at a blend ratio of ∿1/10.

Two series of runs were made with impregnated carbon (same material lot currently planned for use at the SYNTHANE 72 TPD pilot plant; namely, Katalco 7-2, which is equivalent to Pittsburgh FCA) at a superficial velocity and pressure equal to the SYNTHANE design values.

In the first series (Run 9), beds containing 0.8 g (3.2 cm depth) and 1.6 g (6.4 cm depth), respectively, were used. Various reasons prompted initial use of such shallow beds, with the main one based on our initial crude estimate of possible high bed capacity and long run duration. Since we were not aware of any published data regarding performance applicable to our specific system and needs, use was made of the published isotherm equilibrium data for CS_2 on an unimpregaated activated carbon (Grant, R. J., <u>et al</u> (8)) as a guide to possible performance. This was done in recognition of the fact that such data have, in general, not proven to be applicable in much of our work. Based on these data, ball-park estimates of potential breakthrough capacities in the range of 5 wt % of carbon charged, or higher, were thought possible for feeds of ∿12 ppm CS_2 at 6900 kPa (1000 psig). Such capacities translate into potential run times on the order of 7 hours (or higher) and 14 hours (or higher) for the two beds in question. When the beds were run, breakthrough in both cases occurred in less than 1.5 hours. Because of potential system transient effects, such short breakthrough times can lack desired accuracy. Coupling this with the sensitivity of capacity to an accurate measure of breakthrough time, the reliability of results (especially for the shallower bed) based on such short breakthrough times was questionable.

Accordingly, a second run series (Run 11) was made using beds of 3.2 g (12.8 cm depth) and 6.4 g (25.6 cm depth). (As an aside, another run series (Run 10) was made, but was more qualitative in nature and served as a preliminary guide to the deeper bed series which followed.) For the Run 11 series, CS_2 average feed level prior to breakthrough was ∿3 ppm to an average level of ∿12 ppm for Run 9. Breakthrough times of ∿3.4 hours and 6.3 hours were found for the two beds run.

Operating conditions for both series of runs are summarized in Table 4.7. Transient histories of CS_2 effluent levels are shown in Figure 4.7. In all cases, no detectable CS_2 (<0.1 ppmv) was found in effluents prior to breakthrough. For the 12.8 cm and 25.6 cm beds used in Run 11, capacity levels at breakthrough were approximately 0.7 wt % of carbon charged. Bed capacities were put on a common basis by estimating the dynamic equilibrium capacity of a fully saturated bed by using the idealized technique previously discussed. This involves adjusting the breakthrough capacity by the ratio of total run time for effluent to reach 50% of feed level to the time to reach breakthrough. Use of this approximate method resulted in maximum adsorptive capacities (in theory, approachable in very long beds) of 0.95 and 0.80 wt % of carbon charged for the 12.8 cm and 25.6 cm beds, respectively. Taking into account the concentration of CS_2 fed, these maximum capacities translated into approximate maximum volume of gas (STP) treated/volume of carbon charged of 109,000 and 95,000, respectively.

The above capacities were lower than those reported in the past for H_2S, CH_3SH, and thiophene. However, the maximum vol. gas treated/vol. carbon charged parameter was approximately twice the 57,000 figure found for COS run at an average 150 ppm feed concentration in a 49 cm bed. It should be pointed out that a 150 ppm COS level is nearly twice the estimates of maximum levels expected. However, reducing COS feed levels by 50% would not be expected to double the volume of gas treated in as much as adsorption capacity is generally proportional to partial pressure of adsorbate, and much of the benefit gained by such a reduction could be cancelled.

In summary, the experimental results indicated that the impregnated carbon is capable of removing expected maximum CS_2 concentrations down to target levels when it is present as the sole sulfur species in simulated synthesis gas processed at a pressure and superficial velocity equal to that eventually planned for the 72 TPD pilot plant. In terms of maximum volume of gas treated/volume of carbon charged, its capacity is less than that found for H_2S, CH_3SH, and thiophene, but greater than that found for COS, which remains as the sulfur species which would be expected to limit adsorption tower service time. Multicomponent sulfur specie experimentation, discussed next, provided the crucial test for the impregnated carbon system, and information on the influence of combined sulfur species on the removal of individual components.

4.3 Multicomponent Adsorption Data

The true capacity of the metal impregnated carbon adsorbent for the sulfur compounds of interest can only be determined by tests using the full spectrum of compounds simultaneously. Thus, multicomponent adsorption tests were made and are discussed below.

4.3.1 Four Component Sulfur Blends - Carbonyl Sulfide, Carbon Disulfide, Thiophene, Methyl Mercaptan

Experimentation was carried out directed at simultaneous removal of COS, CS_2, C_4H_4S (thiophene), and CH_3SH in simulated synthesis gas using

TABLE 4.7

REMOVAL OF CS_2 IN SIMULATED SYNTHESIS GAS USING METAL-IMPREGNATED ACTIVATED CARBON (RUN 9, 5277-7; RUN 11, 5277-12)

Carbon: Katalco 7-2 (12-30 mesh); 0.53 g/ml
Impregnants (as metals) = 8.0% Cu; 2.7% Cr

Simulated Synthesis Gas①: $H_2 \sim 45\%$; $CH_4 \sim 35\%$; $CO \sim 13.2\text{-}13.5\%$; $N_2 \sim 4.5\text{-}4.8\%$; $CO_2 \sim 1\%$; $C_2H_6 \sim 1\%$; $H_2O \sim 0.05\text{-}0.07\%$

Pressure: 6900 kPa (1000 psig)

Temperature: 33.2 ± 0.4°C

Superficial Velocity: 1.36 cm/sec (at run conditions)

Vol. Feed Rate: 41.7 std. ml/sec

Bed Diameter: 0.775 cm

	Run 9②		Run 11	
	React. 1	React. 2	React. 1	React. 2
CS_2 Avg. Feed (ppmv)③	10.9	11.1	14.3	13.9
Carbon Charged (g)	0.80	1.60	3.20	6.40
Bed Recovered (g)	0.82	1.64	3.48	7.00
Bed Depth (cm)	3.2	6.4	12.8	25.6
Space Velocity, STP (v/v/hr)	99,500	49,700	24,900	12,400
Breakthrough Time (hrs)	1.05	1.38	3.37	6.30
Stoich. Breakthrough Time (hrs)④	1.70	2.23	4.39	7.65
Effluent CS_2 Before Breakthrough (ppmv)	<0.1	<0.1	<0.1	<0.1
CS_2 Capacity @ Breakthrough (wgt % of C)	0.69	0.46	0.73	0.66
Approx. Max. CS_2 Capacity (wgt % of C)⑤	1.12	0.75	0.95	0.80
Vol. Gas (STP)/Vol. Carbon @ Breakthrough	104,400	68,800	83,700	78,300
Approx. Max. Vol. Gas (STP)/Vol. Carbon⑤	169,000	111,000	109,000	95,100

1. CO and N_2 levels are slightly lower and higher (∿1.7% absolute) than target levels due to dilution by CO-free, N_2-supplemented, CS_2 carrier gas.

2. Run 9 results, especially for Reactor 1, judged less reliable than Run 11 results due to short bed used (see discussion in text).

3. Time-averaged feed concentration prior to breakthrough.

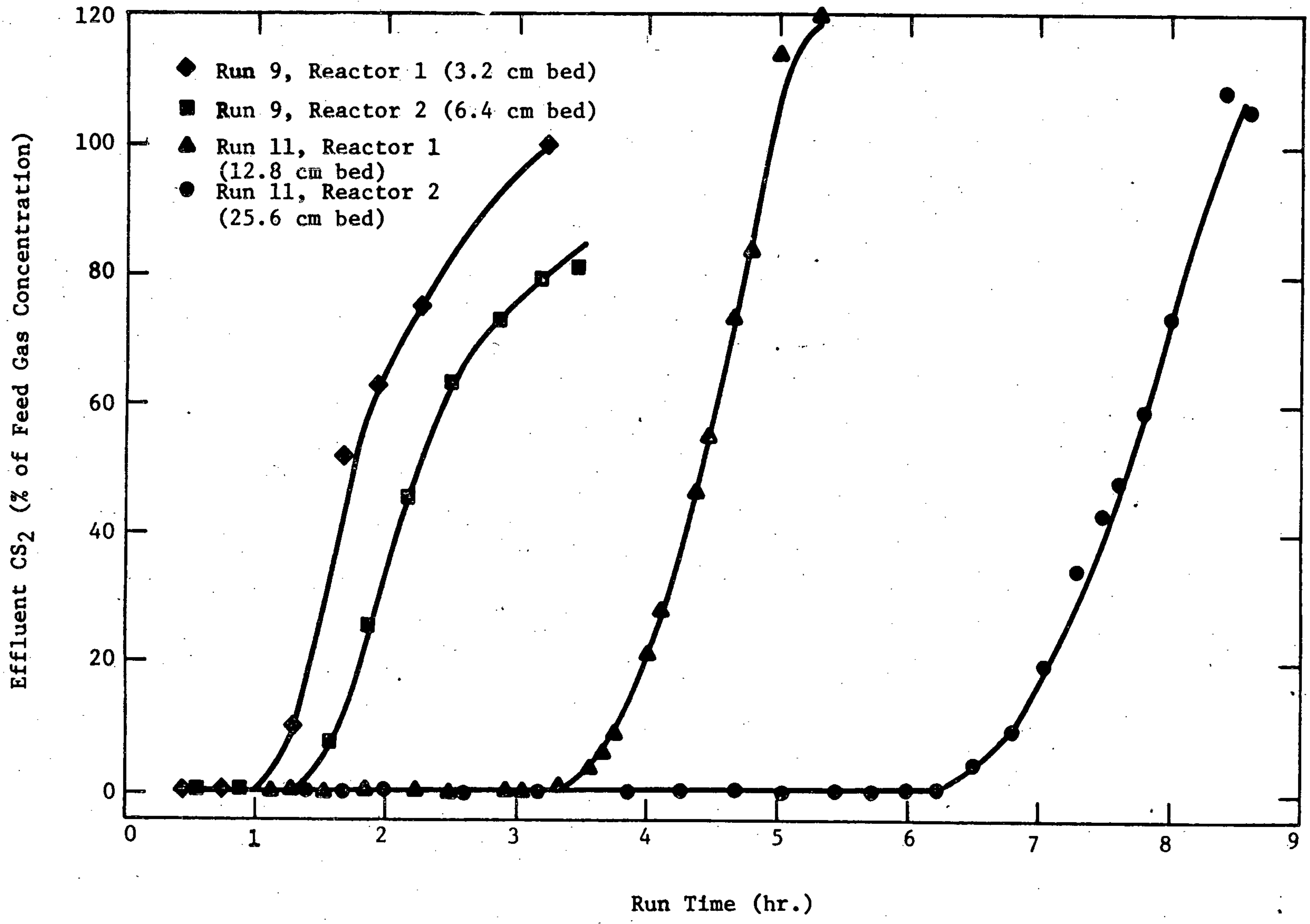
4. Time for effluent concentration to reach 50% of concentration in feed gas (see, e.g., Lukchis, G.M., Chem. Eng'g., June 11, 1973, p. 111).

5. Calculated by multiplying breakthrough result by Stoichiometric Breakthrough Time/Breakthrough Time (see reference cited in footnote 4 for further details). **Result represents approximate saturation levels, or loadings expected in an infinitely long bed.**

FIGURE 4.7

REMOVAL OF CS_2 IN SIMULATED SYNTHESIS GAS VIA METAL-IMPREGNATED ACTIVATED CARBON

Run 9,5277-7; Run 11,5277-12 (See Table 4.7 for Run Details)



metal-impregnated activated carbon. The four sulfur compounds were contained in an N_2 carrier gas which was fed via the armored rotameter sulfur feed system into water-saturated, sulfur-free simulated synthesis gas at a blend ratio of ∿1/10. For various reasons, previously discussed, multicomponent sulfur specie experimentation was first carried out using 4-component (no H_2S) sulfur feeds, with 5-component work to be done subsequently.

The metal-impregnated carbon used was Katalco 7-2 (equivalent to Pittsburgh FCA) which is the same material planned for the SYNTHANE 72 TPD pilot plant. Conditions of pressure (6900 kPa (1000 psig)) and superficial velocity (1.36 cm/sec) were maintained at levels eventually planned for the SYNTHANE facility. Concentration of three of the four sulfur compounds in synthesis feed gas was within target levels. In the case of methyl mercaptan, levels approximately twice the target feed levels were used.

Two parallel beds were charged with impregnated carbon at levels of 3.2 g and 9.6 g, resulting in bed depths of 12.8 and 38.4 cm, respectively. Because considerable time (∿25 minutes) is required to analyze a single sample containing all of the above sulfur compounds via the flame photometric g.c., experimentation was limited to two beds only. This allowed monitoring of feed and effluent levels to be manageable, and minimized the possibility of "missing" all or part of a breakthrough, as well as increased our response time with respect to making necessary corrections to maintain feed concentrations at desired levels.

Run conditions and results are summarized in Table 4.8. Transient histories of the effluent levels for each of the sulfur compounds for the two beds are shown in Figures 4.8 and 4.9, respectively. Prior to breakthrough, effluent levels were below detectability limits of the g.c. which were <0.1-0.2 ppm for most of the sulfur species.

The order of breakthrough found was COS first, then CS_2 and thiophene. No breakthrough was noted for CH_3SH during the entire period each bed was kept on stream. The above order was that expected based on results obtained with the above compounds as single sulfur specie feeds. The capacities (as wt % of carbon charged) at breakthrough are given in Table 4.8. Since concentrations of each sulfur compound differ with respect to each other, a more direct measure of relative system capacity is the quantity Volume of Gas (STP) Treated/Volume of Carbon Charged. The values of this parameter obtained at breakthrough, for the two beds run, are given in Table 4.8 for the three species for which breakthrough was observed. They range from ∿22,000 for COS to ∿230,000 for thiophene.

Another point of interest to note from the breakthrough curves depicted in Figures 4.8 and 4.9 is the maxima exhibited by some of the component breakthrough curves. Such a phenomenon is not unusual, however, when multiple adsorbates are present in a fuel. The observation can be explained in terms of some displacement of a small portion of adsorbed CS_2 or thiophene by other adsorbing gases in the gas mixture.

In order to eliminate the influence of bed length, it is also possible to estimate the dynamic equilibrium capacity of a fully saturated bed, or the capacity approachable in an infinitely long bed. The technique,

TABLE 4.8

REMOVAL OF COS, CS_2, THIOPHENE, AND CH_3SH IN SIMULATED SYNTHESIS GAS USING METAL-IMPREGNATED ACTIVATED CARBON (RUN 12, 5277-22)

Carbon: Katalco 7-2 (12-30 mesh); 0.53 g/ml; Impregnants (as metals) = 8.0% Cu; 2.7% Cr

Simulated Synthesis Gas①: $H_2 \sim 40.9\%$; $CH_4 \sim 31.8\%$; $CO \sim 13.6\%$; $N_2 \sim 11.8\%$; $CO_2 \sim 0.91\%$; $C_2H_6 \sim 0.91\%$; $H_2O \sim 0.05\text{-}0.07\%$

Pressure = 6900 kPa (1000 psig); Temperature = 33.5 ± 0.5°C; Bed Diameter = 0.775 cm

Superficial Velocity (actual) = 1.36 cm/sec; Vol. Feed Rate = 41.7 std. ml/sec

	Reactor 1				Reactor 2			
Carbon Charged (g)	3.20				9.60			
Bed Recovered (g)	3.62				11.39			
Bed Depth (cm)	12.8				38.4			
Space Velocity, STP (v/v/hr)	24,900				8,290			
	COS	CS_2	C_4H_4S	CH_3SH②	COS	CS_2	C_4H_4S	CH_3SH②
Avg. Feed Before Breakthrough (ppmv)③	80.0	8.4	37.2	45.9	82.0	8.7	38.3	47.9
Avg. Feed During Breakthrough (ppmv)④	85.4	8.7	38.0		88.2	8.8	43.0	
Breakthrough Time (hr)	0.88	3.85	8.85	>22.6	2.77	11.4	27.4	>31.0
Stoich. Breakthrough Time (hr)⑤		4.83	10.3			13.2	29.2	
Effluent Concen. Before Breakthrough⑥	<0.2	<0.1	<0.1	<0.3-0.4	<0.2	<0.1	<0.1	<0.3-0.4
Capacity at Breakthrough (wt% of C)	0.85	0.49	5.49	>9.87	0.91	0.49	5.82	>4.72
Approx. Max. Capacity (wt% of C)⑦	5.61	0.61	6.41		6.01	0.57	6.22	
Vol. Gas (STP)/Vol. Carbon @ Breakthrough	22,000	95,700	220,000	>561,000	22,900	94,100	227,000	>257,000
Approx. Max. Vol. Gas (STP)/Vol. Carbon⑦	145,000	120,000	257,000		151,000	109,000	242,000	

***Footnotes on next page.**

Table 4.8 Footnotes:

1. Composition of all components, except N_2, ~10% (relative) lower than target levels due to dilution by N_2 carrier gas for sulfur compounds. N_2 levels ~8.8% (absolute) higher than target level.

