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_3SH (1) 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 Rate (3) (std. ml/sec)	41.7
Initial Superficial Velocity (3), actual (cm/sec)	1.36
Initial Space Velocity (3), 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

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 unimpregnated activated carbon (Grant, R. J., et al (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 Gas(1): H_2∿45%; CH_4∿35%; CO∿13.2-13.5%; N_2∿4.5-4.8%; CO_2∿1%; C_2H_6∿1%; H_2O∿0.05-0.07%

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 9(2)		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. Carbon(5)	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).

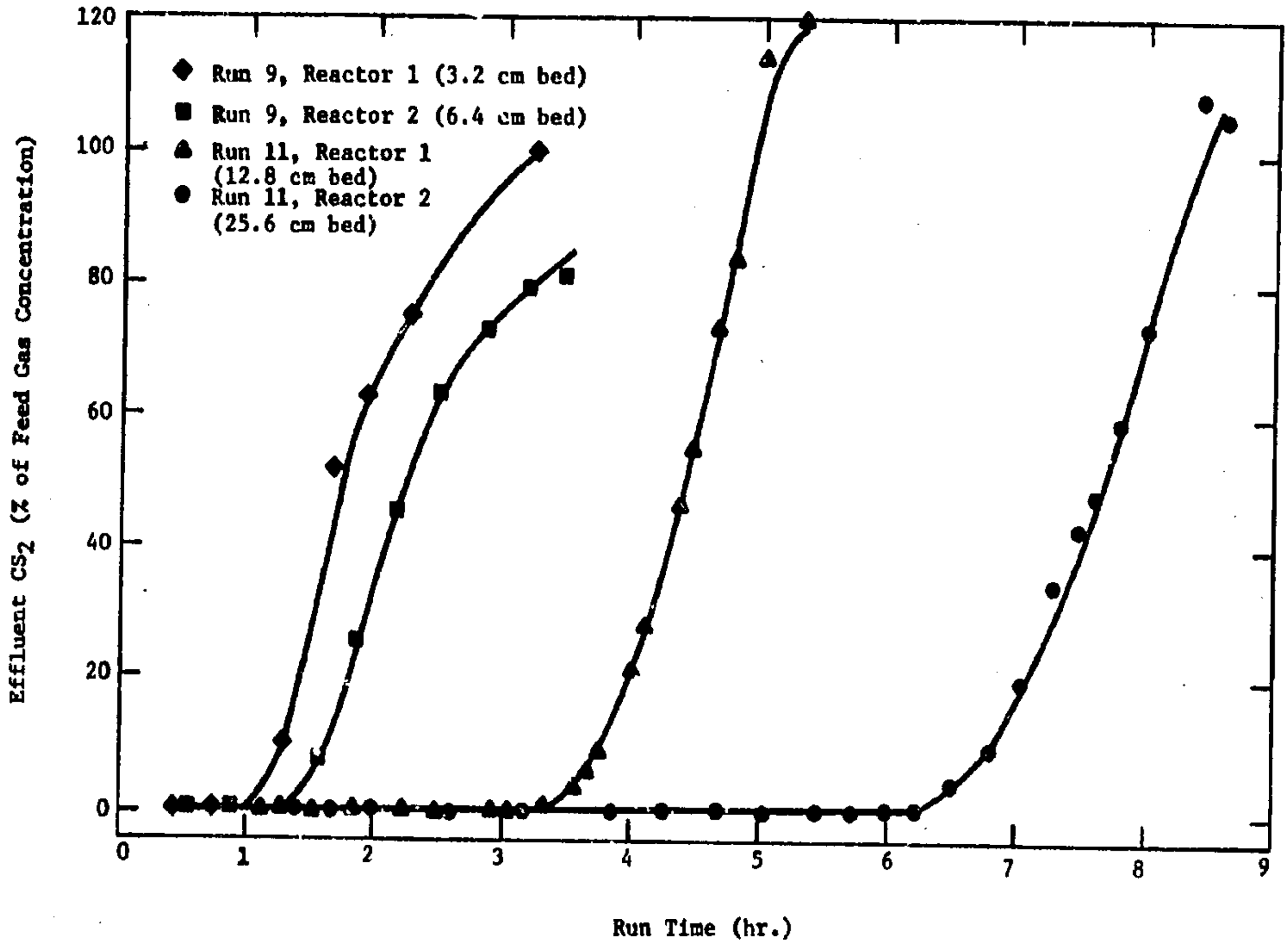
3. Time-averaged feed concentration prior to breakthrough.