2. No breakthrough observed for CH_3SH in either reactor. This is reflected in tabulated results.

3. Time-averaged feed concentration prior to breakthrough.

4. Time-averaged feed concentration during period bounded by initiation of breakthrough to point where effluent concentration = feed gas concentration.

5. Time for effluent concentration to reach 50% of concentration in feed gas (see, e.g. Lukchis, G. M., Chem. Eng'g., June 11, 1973, p. 111). Not calculated for COS. See discussion in text.

6. Levels indicated represent detectability limits for the specific g.c. conditions used.

7. The quantities listed represent approximate saturation levels, or loadings expected in an infinitely long bed. For all except COS, value determined by multiplying breakthrough result by Stoichiometric Breakthrough Time/Breakthrough Time (see reference cited in footnote 5 for further details). For COS, value determined by subtracting cumulative effluent COS from cumulative feed COS, up to point where feed concentration $\simeq$ effluent concentration.

FIGURE 4.8

REMOVAL OF COS, CS_2, THIOPHENE, AND CH_3SH IN SYNTHESIS GAS VIA METAL-IMPREGNATED ACTIVATED CARBON
Run 12, 5277-22 (See Table 4.8 for Run Details)

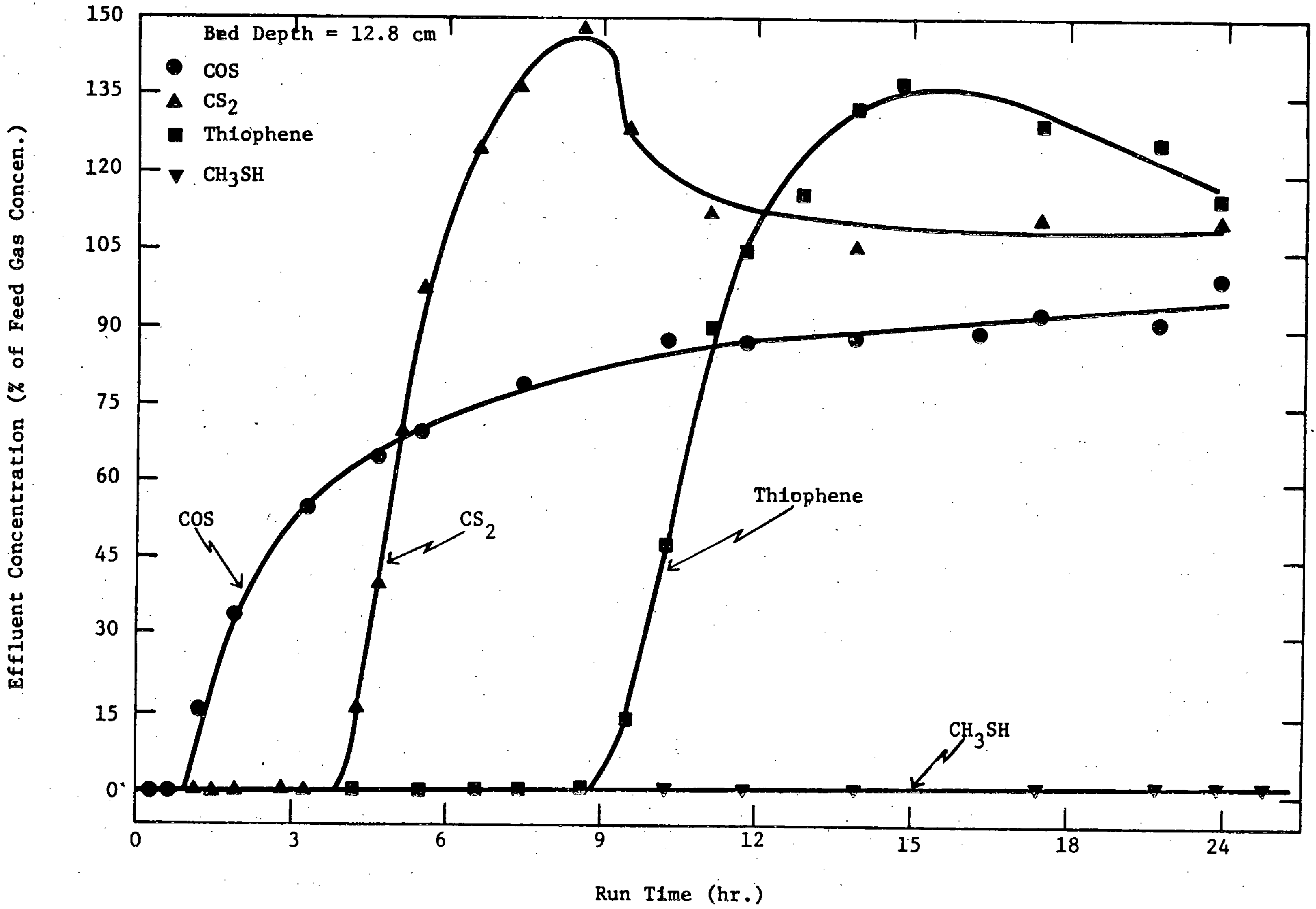
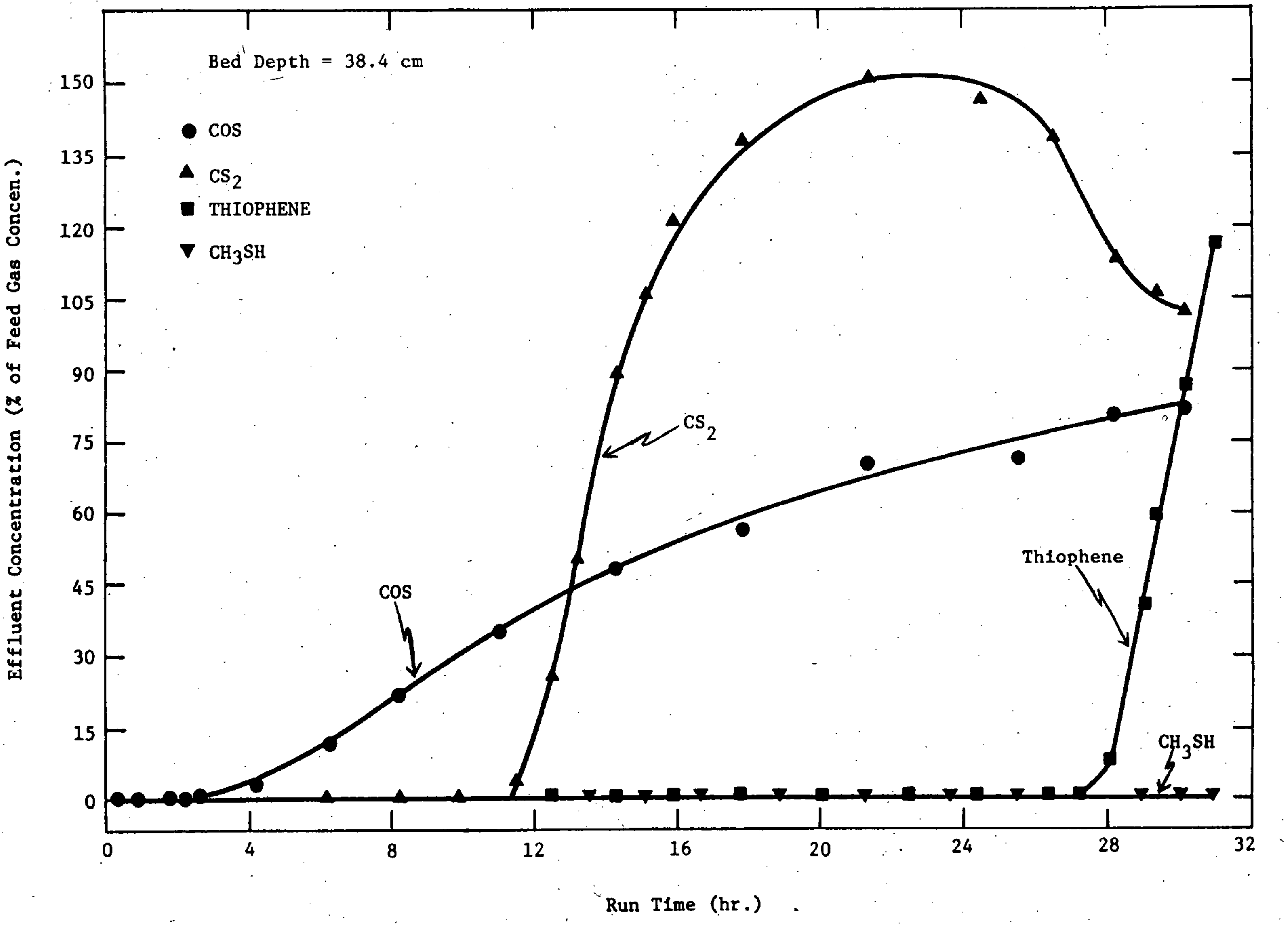


FIGURE 4.9

REMOVAL OF COS, CS_2, THIOPHENE, AND CH_3SH IN SYNTHESIS GAS VIA METAL-IMPREGNATED ACTIVATED CARBON
Run 12, 5277-22 (See Table 4.8 for Run Details)



used for both CS_2 and thiophene, has been discussed and involves multiplying the breakthrough capacity result by the ratio of Stoichiometric Breakthrough Time/Breakthrough Time. For both of these species, the increase in breakthrough capacity ranged only from ∿10-25%. This follows since the breakthrough curves were quite steep indicative of very short mass transfer zones for each of these compounds at the conditions run. This approximate technique is itself only applicable to cases where the bed used is of sufficient length to contain the specie "mass-transfer zone" (see reference cited in footnote 5 of Table 4.8). A bed meets this criterion if the time for a breakthrough curve to fully develop (i.e. the time from initiation of breakthrough to the point where effluent = feed concentration) is less than twice the bed breakthrough time. As shown in Figures 4.8 and 4.9, this was the case for CS_2 and thiophene, but not the case for COS which, although breaking through very rapidly, displayed very slowly developing breakthrough curves, or long "mass-transfer zones".

The method used to approximate the saturation capacity for the carbon with respect to COS sorption consisted of subtracting the cumulative effluent COS from the cumulative feed COS, from the beginning of the run up to the point where feed concentration ≃ effluent concentration. This exercise resulted in a value of Maximum (i.e. saturation) Volume of Gas (STP) Treated/Volume of Carbon Charged of ∿150,000 for COS and the deepest bed used, compared to the ∿23,000 breakthrough figure found for COS at the conditions addressed. The actual value obtainable in a finite-size, commercial scale bed would be less than this 150,000 figure, and would depend on the length of the bed, as well as the length of the "mass-transfer zone". This latter quantity is difficult to estimate from experimentation based on beds whose length is less than the mass-transfer zone, as was the case in our work. However, it would appear, based on rough approximations and the results obtained with the 4-component feeds, that breakthrough of both COS and CS_2 could occur at approximately comparable times when fed at 80 and 8 ppmv levels, respectively, to a bed whose length was equal to the 5.2 m (17 ft.) planned for the SYNTHANE pilot plant.

In summary, the experimental results with the four sulfur component feed indicate that the impregnated carbon is capable of removing expected maximum COS, CS_2, thiophene, and CH_3SH concentrations down to target levels when they are present together in simulated synthesis gas processed at a pressure and superficial velocity equal to that planned for the SYNTHANE pilot plant. Capacity levels, as volume gas treated/volume of carbon charged for the three species for which breakthrough was observed (COS, CS_2, and thiophene) were similar to those found during single specie experimentation, except for COS. In this case, the saturation capacity level was higher than previously found for the single component work, and is of such a magnitude that COS and CS_2, at their expected levels, could have approximately equal breakthrough times in a bed of length equal to that planned for SYNTHANE. Better predictions of system performance will be possible based on the five sulfur component work discussed next.

4.3.2 Five Component System - Carbonyl Sulfide, Carbon Disulfide, Thiophene, Methyl Mercaptan and Hydrogen Sulfide

Experimentation was conducted involving simultaneous removal of COS, CS_2, C_4H_4S (thiophene), CH_3SH, and H_2S in simulated synthesis gas using metal-impregnated activated carbon. Dynamic blending of three gas streams in association with the use of two armored rotameter sulfur feed systems was done to obtain the ultimate feed gas stream. Four of the five sulfur compounds (all except H_2S) were contained in a CO-free, N_2-supplemented simulated synthesis gas, while the H_2S was fed in a 45% H_2/55% N_2 carrier gas. These, in turn, were mixed with water-saturated, sulfur-free simulated synthesis gas. The blend distribution used was 2 parts of the four sulfur compound stream, 1 part of the H_2S-containing stream, and 16 parts of the sulfur-free synthesis gas stream. Four of the five sulfur compounds were essentially at target concentration levels. Methyl mercaptan, however, was fed at approximately twice its target level.

The metal-impregnated carbon used was Katalco 7-2 (equivalent to Pittsburgh FCA) which is the same material planned for the SYNTHANE 72 TPD pilot plant. Operating pressure (6900 kPa (1000 psig)) and superficial velocity (1.36 cm/sec) were kept at levels eventually planned for the SYNTHANE pilot plant unit.

Two parallel beds containing 3.2 g (12.8 cm depth) and 9.6 g (38.4 cm depth) of metal-impregnated carbon were run. Run conditions and results are summarized in Table 4.9. Transient histories of effluent concentrations for each of the sulfur compounds for the two beds are shown in Figures 4.10 and 4.11, respectively. Prior to breakthrough, effluent levels were below 0.1-0.2 ppmv for most of the sulfur species.

Since feed concentrations of each sulfur compound differ with respect to each other, the most direct measure of relative system capacity is the quantity Volume of Gas (STP) Treated/Volume of Carbon Charged. The values of this parameter obtained at breakthrough for each sulfur specie and both beds are given in Table 4.9. In addition, an estimate of the maximum value of this parameter, or the value expected in an infinitely long bed, is also shown. This was calculated using techniques previously discussed (and footnoted in Table 4.9). In essence, it approximates the dynamic equilibrium capacity in a fully saturated bed, and thus, in theory, eliminates the influence of bed length for comparative purposes.

When this saturation parameter is compared, with respect to both beds, for COS, CS_2, and thiophene, relatively good agreement was found, as indicated in Table 4.9. For both CH_3SH and H_2S, agreement was not very good. Since results obtained with a deeper bed are generally more reliable, and, in this particular case also tend to be more conservative, they will be taken as the more accurate measure of removal capacity for both CH_3SH and H_2S.

As shown in Table 4.9, for the deeper bed (38.4 cm) run, the treatment capacities for COS and CS_2, at the concentrations fed, were approximately equal, being on the order of 90,000 volumes of gas (STP)/ volume of carbon. Similarly, thiophene, CH_3SH and H_2S had saturation capacities ranging from ~180,000 to ~210,000 volumes of gas (STP)/volume of carbon. Thus, COS and CS_2, when fed at the concentrations addressed, would be expected to represent the limiting species in very long beds.

TABLE 4.9

REMOVAL OF COS, CS_2, THIOPHENE, CH_3SH, AND H_2S IN SIMULATED SYNTHESIS GAS USING METAL-IMPREGNATED ACTIVATED CARBON (RUN 16, 5277-44)

Carbon: Katalco 7-2 (12-30 mesh); 0.53 g/ml; Impregnants (as metals) = 8.0% Cu; 2.7% Cr

Simulated Synthesis Gas①: $H_2 \approx 45.0\%$; $CH_4 \approx 33.2\%$; $CO \approx 12.6\%$; $N_2 \approx 7.3\%$; $CO_2 \approx 0.95\%$; $C_2H_6 \approx 0.95\%$; $H_2O \approx 0.05-0.07\%$

Pressure = 6900 kPa (1000 psig); Temperature = 33°C ± 0.5°C; Bed Diameter = 0.775 cm

Superficial Velocity (actual) = 1.36 cm/sec; Vol. Feed Rate = 41.7 std. ml/sec

	Reactor 3					Reactor 2				
Carbon Charged (g)	3.20					9.60				
Bed Recovered (g)	3.93					11.65				
Bed Depth (cm)	12.8					38.4				
Space Velocity, STP (v/v/hr)	24,900					8,290				
	COS	CS_2	C_4H_4S	CH_3SH	H_2S	COS	CS_2	C_4H_4S	CH_3SH	H_2S
Avg. Feed Before Breakthrough (ppmv)②	73.0	9.8	38.0	49.3	28.5	76.1	10.5	38.0	50.3	27.6
Avg. Feed During Breakthrough (ppmv)③	83.0	10.4	38.0	51.1	27.2	84.3	10.5	40.0	57.0	26.3
Breakthrough Time (hr)	0.33	2.17	7.00	11.4	12.3	1.50	9.38	22.4	21.5	22.3
Stoichiometric Breakthrough Time (hr)④		3.46	8.10	12.3	18.5		10.9	25.9	22.2	22.5
Effluent Concentration Before Breakthrough⑤	<0.2	<0.1	<0.1	<0.3-0.4	<0.2	<0.2	<0.1	<0.1	<0.3-0.4	<0.2
Capacity at Breakthrough (wt % of C)	0.30	0.32	4.43	5.35	2.45	0.46	0.50	4.73	3.43	1.40
Approx. Maximum Capacity (wt % of C)⑥	2.78	0.51	5.13	5.79	3.69	3.41	0.55	5.46	3.54	1.41
Volume Gas (STP)/Volume Carbon @ Breakthrough	8,290	53,900	174,000	283,000	314,000	12,400	77,800	186,000	178,000	184,000
Approx. Maximum Volume Gas (STP)/Volume Carbon⑥	78,300	85,800	201,000	307,000	473,000	92,400	90,600	214,000	184,000	186,000

***Footnotes on next page.**

Table 4.9 Footnotes:

1. Component compositions differ slightly from target values due to dilution by carrier gases for sulfur compounds.

2. Time-averaged feed concentration prior to breakthrough.

3. Time-averaged feed concentration during period bounded by initiation of breakthrough to point where effluent concentration = feed gas concentration.

4. Time for effluent concentration to reach 50% of concentration in feed gas (see, e.g., Lukchis, G. M., Chem. Eng'g., June 11, 1973, p. 111). Not calculated for COS (see discussion in text).

5. Levels indicated represent detectability limits for the specific gas chromatograph conditions used.

6. The quantities listed represent approximate saturation levels, or loadings expected in an infinitely long bed. For all except COS, each value determined by multiplying breakthrough result by Stoichiometric Breakthrough Time/Breakthrough Time (see reference cited in footnote 4 for further details). For COS, value determined by subtracting cumulative effluent COS from cumulative feed COS, up to point where feed concentration $\simeq$ effluent concentration.

FIGURE 4.10

REMOVAL OF COS, CS_2, THIOPHENE, CH_3SH, AND H_2S IN SYNTHESIS GAS VIA METAL-IMPREGNATED ACTIVATED CARBON
Run 16, 5277-44 (See Table 4.9 for Run Details)

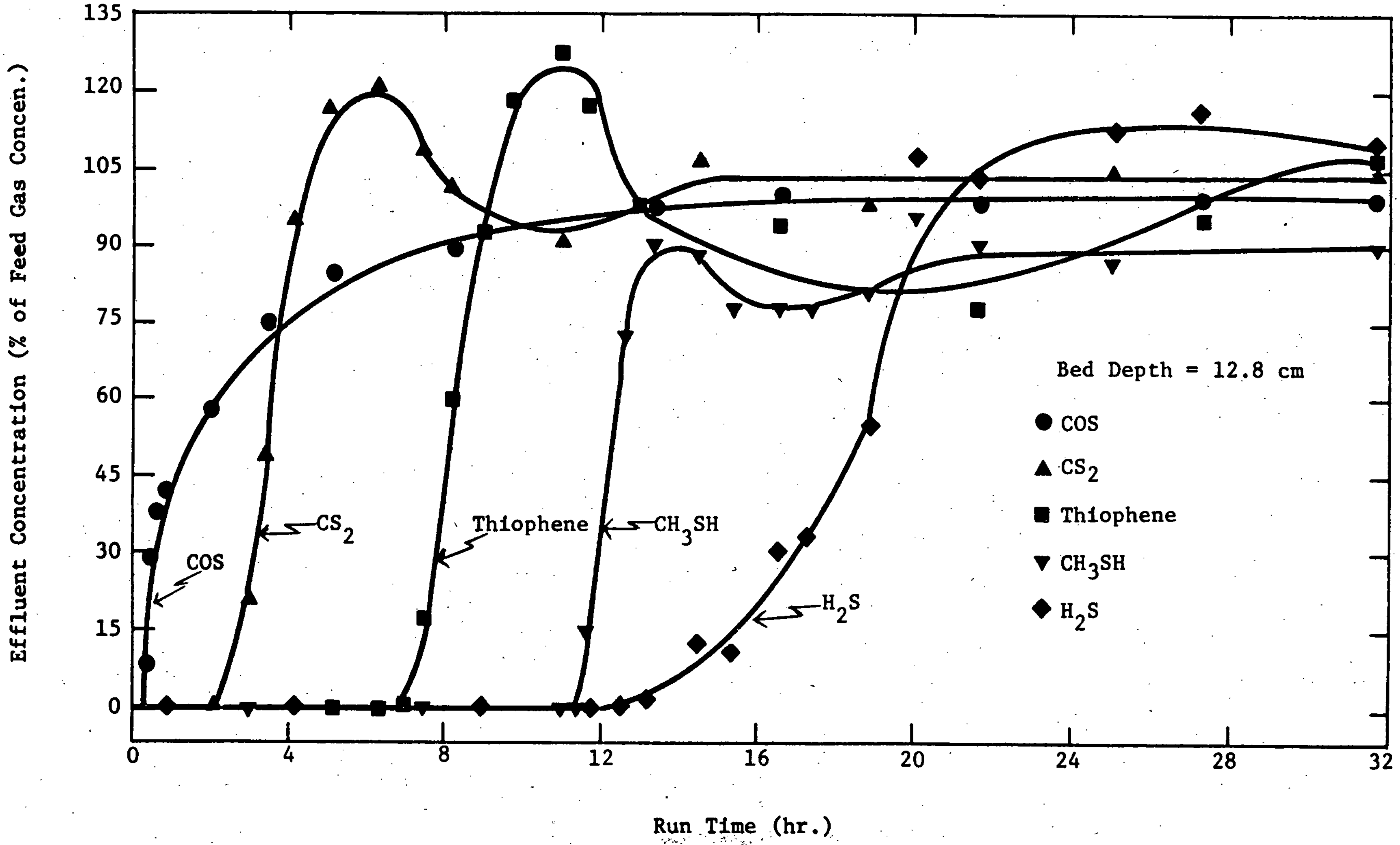
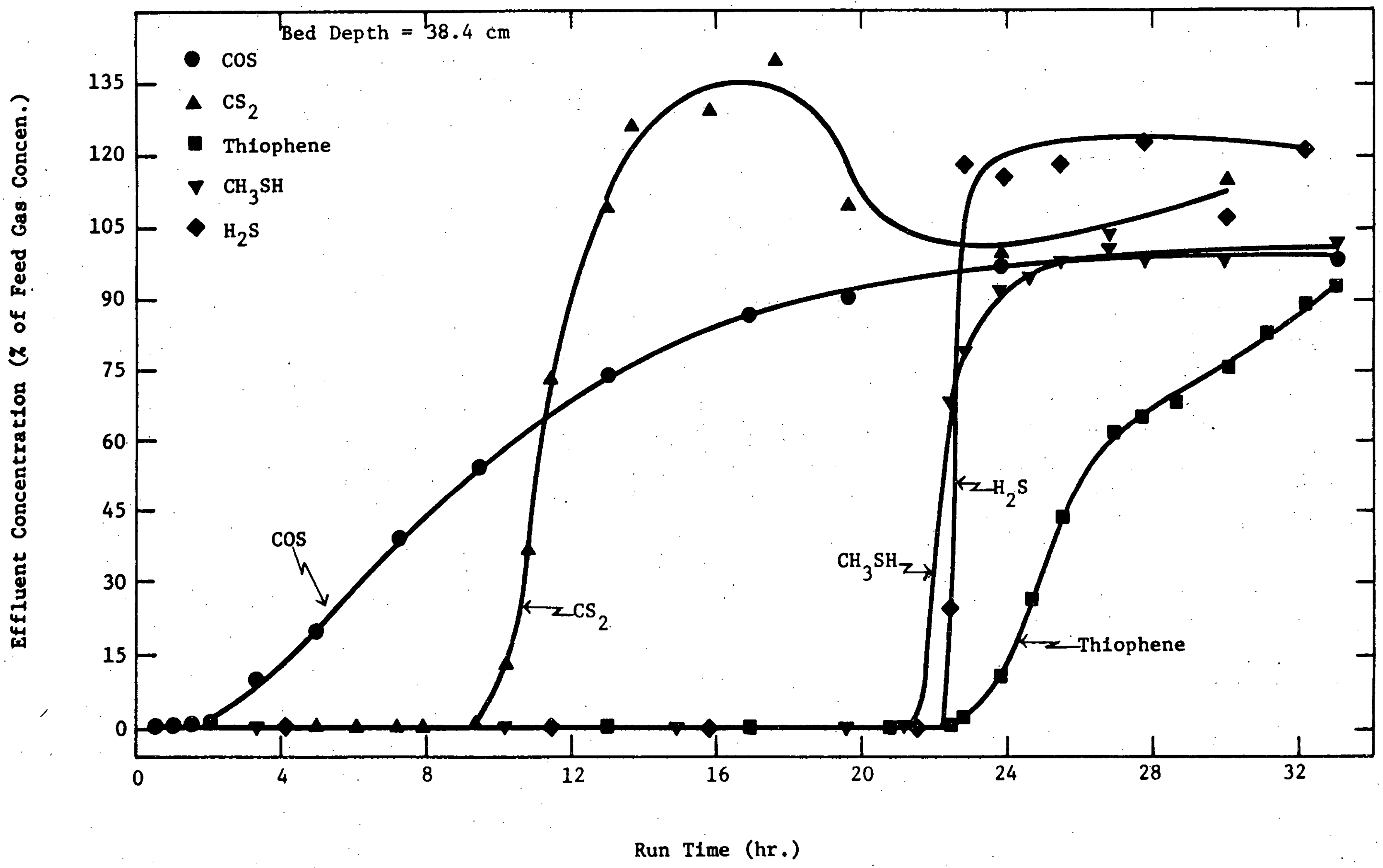


FIGURE 4.11

REMOVAL OF COS, CS_2, THIOPHENE, CH_3SH, AND H_2S IN SYNTHESIS GAS VIA METAL-IMPREGNATED ACTIVATED CARBON
Run 16, 5277-44 (See Table 4.9 for Run Details)



One of the more surprising and interesting results obtained with this five sulfur compound work involves the large difference noted regarding capacity for H_2S and CH_3SH removal compared to that obtained when each was present as the sole sulfur species in the single sulfur component work. The capacities found in the multicomponent work were over an order of magnitude lower than in the single component work. It would appear that the conversion mechanisms that were speculated as being responsible for the very high removal levels found in the earlier work are not operative in a multicomponent sulfur specie feed mode.

Differences between single sulfur component and five sulfur component capacity estimates with respect to the other sulfur compounds are much less drastic. For thiophene, the 214,000 vol. gas/vol. carbon saturation parameter given in Table 4.9 for a 38 ppmv feed level in the five sulfur compound blend contrasts with a 298,000 value obtained for a 52 ppmv feed level in the single sulfur specie work. For CS_2, the 90,600 figure of Table 4.9 (at 10.5 ppmv feed) contrasts with a 94,800 figure (at 14.0 ppmv feed) obtained in the single component work. Both of the above are indicative of the capacity losses due to competitive adsorption present in the five sulfur component system. For COS, the 92,000 figure given in Table 4.9 (for ∿80 ppmv feed) compares with a 57,000 saturation value (at ∿150 ppmv) obtained in the single component work. Such an "apparent" rise in saturation capacity, given the fact that COS feed concentration in the present work was approximately half that used in the single sulfur component work, presumably reflects the fact that the adsorption is less than first order but greater than zero order in COS partial pressure.

The data obtained with the five sulfur component feed were used to predict performance and cost of the SYNTHANE towers. The results of this cost analysis are briefly discussed in Section 5 of this report.

4.4 Analysis of Reproducibility of Sulfur Compound Adsorption

Replicate sulfur compound adsorption data were obtained as a general rule. This was done by using several different adsorbent bed lengths in each set of experiments, which also aided in establishing practical sizes which would breakthrough in reasonable times. There was no way of estimating approximate breakthrough times for the various sulfur compounds in multicomponent adsorption runs prior to actually making such runs. However, since process experimental test conditions were identical for the various reactors containing different lengths of metal impregnated activated carbon, the results from the different length adsorption reactors provided a means of estimating the precision of the experimental results. This can be done by comparing the estimated maximum volume of gas (at STP)/Volume of carbon that can be treated before breakthrough takes place for that specific gaseous component. As indicated in reference (14), this quantity represents the approximate saturation level of a specific adsorbed component that would be expected in an infinitely long bed and is thus independent of adsorption bed length.

Table 4.10 summarizes the results of the precision analysis made on specific sulfur compound adsorption data resulting from single, four and five component adsorption runs respectively. "Replications" correspond to runs made at identical process conditions using adsorption reactors of different lengths.

TABLE 4.10

TRACE SULFUR COMPOUND ADSORPTION DATA PRECISION ANALYSIS

Number of Components in Blend			Approximate Maximum Volume Gas at (STP)/Volume Carbon Trace Sulfur Component				
		H_2S	COS	CS_2	C_4H_4S	CH_3SH	
Five		473,000	78,300	85,800	201,000	307,000	
		186,000	92,400	90,600	214,000	184,000	
	$\bar{x}$	329,500	85,350	88,200	207,500	245,500	
	s	202,900	9,970	3,400	9,192	86,973	
	$\frac{s}{\bar{x}}$ x 100	62%	11.7%	3.9%	4.4%	35.4%	Average precision for five component run 23.5%
Four		not present	145,000	120,000	257,000	no break-thru occurred	
			151,000	109,000	242,000		
	$\bar{x}$	-	148,000	114,500	249,500	-	
	s	-	4,243	7,778	10,607	-	
	$\frac{s}{\bar{x}}$ x 100	-	2.9%	6.8%	4.3%	-	Average precision for four component run 4.7%
Single		101,000	51,300	169,000	319,000	insufficient data	
		140,000	35,300	111,000	212,000		
		80,000	57,100	109,000	298,000		
				95,100			
	$\bar{x}$	107,000	47,900	121,000	276,330		
	s	30,447	11,295	32,756	56,697		
	$\frac{s}{\bar{x}}$ x 100	29%	24%	27%	21%		Average precision for single component run 25.3%

Overall average precision of all runs - 17.8%

Normalized experimental precision was obtained by dividing the standard deviation of each run population (i.e. results for each component in single, four and five component runs respectively) by the mean value of that population. Though the sample population was quite small, (two to four replications) the results can give an estimate of the experimental precision involved in the experimentation during this program. The average run precision was observed to vary from about 4.7% for the four component run, to 23.5% for the five component run to 25.3% for the single component run. The overall average precision (obtained by taking the arithmetic average of all the individual results for one, four and five component runs respectively is 17.8%.