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 Gas[1]: $H_2 \sim 40.9\%$; $CH_4 \sim 31.8\%$; $CO \sim 13.6\%$; $N_2 \sim 11.8\%$; $CO_2 \sim 0.91\%$; $C_2H_6 \sim 0.91\%$; $H_2O \sim 0.05$-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

	Reactor 1				Reactor 2			
	COS	CS_2	C_4H_4S	CH_3SH[2]	COS	CS_2	C_4H_4S	CH_3SH[2]
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 Breakthrough[6]	<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. Carbon[7]	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)

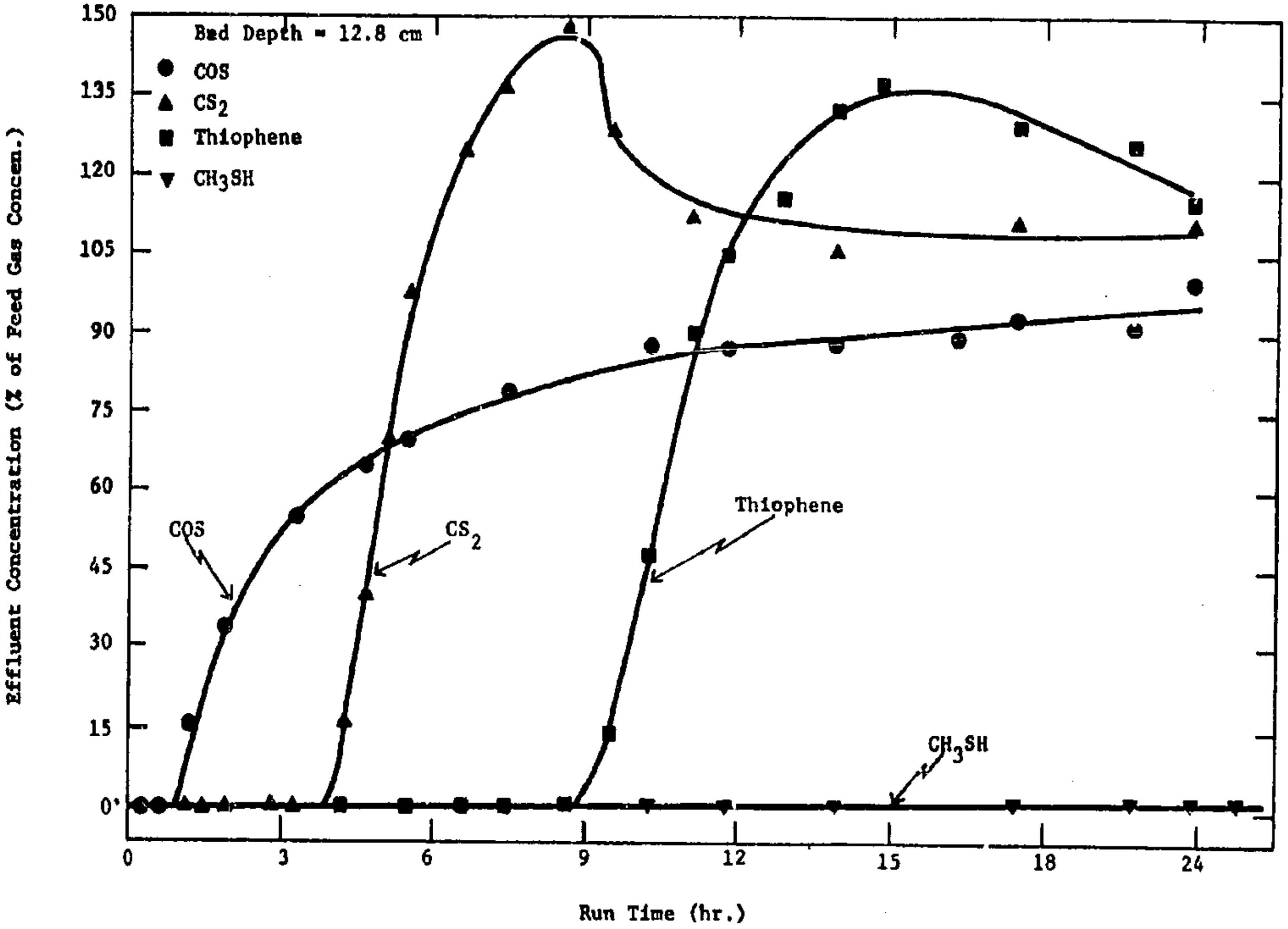
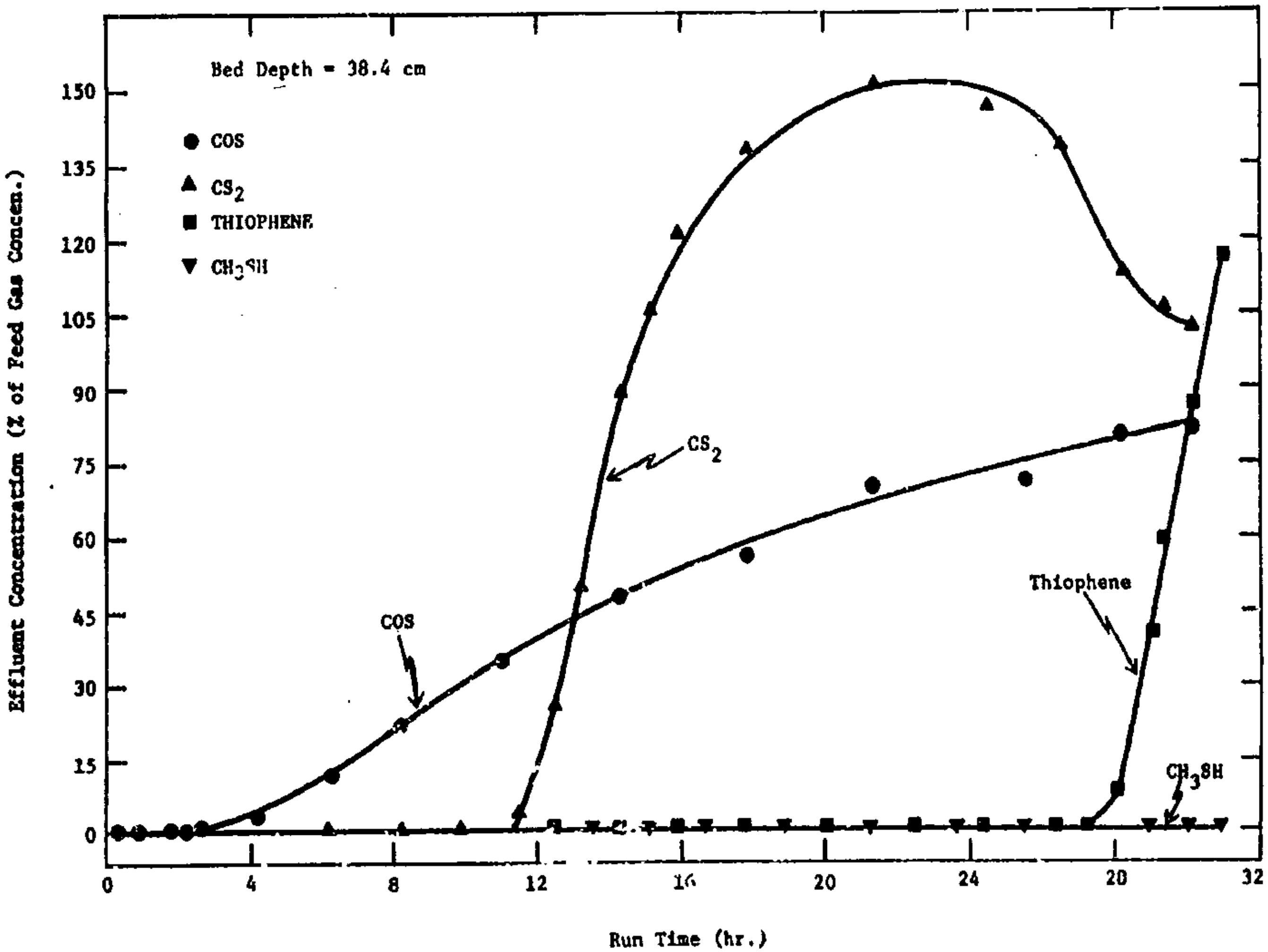


FIGURE 4.9

REMOVAL OF COS, CS_2, THIOPHENE, AND CH_3SH IN SYNTHESIS GAS VIA METAL-IMPREGNATED ACTIVATED CARBON
Run 12, 5277-27 (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 20 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 1G, 5277-44)