5. ECONOMIC AND ENVIRONMENTAL ASSESSMENT

This section briefly discusses the cost of the sulfur guard process and some of the environmental considerations resulting from its use.

5.1 Sulfur Guard Process Costs

Based on the present size of equipment to hold the metal impregnated activated carbon in the SYNTHANE 72 TPD pilot plant, the sorbent annual requirements would be about 113,000 lbs based upon replacement every five days, i.e., one day before the estimated breakthrough of COS. Based on present costs for Katalco 7-2 metal impregnated carbon, this would translate into an annual sorbent cost of about $150,000/year (fob Pittsburgh) not including labor and turnaround costs. See attached letter of quotation in Appendix B.

5.2 Environmental Considerations -- Sorbent Disposal Options

It has been estimated that the sorbent will contain approximately 4% sulfur shortly before the anticipated COS breakthrough (i.e., about five days of running at the SYNTHANE facility). This will be in the form of a mixture of adsorbed COS, CS_2, and thiophene and sulfides of the impregnated metals (CuS) formed from H_2S and CH_3SH. A few possibilities exist for disposal/reclamation of the spent sorbent material. These include:

- Regeneration of Sorbent

The feasibility of regenerating spent sorbent for reuse in this application has not been evaluated experimentally. However, this does present a possible approach which should be explored. Regeneration theoretically involves careful calcining followed by treatment with a reducing gas. This could be done by the sorbent manufacturer or conceivably on-site at the SYNTHANE Facility. It is recommended that the practical feasibility of sorbent regeneration be evaluated in continued studies of this area.

- Burning as a Fuel

The spent sorbent would contain mostly carbon, about 4 wt % sulfur and metal oxides. The high heating value of the carbon makes use as a fuel a possibility. However, because of the relatively high sulfur level, a SO_2 scrubber would be needed downstream of the furnace/boiler to limit this effluent to acceptable levels (i.e., to less than 1.2 lb $SO_2/10^6$ BTU's). Also, because of the relatively high cost of the sorbent (Katalco 7-2), one can only recover about 1% of the initial cost of the sorbent through use of its fuel value.

- Re-Sale to Sorbent Manufacturers

Even if the sorbent cannot be regenerated for use in this application, it may still have value after treatment as a sorbent for another application. Thus, this option should be evaluated if the identified sulfur guard process is used.

In addition to sorbent disposal, another potential environmental problem is "flashing" of some of the adsorbed sulfur gases during depressurization of a reactor. Oxidation of the effluent to SO_2 and subsequent removal with an existing SO_2 tail gas process is a possible approach to this problem. Since the SYNTHANE process utilizes oxygen, this may be a viable approach. However, additional experimental work would be required to establish feasibility.

5.3 Rectisol vs. Benfield Processes

Vendor quotations were received for gas purification plants from Lotepro Corporation (Rectisol Process) and from Benfield Corporation on their process. These quotations, presented in Appendix C, indicate that the Rectisol process is about 30% more expensive than the Benfield process for units applicable to the 72 TPD SYNTHANE pilot plant. This comparison is made without including offsite steam or power generation, cooling water, compressed air, etc.

6. SUMMARY AND CONCLUSIONS

The development of a viable large scale methanation process could make an important contribution to our future energy needs. However, before catalytic methanation can be used for the commercial production of synthetic natural gas from synthesis gas, the problem of methanation catalyst deactivation must be solved. The nickel catalyst used is easily poisoned by sulfur compounds. It was the purpose of this program, conducted under DOE Contract No. E(36-2)-0059, to identify and develop a viable and effective pre-methanation purification system to protect the methanation catalyst and thereby promote viable coal gasification by the SYNTHANE process.

During this program, a review and analysis was made of state of the art gaseous sulfur compound removal processes. Processes for the removal of both bulk and trace sulfur compounds were analyzed, and evaluated as to their applicability for use in a premethanation purification subsystem for the DOE SYNTHANE gasification process. On the basis of this extensive review, a system was selected for a detailed laboratory evaluation to obtain needed design data.

A copper-chromium oxide impregnated activated carbon was selected as the test sorbent and evaluated for its ability to remove specified levels of H_2S, COS, CS_2 mercaptans and thiophenes. The levels used of these respective sulfur compounds was dictated by the anticipated performance of the Benfield Hot Potassium-Carbonate Process selected for bulk removal of acid gases in the Synthane Process.

Experimental runs were made using single component and multicomponent sulfur compound gaseous mixtures in a simulated synthesis gas. Adsorption breakthrough curves were evaluated and estimates were made of the time for breakthrough to occur, and the approximate maximum values of volume of gas that could be processed/volume of carbon used. Using this data, estimates of sorbent requirements, costs and environmental handling constraints were made for a system to be used in the 72 TPD SYNTHANE pilot plant.

Based on the results of this study, the following conclusions may be drawn:

- Essentially target purity levels (<0.1 ppmv) are achievable for each compound at processing conditions using metal impregnated activated carbon Katalco 7-2 (same as Pittsburgh Chemical Co. FCA adsorbent).
- Projected sorbent bed life for the SYNTHANE pilot plant would be about 6 days based on present planned processing conditions. Carbonyl sulfide is expected to be the limiting impurity with regard to bed life, followed closely by carbon disulfide. Projected cost of sorbent would be about $150,000/year based on replacement every 5 days.

- Katalco 7-2 metal impregnated activated carbon shows relatively high capacity for H_2S adsorption followed by CH_3SH, Thiophene, CS_2 and COS in that order.

- Physical adsorption is probably the dominant mechanism in removal of COS, CS_2 and thiophene; adsorption and chemical conversion mechanisms probably are the dominant mechanisms in H_2S and CH_3SH removal.

- A drastic reduction in removal capacity of H_2S and CH_3SH was found in the five component species feedwork compared to that found in the single sulfur component work. Some reduction in CS_2 and thiophene was also observed in the multicomponent runs relative to single sulfur component work.

- Further work is required to:

    - Demonstrate that the identified metal impregnated activated carbon sulfur guard system can protect a catalytic methanator for the projected time.

    - Develop a regeneration technique for the metal impregnated activated carbon.

    - Evaluate environmental effects of sorbent disposal/ regeneration.

    - Investigate other sorbents and/or catalysts for improved multicomponent adsorption characteristics.

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APPENDIX A

COST QUOTATION FOR KATALCO 7-2 ACTIVATED CARBON

Plant Telephone
312-767-6884

Katalco
CORPORATION

Process Catalysts

29[illegible] Butterfield Rd • Oak Brook Illinois 60521 • Area 312-887-1120

November 7, 1977

Mr. Martin Lieberman
Exxon Research and
Engineering Company
Post Office Box 8
Linden, New Jersey 07036

Katalco Quotation #K-77-74

Dear Mr. Lieberman:

As per our recent telephone conversation, I am submitting a quotation for Katalco 7-2, activated carbon. The following quotation contains price, delivery, packaging, and shipping information.

Unfortunately, Katalco does not, nor do I know of anyone who purchases spent carbon. It would be advantageous to include a facility to steam-air regenerate the carbon on site, or to investigate the use of another sulfur removal system, such as cobalt-moly/zinc oxide. Katalco would be pleased to investigate these alternatives with you.

Thank you for your interest in Katalco catalysts. If I can be of any further service, please do not hesitate to contact me.

Very truly yours,

A. V. Kinal

A. V. Kinal,
Sales and Service Representative

AVK/jh

Attachment

KATALCO CORPORATION

EXXON RESEARCH AND ENGINEERING COMPANY
LINDEN, NEW JERSEY

CATALYST AND QUANTITY

Katalco 7-2 Impregnated Activated Carbon - Approximately 3,600 ft^3
(To be Utilized over a Period of One Year)

Size: 12 x 30 Mesh Bulk Density: 33 lbs/ft^3

PRICE

The price of Katalco 7-2 is $40.00 per cubic foot, f.o.b. Pittsburgh
(This Price is Applicable to Quantities Over 900 ft^3)

Total Price for 3,600 ft^3 - $144,000, f.o.b. Pittsburgh

DELIVERY

Delivery can be made to the Bruceton, Pennsylvania site four weeks after receipt of purchase order. Delivery can be adjusted to accommodate your requirements, i.e., one delivery per month (300 ft^3) for one year, or as required.

PACKAGING

The Activated Carbon is packaged in 55 gallon fiber drums, each drum containing 6.7 ft^3 of carbon. Net weight of carbon per drum is 220 lbs.

TERMS

Our usual terms are Net 30 Days.

APPENDIX B

COST ESTIMATES FOR RECTISOL AND BENFIELD SULFUR GAS REMOVAL PROCESSES

EXXON RESEARCH AND ENGINEERING COMPANY

P.O. BOX 8, LINDEN, N. J. 07036

GOVERNMENT RESEARCH LABORATORIES
M. BERGER
Director
J. W. HARRISON
Director
Energy and Environmental Research Laboratory

November 26, 1975

Mr. H. Haberland
LOTEPRO Corporation
1140 Avenue of the Americas
New York, New York 10036

Dear Mr. Haberland:

Per our conversation of October 10, I would like to request your estimate of both investment and operating costs, in as much detail as conveniently possible, of a Rectisol plant to purify the gas stream described in the attached table. These estimates are requested in connection with our contract (No. E(36-2)-0059) with the United States Energy Research and Development Administration. In this regard, we are endeavoring to establish methods and costs for lowering the sulfur content of a gas stream generated by a "Synthane" coal gasification system to a level of less than 0.1 ppm required for feeding to methanation. We understand that the Rectisol system is probably capable of achieving such a requirement.

Along with the cost information described above, I would appreciate your estimate of the compositions of streams leaving the Rectisol system (product gas, as well as CO_2 and H_2S-enriched regenerator effluents) and a general description of the facilities comprising the system (including, if possible, your recommendation for a sulfur recovery system to handle regenerator effluent).

I would be most grateful for any priority that you could assign this matter. Again, thank you for your regard and cooperation.

Very truly yours,

C. D. Kalfadelis /EPI

C. D. Kalfadelis

CDK/cab

Attachment

cc: E. P. Iaccarino
H. Shaw

Feed Gas to Acid Gas Treatment

Flow Rate = 74,000 moles/hr
Pressure = 965 psig
Temperature = 225°F

Composition

H_2 = 27.9%
CO = 9.0
CO_2[1] = 35.9
CH_4 = 21.9
C_2H_6 = 0.7
N_2 = 1.6
H_2O = 2.0

Sulfur Comp'ds.* = 1.0

*Hydrogen Sulfide = 9800 ppm
Carbonyl Sulfide = 150
Thiophene = 31
Methyl Thiophene = 10
Dimethyl Thiophene = 10
Carbon Disulfide = 10
Methyl Mercaptan = 60

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[1] Treated gas should contain $\leq$ 1-2% CO_2.

Lotepro CORPORATION
1140 AVENUE OF THE AMERICAS • NEW YORK, N. Y. 10036 • (212) 575-7878

December 31, 1975

EXXON Research and Engineering Co.
P.O. Box 8
Linden, New Jersey 07036

Attn: Mr. C. D. Kalfadelis

Re: Rectisol System for Sulfur and CO_2
Removal from Synthane - Coal Gasification Gas
Your letter dated Nov. 26, 1975

Dear Mr. Kalfadelis:

We have prepared a material balance and utility list for a Rectisol system designed to purify the given gas stream. This system has been especially designed for high methan recovery.

We estimate the following utility consumption.

Refrigeration:	54 MMBTU/HR @ -49°F
Steam:	84 MMBTU/HR @ 50 psig 48 MMBTU/HR @ 100 psig
Cooling Water:	2178 USGPM @ 18°F temp. rise does not include the refrigeration unit.
Electric Energy:	9510 KW, does not include the refrigeration unit.
Methanol Losses:	400 LBS/HR

The large flows that have to be handled require to build the plant in three parallel trains. Based on that assumption we estimate the investment cost for the turnkey unit to be

$35,000,000.-

The accuracy of this estimate if ± 20%
Each train consists of:

1 Wash tower for sulfur removal
1 Wash tower for CO_2 removal
2 Regeneration towers for CH_4- Recovery
Pumps
1 Refrigeration unit
1 Recycle compressor
Heat exchangers
1 Water Methanol separation

The Rectisol system can purify the gas stream to a sulfur level of less than .1 ppm. It also can enrich the sulfur in a sulfur fraction that can be fed directly to a Clauss-unit for conversion into elemental sulfur.

The CO_2-tailgas will contain no more than 5 ppm of sulfur.

Rectisol also dries the gas. Therefore, the material balance has been set up for dry gas. The water is removed and delivered as pure water at battery limits.

If you have any questions please feel free to call the undersigned.

Best regards,
LOTEPRO CORPORATION

Juergen Bokaemper

JB/ub
Encl.

LOTEPRO CORP.

MATERIAL-BALANCE

PROJECT: EXXON SYNTHANE
DATE: 12/30/75 BY:
PAGE 1 OF 1 PAGES

TOTAL GAS FLOW RATE 74,000 LBMH

Gas Component	Feedgas		Purified gas		Sulfur-tailgas		CO_2-tailgas	
	Vol.%	LBMH	Vol.%	LBMH	Vol.%	LBMH	Vol.%	LBMH
H_2	28.5		45.1		0.1		0.4	
CO	9.2		14.7		0		0.1	
CH_4	22.4		35.5		0.2		0.2	
C_2H_6	0.7		0.2		0.4		1.7	
N_2	1.6		2.5		0		0	
CO_2	36.6		2.0		74.3		97.6	
Total Sulfur Compound	1.0		<.1 ppm		25.0		<5 ppm	
	100.0	72,618	100.0	45,638	100.0	2,904	100.0	24,076
Psig		965		935		20		1
°F		100		90		100		90

EXXON RESEARCH AND ENGINEERING COMPANY
P.O. BOX 8, LINDEN, N.J. 07036

GOVERNMENT RESEARCH LABORATORIES
M. BERGER
Director
J. W. HARRISON
Director
Energy and Environmental Research Laboratory

November 26, 1975

Dr. Homer Benson
Benfield Corporation
615 Washington Road
Pittsburgh, Pennsylvania 15228

Dear Dr. Benson:

Per our conversation of October 10, I would like to request your estimate of both investment and operating costs, in as much detail as conveniently possible, of a Benfield plant to purify the gas strean described in the attached table. These estimates are requested in connection with our contract (No. E (36-2)-0059) with the United States Energy Research and Development Administration. In this regard, we are endeavoring to establish methods and costs for lowering the sulfur content of a gas stream generated by a "Synthane" coal gasification system to a level of less than 0.1 ppm required for feeding to methanation. We understand that the Benfield system alone is not capable of achieving such a requirement but would require an ancillary sulfur guard system.

Along with the cost information described above, I would appreciate your estimate of the compositions of streams leaving the Benfield system (product gas, as well as CO_2 and H_2S-enriched regenerator effluents) and a general description of the facilities comprising the system (including, if possible, your recommendation for a sulfur recovery system to handle regenerator effluent).

I would be most grateful for any priority that you could assign this matter. Again, thank you for your regard and cooperation.

Very truly yours,

C. D. Kalfadelis

CDK:da
Attachment

cc: E. P. Iaccarino
H. Shaw

Feed Gas to Acid Gas Treatment

Flow Rate = 74,000 moles/hr
Pressure = 965 psig
Temperature = 225°F

Composition

H_2 = 27.9%

CO = 9.0

CO_2[1] = 35.9

CH_4 = 21.9

C_2H_6 = 0.7

N_2 = 1.6

H_2O = 2.0

Sulfur
Comp'ds.* = 1.0

*Hydrogen Sulfide = 9800 ppm
Carbonyl Sulfide = 150
Thiophene = 31
Methyl Thiophene = 10
Dimethyl Thiophene = 10
Carbon Disulfide = 10
Methyl Mercaptan = 60

[1] Treated gas should contain $\leq$ 1-2% CO_2.

Benfield
CORPORATION • 615 WASHINGTON RD., PITTSBURGH PA.

January 12, 1976

Exxon Research and Engineering Company
P. O. Box 8
Linden, New Jersey 07035

Attention: Mr. C. D. Kalfadelis

Reference: Your letter of November 26, 1975, CDK/jep; our PS-1601

Subject: Benfield Unit Information for your ERDA Contract E(36-2)-0059

Gentlemen:

On the basis of the process information accompanying your referenced letter we offer the following information on a Benfield unit to satisfy your product specifications:

a. Estimated total plant installed cost - $26.7 MM
This is a preliminary budget estimate with a range of plus or minus 15%. It is on a battery limits bases without including offsite steam or power generation, cooling water, compressed air, etc. facilities. Installed cost includes equipment (towers, pump, tanks, exchangers, etc.), plus electrical, piping, insulation, instruments, concrete, painting, field labor and indirect costs.

b. Estimate utility requirements per hour:

Steam	0.646 MM lbs.
Power (pumps and fans)	15917 KWH
Cooling water (25°F rise)	3.25 MM U.S. Gal.
Chemical make-up for losses	$7.29

c. Estimated solution inventory $392,000

The analyses of the inlet and outlet gas of the Benfield unit are:

Component	Inlet Volume Percent	Outlet Volume Percent
H_2	28.47	45.6
CO	9.18	14.7
CO_2	36.63	0.15
CH_4	22.35	35.8
C_2H_6	0.71	1.1
N_2	1.64	2.6
H_2S	9800 ppm	<0.5 ppm

Component	Inlet Volume Percent	Outlet Volume Percent
COS	150 ppm	< 3 ppm
CS_2	10 ppm	< 2 ppm
Methyl mercaptans	60 ppm	20 ppm
Thiophenes	51 ppm	80-85 ppm
Total mole (dry)	72520	44886
Water	26663 lbs.	1195 lbs.
Temperature	225°F	122 °F
Pressure	980 psia	973 psia

The analysis of the regenerator effluent is (total regenerator effluent will be approximately 27645 lb. mols/hr.):

Component	Volume Percent
CO_2	96.1
H_2S	2.65
Methyl mercaptan	80 ppm
Other (H_2, CO, CH_4, etc.)	1.2

The Benfield system would consist of two identical trains, each train containing two absorber and two regenerators plus pumps, exchangers, reboilers and condensers.

We have assumed bulk removal of CO_2, H_2S and COS with no selectivity. As a guard chamber and for further removal of the organic sulfur from the product gas we suggest consideration of activated carbon and zinc oxide to reduce the sulfur components to tolerable levels for methanation. If residual COS becomes a problem in downstream purification, we could, at a reasonable extra plant investment, decrease the residual COS to about 0.1 ppm.

If selective removal of H_2S is of interest, we could provide an acid gas that would contain H_2S in the range of 13-20% that would be suitable for a Claus unit feed.

We trust that the foregoing is of some help to you.

Very truly yours,

THE BENFIELD CORPORATION

Homer E. Benson, President

Feed Gas to Acid Gas Treatment

Flow Rate = 74,000 moles/hr
Pressure = 965 psig
Temperature = 225°F

Composition

H_2 = 27.9%

CO = 9.0

CO_2[1] = 35.9

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Sulfur
Comp'ds.* = 1.0

*Hydrogen Sulfide = 9800 ppm
Carbonyl Sulfide = 150
Thiophene = 31
Methyl Thiophene = 10
Dimethyl Thiophene = 10
Carbon Disulfide = 10
Methyl Mercaptan = 60

---

[1] Treated gas should contain $\le$ 1-2% CO_2.

APPENDIX C

ADSORPTION OF SULFUR COMPOUNDS FROM SYNTHESIS GAS
THEORETICAL ANALYSIS

Nicholas Kafes

August, 1976

NSF Faculty Research Participation Project
Grant No. SER 76-04548

Exxon Research and Engineering Company
Government Research Laboratories
Linden, New Jersey 07036

BACKGROUND

An ERDA-sponsored development program was conducted at Exxon's Government Research Laboratories to recommend and define the sulfur guard system to be employed on a coal derived synthesis gas prior to methanation. The contaminants of concern are H_2S, COS, CH_3SH, CS_2, C_4H_4S in the 10 to 100 ppm range. The intent was to effect removal of the organic sulfur compounds by physical adsorption on an activated carbon surface and to effect chemisorption removal of the H_2S by converting a metal oxide impregnant of the carbon to the sulfide. The experimental program that was conducted consists of obtaining dynamic adsorption data for each of the contaminants separately in a synthetic synthesis gas blend. Data was also subsequently obtained with all of the contaminants in the gas blend.

The task assigned to the writer concerned the scaleup of the laboratory data being generated so that a reliable design could be implemented for a large scale commercial operation. An extensive review of the literature was undertaken in order to evaluate methods that could be employed to establish a design basis for such a multi-component adsorption system. Most of the workers in the field, however, have focused their efforts on single component systems under a variety of limiting constraints. The literature is replete with mathematical analyses in an attempt to define the sorbate concentrations as a function of time and distance along the bed. Relatively very little experimental data are being generated. The failure, in general, of these solutions to predict the behavior of adsorption beds with accuracy is a measure of the complexity of the phenomena being analyzed.

For the adsorption of one component from an inert fluid the rate of adsorption at the interface is usually so rapid that it is normally ignored in comparison with boundary layer and solid phase diffusion. These latter two mechanisms have been examined by numerous investigators; however, the relatively rigorous solutions of Rosen (1954) and Vermueker, et. al. (1973) appear most tractable for numerical evaluation. Approximate approaches, depending on a simplification of the transfer mechanisms or mathematical treatment have been proposed but the solutions are still cumbersone and of little direct value in design though they might be of utility in predicting the effect of a particular variable. Worth noting is the solution of Hougan and Marshall (1947), who assume that solid phase diffusion is not important and that the rate of mass transfer is a function of the sorbate concentration in the fluid and the average concentration in the particles. The solution is in graphical form and permits one to approximate the mass transfer breakthrough profile with reasonable effort.

For multicomponent systems, very little was found in the literature, where the interactive effect of the different species on one another is taken into account. A worthwhile piece of experimental work was that of Thomas (1971) on the binary adsorption of ppm levels of C_6H_6 and C_7H_8 on activated carbon. This appears to be on the right track toward the modeling of dynamic multicomponent systems even though the results have limited applicability for design purposes.

DESIGN APPROACH

The writer was asked to put together an approach for a multicomponent adsorption system design and to implement this with available information existing in the literature. The parameters involved could then be subsequently modified as the data becomes available from the development program. The intent was to point up the key factors that dictate the design of the unit.

For a single component system, the determination of the adsorbent bed length requirement in practice, consists of defining the equilibrium zone, where the adsorbent is saturated with sorbate, and the mass transfer zone, where the concentration of the sorbate species falls from the saturation value to zero at the leading edge of the zone.

$$L_o = L_{Equil} + L_{MTZ}$$

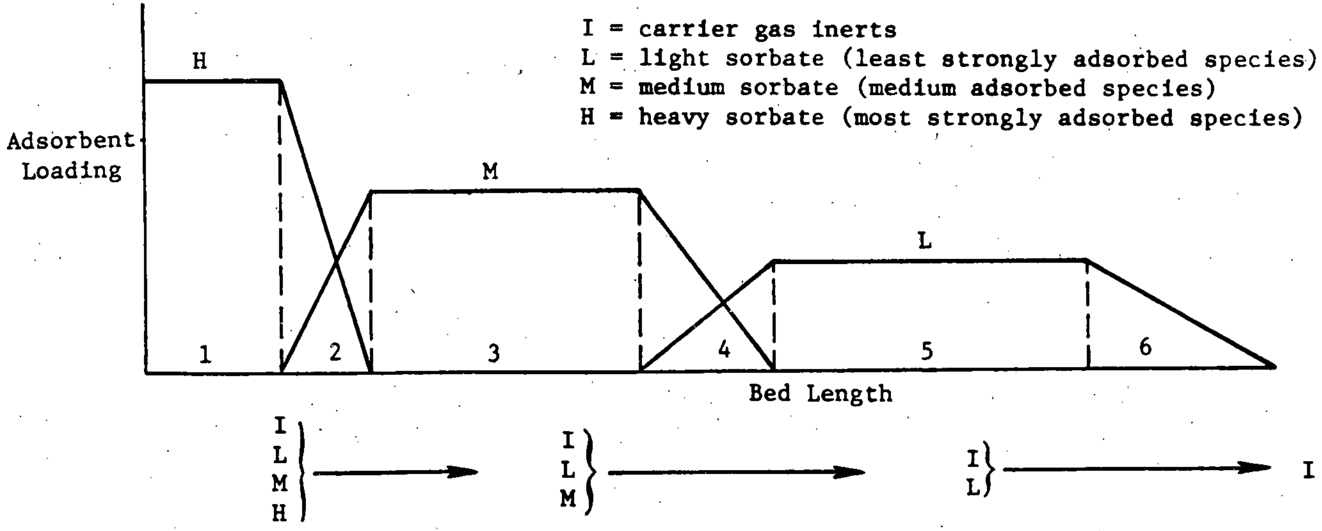
This approach is simplified somewhat, when a stable mass transfer front is exhibited by considering these two zones equivalent to a Length of Equivalent Equilibrium Section and a Length of Unused Bed, Collins (1968), Lukchis (1973). In the mass transfer zone approximately half the adsorbent can be considered to be at its saturation value and half completely unused (experimentally this fraction ranges between .4 to .6).

$$L = (L_{Equil} + \frac{L_{MTZ}}{2}) + \frac{L_{MTZ}}{2} = LES + LUB$$

The equivalent equilibrium section bed requirement can be defined using available isotherm loading data taken under static conditions. These values are frequently derated to account for the dynamic conditions prevailing in the bed. The length of the mass transfer zone is a function of the adsorbent properties, fluid properties, concentration and flow conditions. As previously indicated, the breakthrough profile, or MTZ length, can be reasonably approximated, under certain restricted conditions (isothermal, linear equilibrium relation) using available models such as that of Hougan and Marshall (1947) as described by Fair (1969). The use of a more complex model is not warranted. To establish a firmer basis for design necessitates that the MTZ length be obtained experimentally along with the dynamic saturation loadings for the equilibrium section.

To provide a design basis for a multicomponent system, the approach taken was to account for the individual components of the system in a series fashion. Each of the species is treated in sequence, in the order of their molar polarizability, i.e., from the most strongly adsorbed species to the least strongly adsorbed species. This order is dependent on molecular weight, boiling point, and refractive index of the components involved. This additive procedure has been referred to in the literature, Conviser (1965), Manchanda (1973), Chi (1973), as being successfully employed in the prediction of molecular sieve bed performance for the drying and desulfurization of natural gas, though relatively little detailed information is given. This approach is also recommended by activated carbon vendors for the multicomponent systems where low concentration levels prevail and where no interactive effects are expected.

For a system in which the species are present at ppm levels it is reasonable to expect that a number of stable mass transfer fronts would be manifested as the fluid passes through the bed. If no interaction is assumed between the sorbates, a multicomponent system should exhibit the following type of behavior.



At the inlet side of the bed, zone 1 is completely saturated with the heavy sorbate. In zone 2, the medium sorbate which had previously been adsorbed is being replaced by the heavy sorbate. This zone is an interchange zone and can be considered to be occupied half by the heavy sorbate at its saturation value and half by the medium species at its saturation value. In zone 3 the medium sorbate saturates the bed having completely pushed off the light sorbate. Again in zone 4 an interchange takes place where the medium sorbate is pushing out the light sorbate. In zone 5 the light sorbate saturates the bed and in the zone 6 mass transfer zone the light sorbate concentration drops from its saturation value to zero at the leading edge. The breakthrough point (a measurable concentration level at the loading edge) for the light sorbate usually dominates the design of the bed.

The idealized front profiles shown above can then be replaced by equivalent equilibrium sections for all the species plus a length of unused bed for the least strongly adsorbed contaminant.

$$L = (LES)_{Heavy} + (LES)_{Medium} + (LES)_{Light} + (LUB)_{Light}$$

There are no lengths of unused bed for the heavy and medium sorbates since the mass transfer zones for the species involved are fully occupied.

The above model assumes that there are no interactive co-adsorption effects taking place. This is somewhat unrealistic, however the adsorbent requirement calculated by considering the individual species separately should be on the conservative side particularly if the components exhibit different adsorptive tendencies toward the adsorbent. The major uncertainty with the above approach, for the situation at hand, involves the so called inert constituents of the carrier gas. If the carrier gas has a constituent with an adsorption affinity close to the lightest sorbate, these will be competition for the same adsorption sites such as to effect a much lower loading value for the light sorbate relative to the equilibrium isotherm value. This will result in a much larger adsorbent requirement when designing for light sorbate removal.

CASES INVESTIGATED

For the multicomponent system under consideration, a number of situations were calculated according to the possible modes of operation proposed for the sulfur guard system. Three base cases were implemented with further variations for contaminant level and design velocity.

Case I - involves the use of a virgin, unimpregnated activated carbon to remove all five sulfur species by physical adsorption.

Case II - involves the use of an impregnated activated carbon to remove the four organic sulfur species C_4H_4S, CS_2, CH_3SH, COS by physical adsorption and the H_2S species by a parallel chemisorption mechanism.

Case III - involves the use of an impregnated activated carbon to remove the three heaviest organic sulfur species, C_4H_4S, CS_2, CH_3SH by physical adsorption and the H_2S by chemisorption.

The cases were calculated for the following stream composition, contaminant levels, flow quantity and operating conditions.

For the adsorbent bed the following parameters were fixed"

Breakthrough time	θ_B = 24 hours
Adsorbent mesh size	4 x 10 mesh
Superficial velocity	**V* = 6.7 cm/sec**

***This is about 5x the design value used in the experimentation. However, this should have only a minor effect on predicted performance.**

	Mol.%		Contaminant (ppm)	Operating Conditions
H_2	45.0			
N_2	2.7	C_4H_4S	45	
CO	14.7	CS_2	12	T = 90°F
CO_2	1.0	CH_3SH	25	
CH_4	35.4	COS	80 (10)	P = 1000 psig
C_2H_6	1.0	H_2S	25	
H_2O	.2			
	100.0		187 (117)	

Mols/hr. = 45000 (flow quantity for a 250 M SCFD plant).

Pressure drop considerations dictate the mesh size and superficial velocity employed. These values were set for Case II, the most important of the above cases with design velocity changes being considered for the other cases.

The adsorbent particle size employed in the Exxon development program is a 12 x 30 mesh impregnated activated carbon necessitated by the small diameter take being tested. For a large scale commercial unit, however, this particle size would not be practical. The ensuing pressure drop would be three to four times larger than for the 4 x 10 mesh size carbon. Alternately, a very low superficial velocity would have to be employed leading to an excessive vessel diameter or a large number of vessels. At the SYNTHANE pilot unit, a very low velocity, .044 ft/sec., is to be employed with the 12 x 30 mesh impregnated activated carbon. The effect of particle size on the mass transfer characteristics is not too discernable. Equilibrium loadings are essentially unaffected, though a larger particle size will bring about a lengthening of the breakthrough profiles.

Values for the equilibrium loadings (static isotherm data) are available in the literature, Grant (1960, 1962) for H_2S, COS, CH_3SH and

CS_2 on a 4 x 10 mesh virgin activated carbon which has properties similar to the carbon being tested. The equilibrium loading for thiophene, C_4H_4S, was estimated using the generalized Polanyi correlation which fairly accurately describes the behavior of the other sulfur species of the system.

With these loadings and the mass rate of the individual species given, the absorbent volume equilibrium requirement for each of the components is readily calculated for the chosen breakthrough time. For a specified superficial velocity the cross sectional area for the system is fixed and hence the lengths of the equivalent equilibrium sections can be determined. The length of the unused bed for the lightest sorbate is obtained from the breakthrough profile which can be calculated for a given superficial velocity and particle size.

For Case I, the above noted equilibrium values were used directly to establish the equivalent equilibrium section lengths. The length of the unused bed for H_2S, the lightest sorbate, was calculated from the Hougen, Marshall prediction for the breakthrough curve. Eight vessels with dimensions D = 12 ft, L = 59 ft, would be required (four adsorbing, four regenerating). The superficial velocity is .165 ft/sec with a bed pressure drop of 2.4 psi. The results for this case are subject to some uncertainty due to the coadsorption of the ethane and carbon dioxide constituents of the carrier gas, which have an adsorption affinity relatively close to H_2S.

For Case II the lengths of the equivalent equilibrium sections were calculated using the above noted equilibrium loading values for the organic sulfur species, derated by 10% to account for loss of adsorption surface due to the copper oxide impregnant. The length of the unused bed for COS, the lightest sorbate, was calculated from the Hougen/Marshall model and added to the bed length. The equilibrium loading value for H_2S chemisorption was predicated by the stoichiometry of the copper present in the carbon. Six vessels with dimensions D = 12 ft, L = 38 ft would be required (three adsorbing, three regenerating). The superficial velocity is .22 ft/sec. with a bed pressure drop of 2.4 psi. The physical adsorption of the organic species controls the design the bed; the parallel chemisorption mechanism for H_2S removal utilizes less than 10% of the bed. The COS contaminant level for this case was taken at 80 ppm corresponding to a low performance Benfield operation located upstream of the sulfur guard system. If a high performance Benfield unit is installed, a 10 ppm COS level can be attained. The above dimensions for the six vessels can then be reduced to D = 12 ft, L = 22 ft. The reasonable confidence in these results can be expected since the carrier gas species, C_2H_6 and CO_2 have adsorption characteristics an order of magnitude different from COS, the lightest sorbate.

For Case III the calculations are the same as for Case II except that CH_3SH is the light sorbate breakthrough constituent. It is anticipated that COS will be removed with an HDS unit. This is a relatively easy cleanup operation requiring four vessels with dimensions D = 12 ft., L = 17 ft. (two adsorbing, two regenerating). The superficial velocity is .33 ft/sec. with a bed pressure drop of 1.9 psi. Again, as for Case II, physical adsorption of the organic species controls the design; the H_2S chemisorption mechanism utilizes less than a third of the bed. Confidence in the calculations for this case is high since essentially no interference is expected from C_2H_6 and CO_2; the CH_3SH has a considerably larger adsorption affinity than these two species.

The results for the three cases are summarized in the following tabulation. No over design is included at this point. If higher contaminant levels are encountered this would be compensated for, to a considerable degree, by higher equilibrium loadings. However, this loading increase is not directly proportional and extra bed length would be required or alternately a shorter breakthrough cycle can be used for the period of higher contaminant levels. For the impregnated carbon cases, the H_2S level is not controlling and a large concentration increase can be easily contained.

The superficial velocities employed, are in the ball park, and yield reasonable bed pressure drops (on low side) for the 4 x 10 mesh carbon chosen. Vessel diameter was limited to 12 feet; shop fabrication of a larger number of these vessels was assumed more economic than field fabrication of a lesser number of larger diameter vessels. Modifications in the system design, however, can be readily implemented for changes in superficial velocity/diameter/number of vessels.

Time ran out with regard to pursuing an investigation of interactive co-adsorptive effects of the carrier gas constituents. This type of data is simply not available for the species involved. However, co-adsorption equilibrium calculations of binary pairs by the methods of Myers (1965) or You (1971) might be combined to yield some prediction of these effects. The development program as it is presently constituted, single component runs plus five component runs, is suitable to provide a basis for direct scale up for a large commercial size unit. However, it will be difficult to ascertain specific interactive effects from the data. It would be informative if binary and ternary runs would be executed, particularly for the more critical light sorbates, H_2S, COS, CH_3SH, with and without the interfacing carrier gas species C_2H_6 and CO_2.

RESULTS

[D = 12 ft]

[4x10]
[mesh]

Case	Breakthrough Contaminant	Number of Vessels on Line	Vessel Length (ft)	Superficial Velocity (ft/sec)	Bed Pressure Drop (psi)	Design Confidence Level
I	H_2S	4	59	.165	2.4	Low
II	COS 80 ppm (10 ppm)	3	38	.22	2.4	Good
III	CH_3SH	2	17	.33	1.9	High

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APPENDIX

OF

CALCULATIONS

GAS - AVERAGE MOLECULAR WEIGHT AND DENSITY

89.6°F
T = 32°C = 305°K
P = 1014.7 psia = 69 atm

	Mole %	M (lbs/mol)	Pc (atm)	Tc (°C)	Tc (°K)
H_2	45.0	2.016	12.8	-239.9	33.3
H_2	2.7	28.02	33.5	-147.1	126.1
CO	14.7	28.01	35.0	-139.0	134.2
CO_2	1.0	44.01	73.0	31.1	304.3
CH_4	35.4	16.04	45.8	-82.5	190.7
C_2H_6	1.0	30.07	48.8	32.1	305.3
H_2O	.2	18.016	218.4	374.15	647.3
	100.0				

$M_{aoe} = 12.24$ $(Pc)_{aoe} = 29.68$ atm $(Tc)_{aoe} = 113°K$

Reduced Conditions $P_r = \frac{P}{Pc} = 2.33$ $T_r = \frac{T}{Tc} = 2.70$

Compressability $Z = 1.02$

Density $C = \frac{PM}{ZRT}$

$$C = \frac{1014.7\ (12.24)}{(1.02)(10.73)(549.6)} = 2.06\ \frac{\text{lbs.}}{\text{ft}^3}$$

VESSEL DIAMETERS - TO PROCESS GAS AT DIFFERENT VELOCITIES

$T = 90°F$	$M = 12.24$ lb/mol
$P = 100$ psig	$d = 2.06$ lb/ft^3
Molal rate	$\mu_T = 45000$ Mols/hr.
Mass rate	$\dot{m} = \mu M = 550800$ lbs/hr
Volumetric rate	$Q = \frac{\dot{m}}{d} = 267000 \frac{ft^3}{Hr} = 74.27 \frac{ft^3}{sec}$
Cross sectional Area	$S = \frac{Q}{V}$
Diameter	$S = \frac{\pi D^2}{4}$ $\quad D = (S/.785)^{\frac{1}{2}}$

(Multiple of SYNTHANE Value)	Velocity ($\frac{ft}{sec}$)	Crossection Area (ft^2)	Diameter (Single Vessel) (ft)	(Two Vessels)	(Three Vessels)	(Four Vessels)
1	.044	1688	46.4	32.8	26.8	23.2
2	.088	844	32.8	23.2	18.9	16.4
4	.176	422	23.2	16.4	13.4	11.6
5	.220	337	20.7	14.7	12.0	10.4
6	.264	281	18.9	13.4	10.9	9.5
8	.352	211	16.4	11.6	9.5	8.2

PRESSURE DROP - 4 x 10 MESH CARBON

= 90°F

= 1000 psig

$d = 2.06 \frac{\text{lb}}{\text{ft}^3}$

$\mu = .0126$ cp

$V = .22 \frac{\text{ft}}{\text{sec}} = 13.2 \frac{\text{ft}}{\text{min}}$ (superficial velocity)

$E = .39$ (bed voidage)

$D_{Pa} = 1.84$ mm (adjusted mean particle diameter)

rgun Equation

$$= (.934)\,\frac{(1-E)^2}{E^3}\left(\frac{\mu V}{D_{Pa}^{\,2}}\right) + 8.86\,(10^{-4})\,\frac{(1-E)}{E^3}\,\frac{V^2 d}{D_{Pa}}$$

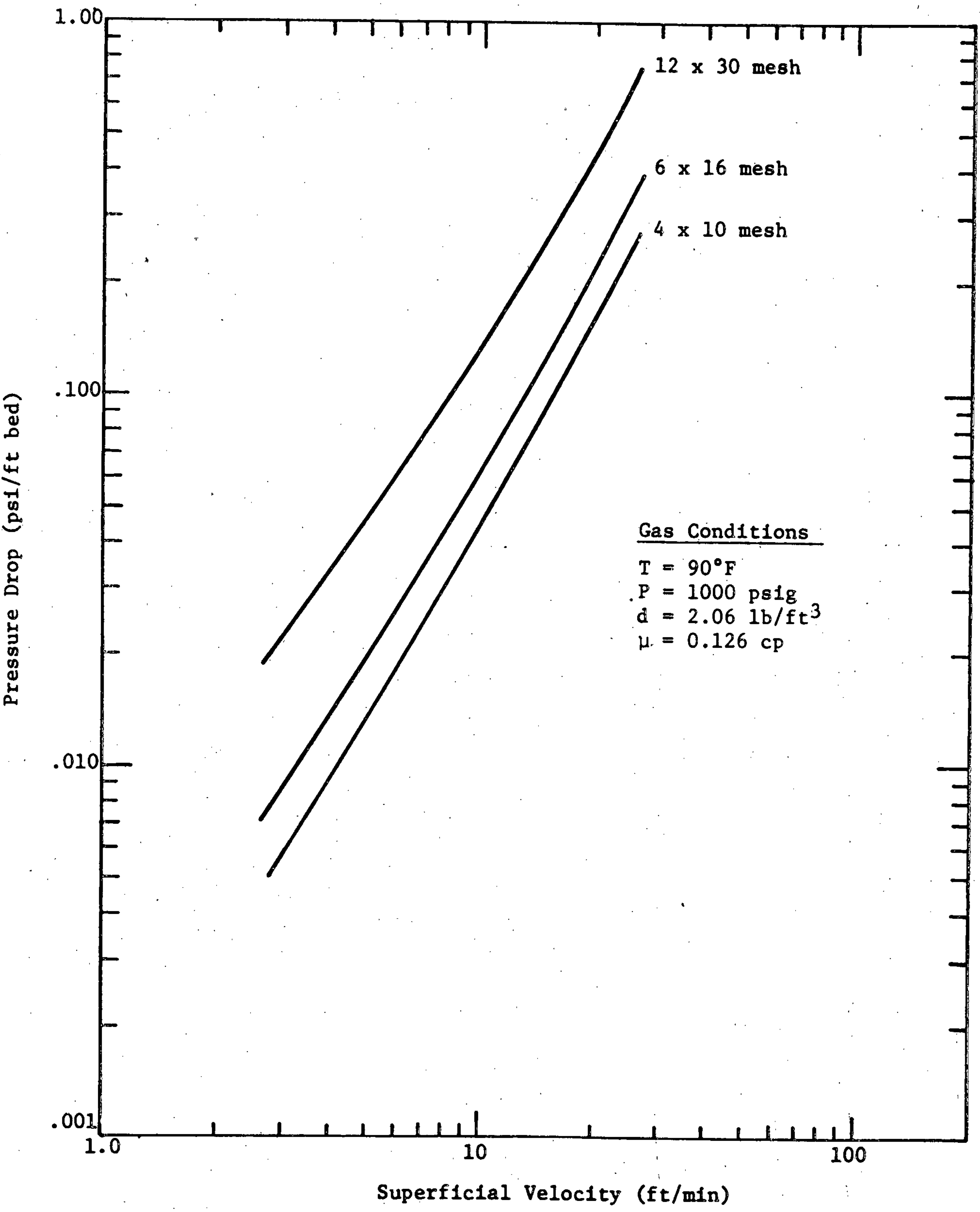
$$= (.934)\,\frac{(.61)^2}{(.39)^3}\,\frac{(.0126)(13.2)}{(1.84)^2} + (.000886)\,\frac{(.61)}{(.39)^3}\,\frac{(13.2)^2(2.06)}{(1.84)}$$

$$= .288 + 1.777 = 2.065\,\frac{\text{inches } H_2O}{\text{ft-bed}}$$

$$= \left(\frac{2.065}{12}\right)\left(\frac{62.4}{144}\right) = .075\,\frac{\text{psi}}{\text{ft-bed}}$$

PRESSURE DROP VS. SUPERFICIAL VELOCITY

BPL Activated Carbon



ATTRITION OF ADSORBENT - DUE TO HIGH GAS VELOCITY

For granular alumina system attrition should not be a problem if momentum as calculated from following relation is less than 30,000.

Momentum = (V) (M) (P)

Superficial Velocity	V = 13.4 ft/min	(.22 ft/sec.)
Molecular Weight	M = 12.2	
System Pressure	P = 69 atm	(1014.7 psig)

Momentum = (13.4) (12.2) (69)

= 11,100

SULFUR COMPOUNDS - PROPERTIES

	ppm Level	Pc (atm)	Tc (°C)	M (lb/mol)	Boiling Pt. °C (1 atm)	Liq. Sp.G.
H_2S	25	88.9	100.4	34.08	-59.6	
C_4H_4S	45	48.0	317.0	84.13	84.4	1.070 15/4
CS_2	12	76.0	273.0	76.13	46.3	1.263 20/4
CH_3SH	25	71.4	196.8	48.10	6.8	.896°
COS	80 or 10	61.0	105.0	60.07	-50.2	1.24^{-87}
	187 (117)					

EQUILIBRIUM LOADINGS

Activated Carbon BPL 2026-54 (4x10 mesh)

				[90°F and Pi]		[90°F Pi = 0.01 psig]
Sulfur Compounds	(ppm)	(Mol. Fract) Yi	(Partial Pressure) Pi Yi Pt	Loading (%) lb/100 lb	Loading W lb/lb	Loading (%) lb/100 lb
H_2S	25	.000025	.0254	.20	.002	.10
C_4H_4S	24	.000045	.0457	(30.5)	.305	21.5
CS_2	12	.000012	.0122	10.0	.10	9
CH_3SH	25	.000025	.0254	3.4	.034	2
COS	80	.000080	.0812	2.5	.025	
	10	.000010	.0102	.78	.0078	.78

Loadings all from experimental data except for C_4H_4S value which was estimated from Polanyi correlation.

T = 90°F

P = 1014.7 psia

THIOPHENE - EQUILIBRIUM LOADING

Polanyi Correlation - Sulfur Family

C_4H_4S (45 ppm) T = 32°C, 305°K P = 1000 psig

M = 84.13 Pi = .0457 psia (partial pressure)

P° = 2.116 psia (vapor pressure at 32°C)

SpG = 1.07 (at 15°C)

SpG = (1.13) est. (at Pi = .0457 psia, .00311 atm)

Liquid Molar Volume at temperature where vapor pressure equals adsorption pressure

$$u_v = \frac{M}{d} = \frac{84.13\left(\frac{gm}{mol}\right)}{1.13\left(\frac{gm}{cm^3}\right)} = 74.45\ \frac{cm^3}{mol}$$

Adsorption Potential Parameter

$$\frac{T}{V_m}\log_{10}\frac{P^\circ}{Pi} = \left(\frac{305}{74.45}\right)\log\frac{2.116}{.0457}$$

$$= 6.83$$

Loading from Sulfur Family Polanyi Plot

27 cm^3 liq./100 gm carbon

w = .27 (1.13)

w = .305 gm liquid/gm carbon

(30.5% loading)

BENZENE - EQUILIBRIUM LOADING

Benzene used as a substitute for thiophene in Pittsburgh carbon computer program. Check to see if benzene loading data fall on Polanyi sulfur family plot.

$\underline{C_6H_6}$ (45 ppm) M = 78.11 T = 32°C 305°K P = 1000 psig

Pi = .0457 psia (partial pressure)

P^o = 2.64 psia (vapor pressure at 32°C)

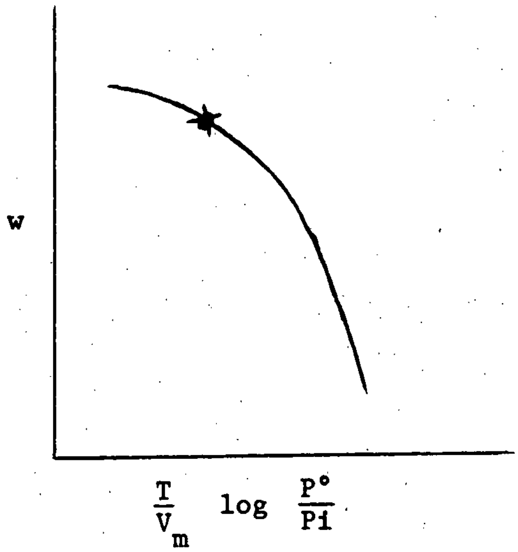
SpG = .879 (at 20°C)

$V_m = \frac{M}{d} = \frac{78.11}{.93} = 84.0$ SpG = .93 (at Pi = .0451 psia .00311 atm)

$$\frac{T}{V_m} \log_{10} \frac{P^\circ}{Pi} = \left(\frac{305}{84.0}\right) \log \frac{2.64}{.0457} = 6.40 \quad \left\{ \begin{array}{l} \text{Adsorption} \\ \text{Potential Parameter} \end{array} \right.$$

$$\left. \begin{array}{l} w = 25 \text{ gms } C_6H_6/100 \text{ gm carbon} \\ w = \frac{.25}{.89} = .281 \frac{\text{cm}^3 \text{ liquid}}{\text{gm carbon}} \end{array} \right\} \begin{array}{l} C_6H_6 \text{loading} \\ \text{on BPL } (4 \times 10) \\ \text{activated carbon} \end{array}$$

If this point is plotted on the Sulfur Family Polanyi correlation it falls on the curve drawn through the sulfur compound data.



EQUILIBRIUM FRONT CALCULATIONS

Breakthrough time	$\theta_b = 24$ hours
Total Molal Flow Rate	$\mu_T = 4500$ lbs/hr.
Total Volumetric Flow Rate	$Q = 74.27$ ft^3/sec.
Density of Adsorbent (lb/ft^3)	Cb
Molecular Weight of Contaminant Species (lb/mol)	Mi
Mole Fraction of Contaminantin Gas (mol/mol)	Yi
Mass Rate of Contaminant (lbs/mol)	Ri_i = YiNTMi
Pickup of Contaminant at Breakthrough (lbs)	$M_i\theta_b$
Equilibrium Loading of Contaminant (lb/lb carbon)	W_i
Carbon Requirement for Contaminant - Mass (lb)	C_{vi} = MiOb/Wi
Carbon Requirement for Contaminant - Volume (ft^3)	C_{vi} = Cmi/Cb
Length of Equivalent Equilibrium Section (ft)	$(LES)_i = C_{vi}/S$

Cross sectional area S based on superficial velocity V chosen

For preliminary purposes take $V = .22 \dfrac{ft}{sec}$

$$S = \frac{Q}{V} = \frac{74.27}{.22} = 337 \text{ ft}^2$$

Diameter if three vessels operate in parallel

$$D = \left(\frac{S/3}{\pi/4}\right)^{\frac{1}{2}} = 12.0 \text{ ft.}$$

Total Length of Bed

$$L_o = \sum_{i=1}^{i=N} (LES)_i + (LUB)_{i=N}$$

$$L_o = \sum_{i=1}^{i=N} \left(\frac{YiNtMi\theta_b}{WiC_bS}\right) + \frac{(LMTZ)i=N}{2}$$

CASE I - Removal of all five sulfur compounds by Physical Adsorption with virgin unimpregnated BPL carbon (4 x 10 mesh)

M_T = 45000 mols/Hr.　　θ_b = 24 hr.　　$C_b = 33\ \mathrm{lb/ft^3}$

@ $V = 0.22\ \frac{ft}{sec}$　　$S = 337\ \mathrm{ft}^2$　　Three vessels in parallel
Diameter = 12.0 ft.

(@ $V = .165\ \frac{ft}{sec}$　　$S = 450\ \mathrm{ft}^2$)　　Four vessels in parallel
Diameter = 12.0 ft.

	Contaminant Conc. Level (ppm)	Y_i	M_i $Y_iN_TM_i$ (lbs/hr)	Pickup θ_bM_i (lbs)	Loading W_i (lb/lb carbon)	Carbon Requirement C_m θ_bM_i/W_i (lbs)	C_v C_m/C_v (ft^3)	LES C_v/S (ft)	
C_4H_4S	45	.000045	170.4	4089	.305	13405	405	1.2	(.9)
CS_2	12	.000012	41.1	987	.100	9870	300	.9	(.7)
CH_3SH	25	.000025	54.1	1299	.034	38200	1160	3.4	(2.6)
COS	80	.000080	216.3	5191	.025	207600	6290	18.7	(14.0)
H_2S	25	.000025	38.3	920	.002	460080	13940	41.4	(31.0)

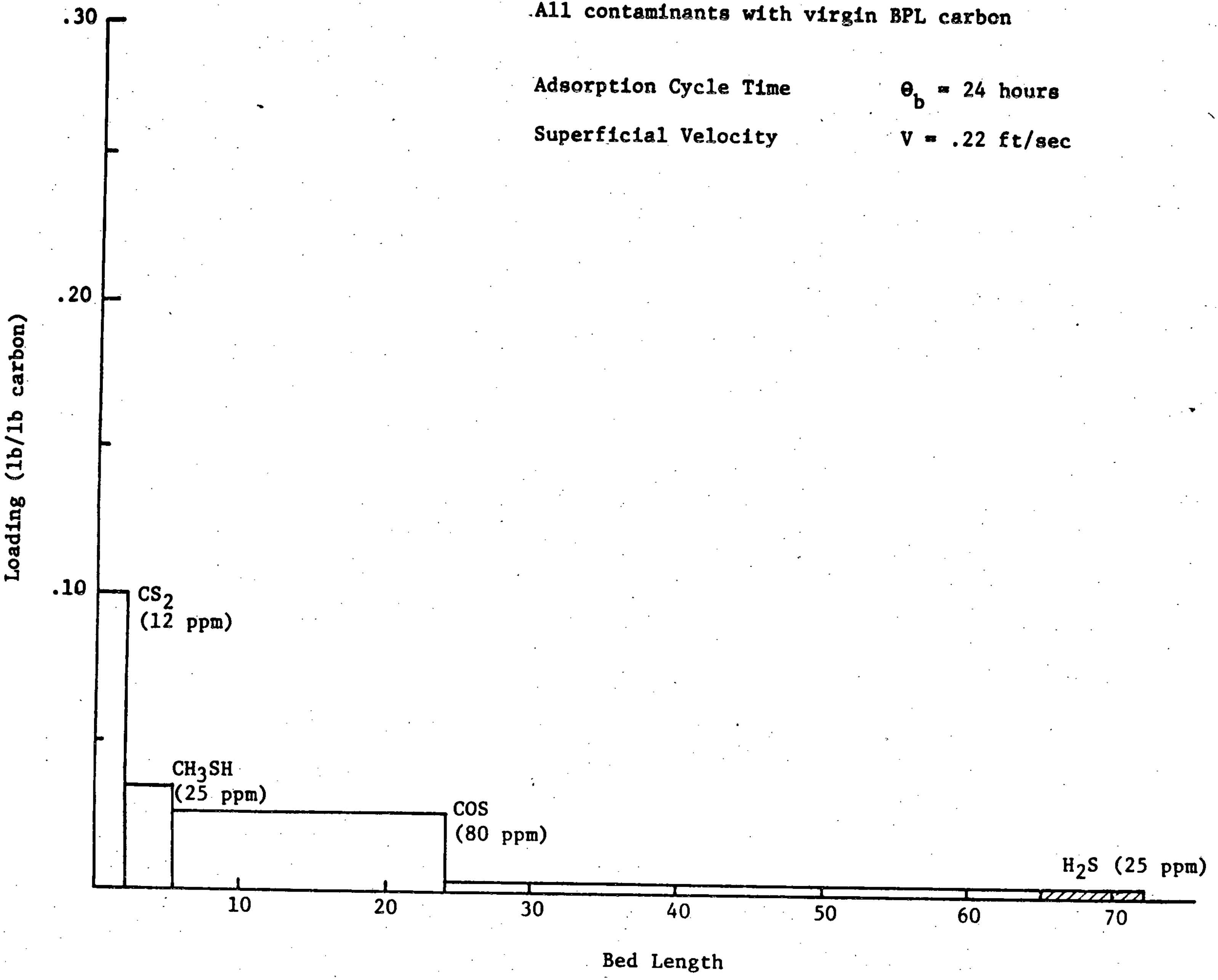
Σ (LES) = 65.6　(49.2)

$(LUB)_{H_2S}$ - Determined from calculation of Breakthrough Curve for H_2S　　$(LUB)_{H_2S}$ = 6.3　(4.8)

L_o = 71.9　(54.0)

$V = .22\ \frac{ft}{sec}$　　$V = .165\ \frac{ft}{se}$

CASE I - PHYSICAL ADSORPTION



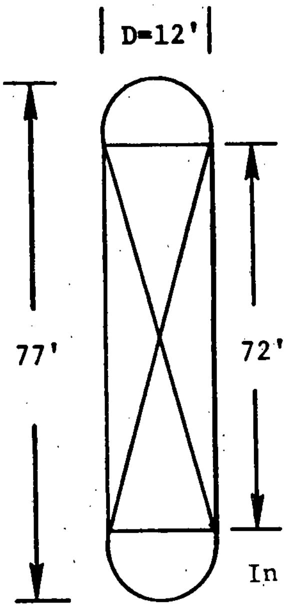
All contaminants with virgin BPL carbon

Adsorption Cycle Time θ_b = 24 hours

Superficial Velocity V = .22 ft/sec

$V = .22 \frac{\text{ft.}}{\text{sec}}$ (5 * SYNTHANE pilot plant)

D = 12.0 ft.
L = 77.0 ft.



Three Vessels in Parallel - Operating
Three Vessels in Parallel - Regenerating/Cooling

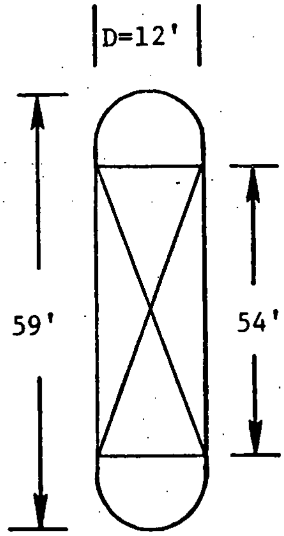
Pressure Drop = .075 psi/ft (4x10 mesh)

$\Delta P = .075\ (72) = 5.4$ psi

In this case a slightly lower velocity should be used.

$V = .165 \frac{\text{ft.}}{\text{sec}}$

D = 12.0 ft.
L = 59.0 ft.



Four Vessels in Parallel - Operating
Four Vessels in Parallel - Regenerating/Cooling

Pressure Drop = .045 psi/ft (4x10 mesh)

$\Delta P = .045\ (54) = 2.4$ psi

PROPERTIES OF ACTIVATED CARBON
(Granular Form)

Mesh Size		4 x 10	12 x 30 (estimated)
Particle Density	C_p (lbs/ft^3)	50	
Bulk Density	C_B (lbs/ft^3)	30	33
Effective Diameter	D_p (ft)	.0110	.0027
External Void Fraction	F_e	.40	.39
External Surface	A_v (ft^2/ft^3)	460	725 (.75)(970)
Specific Heat	C_p (Btu/lb°F)		
Pore Diameter	d_p (avg.)	20	

VISCOSITY OF GAS MIXTURE

	Mol.%	90°F 14.7 psia M (cp)	90°F 1000 psia M (cp)
CH_4	35		.013
H_2	45	.009	(.0099) est.
CO	15	.018	(.0198) est.
	95		

$$M_{aoe} = .0126 \text{ cp x } 2.42 = 0.30 \frac{\text{LB}}{\text{ft/hr}}$$

DIFFUSIVITY OF H_2S IN GAS MIXTURE

$$D_{H_2S} = \frac{.0043\ T^{1.5} \sqrt{\dfrac{1}{M_{H_2S}} + \dfrac{1}{M_G}}}{P \quad V_{H_2S}^{1/3} + V_G^{1/3}\ {}^{2}}$$

$M_{H_2S} = 34.08$

$M_G = 12.24$

$T = 32°C = 305°K$

$P = 1014.7 \text{ psia} = 69 \text{ atm}$

Molar volume as a liquid at its boiling point

$$V_{H_2S} = \frac{M_{H_2S}}{C_{H_2S}} = \frac{34.08 \left(\frac{gm}{gm\ mole}\right)}{.96 \left(\frac{gm}{gm}\right)} = 35.5 \frac{cm^3}{gm\ mole}$$

$$V_G = \frac{MG}{C_G} = \frac{12.24 \left(\frac{gm}{gm\ mole}\right)}{.42 \left(\frac{gm}{cm^3}\right)} = 29.1 \frac{cm^3}{gm\ mole}$$

$$D_{H_2S} = \frac{.0043\ (305)^{1.5} \left(\frac{1}{34.08} \quad \frac{1}{12.24}\right)^{1/2}}{(69)(35.3^{1/3} + 29.1^{1/3})^2} = .00273 \frac{cm^2}{sec}$$

$$D_{H_2S} = .00273 \left(\frac{cm^2}{sec}\right) \frac{3600 \left(\frac{sec}{hour}\right)}{(30.48)^2 \left(\frac{cm^2}{sec}\right)} = .0106 \frac{ft^2}{hr}$$

BREAKTHROUGH PROFILE FOR H_2S - 4 x 10 MESH CARBON

$T = 90°F$

$P = 1014.7$ psia

$V = .22 \frac{ft}{sec}$

$C = 2.06\ lb/ft^3$

$\mu = .030\ lb/ft\text{-}hr$

$D_{H_2S} = .0106 \frac{ft^2}{hr}$

$C_b = 33\ lb/ft^3$

$D_p = .0110\ ft$

$a_o = 460\ ft^2/ft^3$

$$N_{Re} = \frac{D_pG}{\mu} = \frac{.0110\ (1632)}{.030} = 598$$

$G = VC$
$G = (.22)(2.06)(3600)$
$G = 1632\ lb/hr\text{-}ft^3$

$T_D = .03$ for 4 x 10 mesh

$$N_{Sc} = \frac{\mu}{CD} = \frac{.030}{2.06\ (.0106)} = 1.37$$

$$a = \frac{ao\ TD}{(H_{SC})2/3} = \frac{460\ (.03)}{(1.37)2/3} = 11.2$$

Slope of linear isotherm:

$C = Y*/w$

$$C = \frac{6.97\ (10^{-5})}{.002} = .035$$

Loading $w = .002$ lb/lb carbon

Equilibrium
Gas Care
(25 ppm)

$$Y* = \frac{PiMi}{PM_G}$$

$$Y* = \frac{.0254\ (34.08)}{1014.7(12.24)} = 6.97\ (10^{-5})$$

$$b = \frac{acG}{C_b}$$

$$b = \frac{11.2\ (.035)\ (1632)}{33} = 19.3$$

BREAKTHROUGH PROFILE - H_2S (25 ppm)

$a = 11.2$

	$\left(\frac{YoaT}{Yin}\right)$	bO $z=41.4$ $az=464$	O $b=19.3$ (hr)	$\frac{Yact}{Yin}$	bO $Z=47.7$ $AZ=534$	O $b=19.3$ (hr)
O_b	.01	390	20.21	.01	470	24.30
	.10	420	21.76	.10	510	26.42
O_s	.50	460	23.83	.50	540	27.98
	.90	495	25.65	.90	600	31.09

$$LUB = L_o\left(\frac{O_s - O_b}{O_s}\right)$$

$$= 41.4\left(\frac{23.83-20.21}{23.83}\right)$$

$$= 41.4\ (.152)$$

$LUB = 6.3$ ft.

$LES = 41.4$ (Used this value as initial estimate of Z)

$L_o = 47.7$ ft.

$$LUB = L_o\left(\frac{O_s - O_b}{O_s}\right)$$

$$= 47.7\left(\frac{27.98-24.30}{27.98}\right)$$

$$= 47.7\ (.132)$$

$LUB = 6.3$ ft.

$LES = 41.4$

$L_o = 47.7$ ft.

Superficial Velocity } $V = .22\ \frac{ft.}{sec}$

Front Velocity } $U = \frac{Lo}{O_s}$

$$U = \frac{47.7}{27.98}\ \frac{1}{3600}$$

$$U = .00047\ ft/sec$$

CASE II - CHEMISORPTION - H_2S removal $w' = .04$ lb/lb carbon
(Loading value from development program)

PHYSICAL ADSORPTION - COS, CH_3SH, CS_2, C_4H_4S removal
(Equilibrium loadings of BPL derated)
$10' = .90$ (co)

$ri_i = 45000$ mols/hr $\theta_b = 24$ hr. $C_b = 33$ lb/ft^3

@ $V = 0.22$ ft/sec $S = 337$ ft^2 (Three vessels in Parallel)
Diameter = 12.0 ft.

	Contaminant Conc. (ppm)	Level Y_i	M_i $Y_iN_tM_i$ (lbs/hr)	Pickup θ_bM_i (lbs)	Loading W_i (lb/lb carbon)	Carbon Requirement Cm θ_bM_i/W_i (lbs)	Carbon Requirement Cv Cm/C_v (ft^3)	LES C_v/S (ft)
H_2S	25	.000025	38.3	920	.040	23000	697	2.1
C_4H_4S	45	.000045	170.4	4089	.2745	14895	451	1.3
CS_2	12	.000012	41.1	987	.090	10960	332	1.0
CH_3SH	25	.000025	54.1	1299	.0306	42440	1286	3.8
COS	80 (10)	.000080 (.000010)	216.3 (27.0)	5191 (649)	.0225 (.00702)	230670 (92415)	6990 (2800)	20.8 (8.3)

Σ (LES) = 26.9 (14.4

$(LUB)_{cos}$ = 5.6 (2.6)

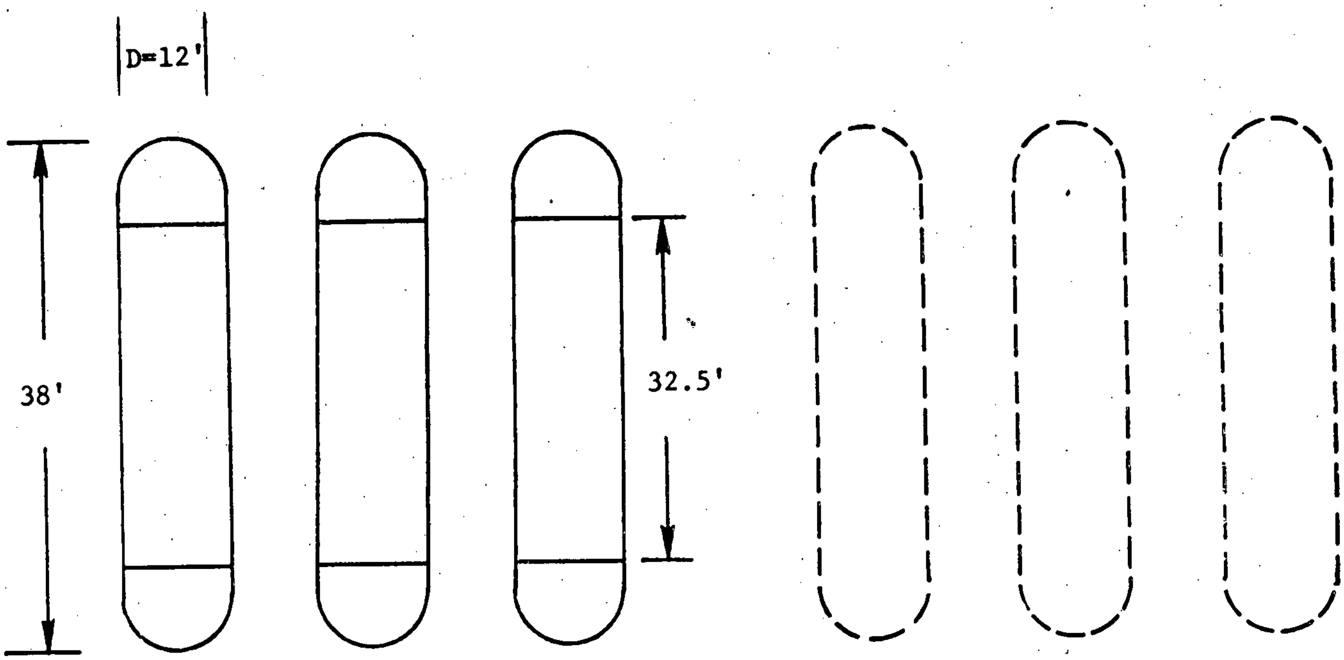
L_o = 32.5 (17.0

COS   80 ppm 10 ppm

$(LUB)_{cos}$ - Determined from calculation of Breakthrough Curve for COS

Three Vessels in Parallel - Operating (D = 12.0 ft.)

Three Vessels in Parallel - Regenerating/Cooling (L = 38.0 ft.)



Pressure Drop = $.075 \frac{\text{psi}}{\text{ft bed}}$ for 4 x 10 mesh carbon

$\Delta P = .075\ (32.5) = 2.4$ psi

The above is for a COS level of 80 ppm.

For a COS level of 10 ppm

Vessel Dimensions would be D = 12.0 ft

L = 22.0 ft

$\Delta P = .075\ (17.0) = 1.3$ psi

DIFFUSIVITY OF COS IN GAS MIXTURE

$$D_{COS} = \frac{.0043\ T^{1.5}\sqrt{\frac{1}{M_{COS}} + \frac{1}{M_G}}}{P\ (V_{COS}^{1/3} + V_G^{1/3})^2}$$

$T = 32°C = 305°K$ $M_{COS} = 60.07$

$P = 1014.7$ psia $= 69$ atm $M_G = 12.24$

Molar Volume as a liquid at its boiling point

$$V_{COS} = \frac{M_{COS}}{CL_{COS}} = \frac{60.07}{1.17} = 51.3\ \frac{cm^3}{gm\ mol}$$

$$VG = \frac{MG}{CLg} = \frac{12.24}{.42} = 29.1$$

$$D_{COS} = \frac{.0043\ (305)^{1.5}\ \left(\frac{1}{60.07}\quad \frac{1}{12.24}\right)^{1/2}}{(60)(51.3^{1/3} + 29.1^{1/3})^2} = .00226\ \frac{cm^2}{sec}$$

$$D_{COS} = .00226\left(\frac{cm^2}{sec}\right) = \frac{3600\ \left(\frac{sec}{hr}\right)}{30.48^2\ \left(\frac{cm}{ft}\right)^2} = .00874\frac{ft^2}{hr}$$

BREAKTHROUGH PROFILE FOR COS - 4 x 10 MESH

$T = 90°F$

$P = 1014.7$ psia

$V = .22$ ft/sec.

$C = 2.06$ lb/ft^3

$M = .030$ lb/ft-hr.

$D_{COS} = .00874 \frac{ft^3}{hr}$

$C_b = 33$ lb/ft^3

$D_p = .0110$ ft

$a_o = 460$ ft^2/ft^3

$$H_{Re} = \frac{D_pG}{\mu} = \frac{.0110\ (1632)}{.030} = 598$$

$G = Ve$

$G = (.22)(2.06)(3600)$

$G = 1632$ lb/hr-ft^2

TD = .030 for 4 x 10 mesh

$$H_{SC} = \frac{\mu}{CD} = \frac{.03}{2.06\ (.00874)} = .168$$

$$a = \frac{av\ TD}{(H_{sc})2/3} = \frac{460\ (.03)}{(1.68)2/3} = 9.75$$

Slope of linear isotherm:

$$C = \frac{Y^*}{w'}$$

Loading w' = .0225 lb/lb carbon

$$C = \frac{3.93\ (10^{-4})}{.0225} = .0175$$

Equilibrium
Gas Conc.
(80 ppm)

$$b = \frac{acG}{Cb}$$

$$b = \frac{9.75\ (.0175)(1632)}{33} = 8.44$$

BREAKTHROUGH PROFILE - COS (80 PPM)

a = 9.75

	Yoat Yin	b0 z=20.8 az=203	0 b=8.44 (hr)	Yoat Yin	b0 z=25.8 az=252	0 b=8.44
0_b	.01	160	18.96		200	23.70
	.10	175			220	26.06
0_s	.50	210	24.88		255	30.21
	.90				285	33.77

$$LUB = Lo \left(\frac{0_s - 0_b}{0_s}\right)$$

$$= 20.8 \left(\frac{24.88-18.96}{24.88}\right)$$

$$= 20.8\ (.238)$$

LUB = 5.0 ft.

LES = 20.8 ft. (used this value as initial estimate of Z)

Lo = 25.8 ft.

$$LUB = Lo \left(\frac{0_s - 0_b}{0_s}\right)$$

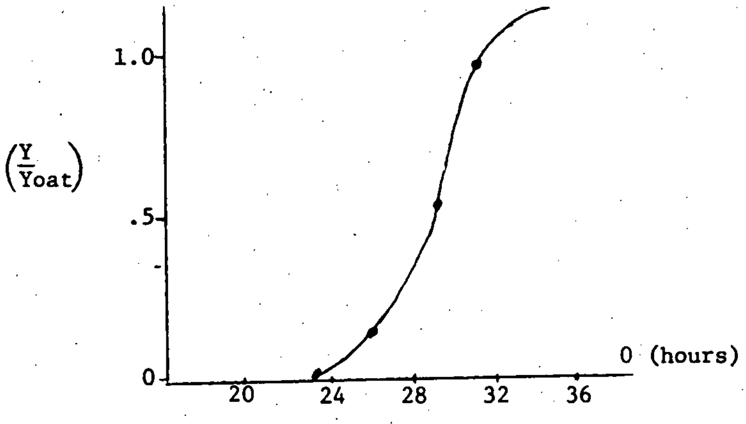
$$= 25.8 \left(\frac{30.21-23.70}{30.21}\right)$$

$$= 25.8\ (.216)$$

LUB = 5.6 ft.

LES = 20.8 ft.

Lo = 26.4 ft.



Superficial Velocity } V = .22 ft/sec.

Front Velocity } $U = \frac{Lo}{0_s}$

$$U = \frac{26.4}{30.21} \; \frac{1}{3600}$$

U = .00024 ft/se

ASE III - CHEMISORPTION - H_2S removal w' = .04 lb/lb. carbon.
(loading value from development program)

PHYSICAL ADSORPTION - CH_3SH, CS_2, C_4H_4S removal (Equilibrium loadings of BPL derated 10%) w' = .90(10)

i_T = 45000 mols/hr. O_L = 24 hr. C_b = 33 lb/ft^3

V = .22 ft/sec S = 337 ft^2 Three Vessels in Parallel
Diameter = 12.0 ft.

(@ V = .33 ft/sec. S = 225 ft^2)
Two vessels in parallel D = 12.0 ft.

	Contaminant Conc. Level (ppm)	Y_i	M_i $Y_iN_tM_i$ (lbs/hr)	Pickup θ_bM_i (lbs)	Loading W_i (lb/lb carbon)	Carbon Requirement		LES C_v/S (ft)	
						Cm θ_bM_i/W_i (lbs)	Cv Cm/Cv (ft^3)		
H_2S	25	.000025	38.3	920	.040	23000	697	2.1	(3.1)
$_4H_4S$	45	.000045	170.4	4089	.2745	14895	451	1.3	(2.0)
S_2	12	.000012	41.4	987	.090	10960	332	1.0	(1.5)
H_3SH	25	.000025	54.1	1299	.0306	42440	1286	3.8	(5.7)

Σ (LES) = 6.1 (9.2)

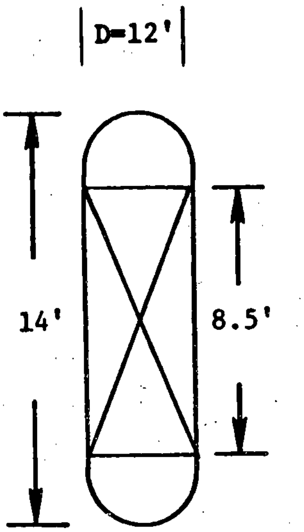
(LUB) = 2.2 (2.8)
CH_3SH

Lo = 8.3 (12.0)

V=.22 $\frac{ft}{sec}$ V=.33 $\frac{ft}{se}$

$V = .22 \frac{ft}{sec}$ (5* SYNTHANE pilot plant)

D = 12.0 ft.
L = 14.0 ft.



Three Vessels in Parallel - Operating
Three Vessels in Parallel - Regenerating/Cooling

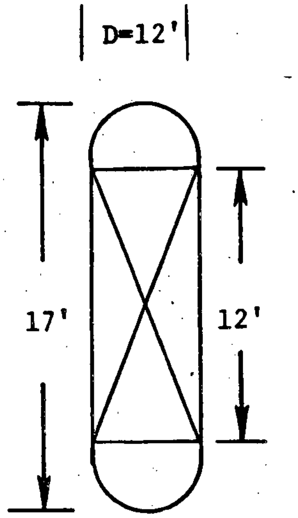
Pressure Drop = .075 psi/ft (4x10 mesh)

$\Delta P = .075\ (8.5) = .64$ psi

In this case a higher velocity can be used

$V = .33 \frac{ft}{sec}$

D = 12.0 ft.
L = 17.0 ft.



Two Vessels in Parallel - Operating
Two Vessels in Parallel - Regenerating/Cooling

Pressure Drop = .16 psi/ft (4x10 mesh)

$\Delta P = .16\ (12) = 1.9$ psi

DIFFUSIVITY OF CH_3SH IN GAS MIXTURE

$$D_{CH_3SH} = \frac{.0043\ T^{1.5} \sqrt{\frac{1}{M_{CH_3SH}} \quad \frac{1}{M_G}}}{P\ (V_{CH_3SH}{}^{1/3} + V_G{}^{1/3})2}$$

$T = 32°C = 305°K$

$P = 1014.7$ psia $= 69$ atm

$M_{CH3SH} = 48.10$

$M_G = 12.24$

$$V_{CH_3SH} = \frac{M_{CH_3SH}}{CL_{CH_3SH}} = \frac{48.10}{.885} = 54.4$$

$$V_G = \frac{MG}{CLG} = \frac{12.24}{.42} = 29.1$$

$$D_{CH_3SH} = \frac{.0043\ (305)^{1.5} \left(\frac{1}{48.10} + \frac{1}{12.24}\right)^{1/2}}{(69)(54.4^{1/3} + 29.1^{1/3})^2} = .00226\ \frac{cm^2}{sec}$$

$$D_{CH_3SH} = .00226 \left(\frac{cm^2}{sec}\right) \frac{3600 \left(\frac{sec}{hr}\right)}{30.48^2 \left(\frac{cm}{ft}\right)^2} = .00874\ \frac{ft^2}{hr}$$

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