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

Simulated Synthesis Gas(1): H_2 ≈ 45.0%; CH_4 ≈ 33.2%; CO ≈ 12.6%; N_2 ≈ 7.3%; CO_2 ≈ 0.95%; C_2H_6 ≈ 0.95%; H_2O ≈ 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 Breakthrough(5)	<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 Carbon(6)	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 ≃ 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)

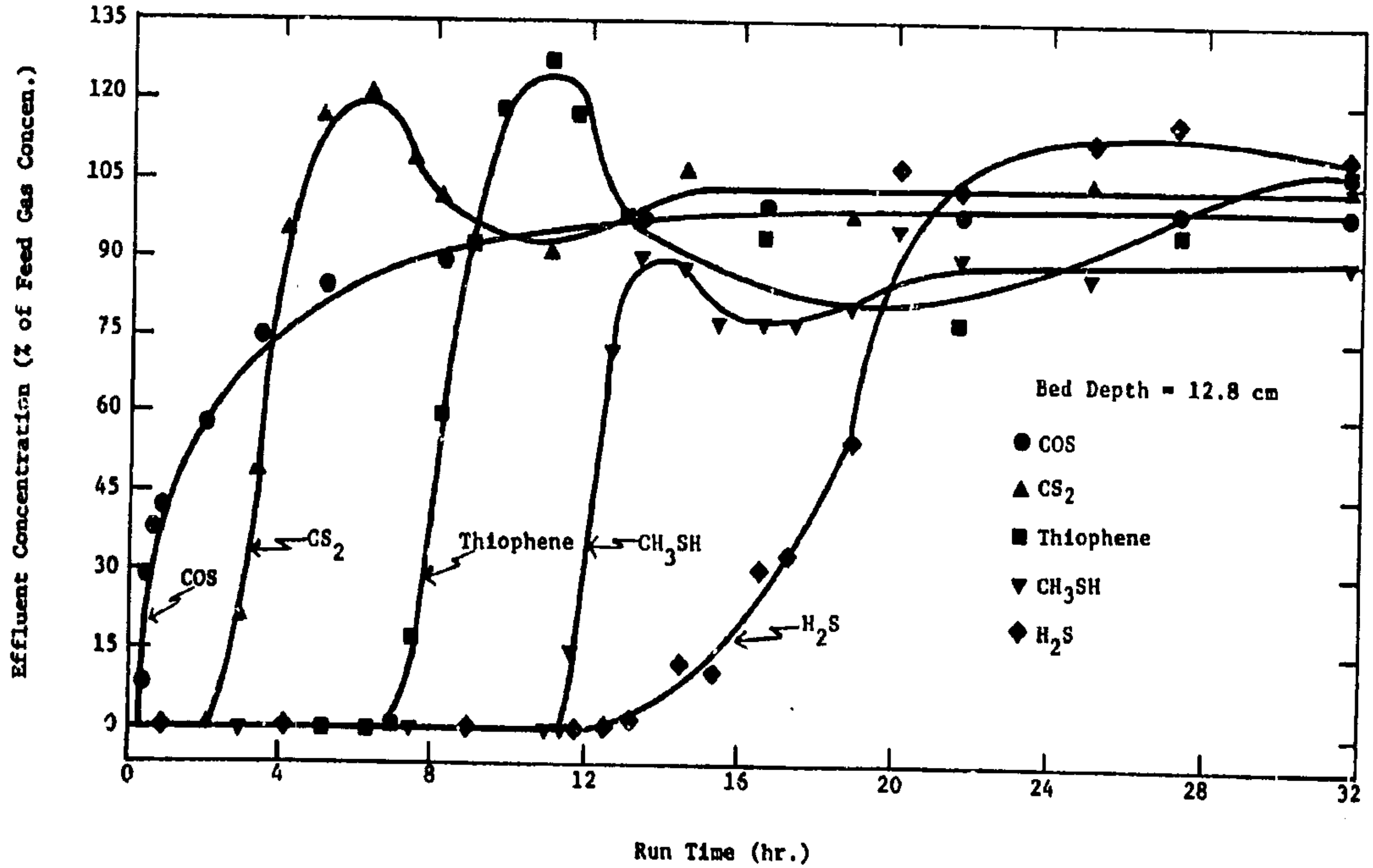
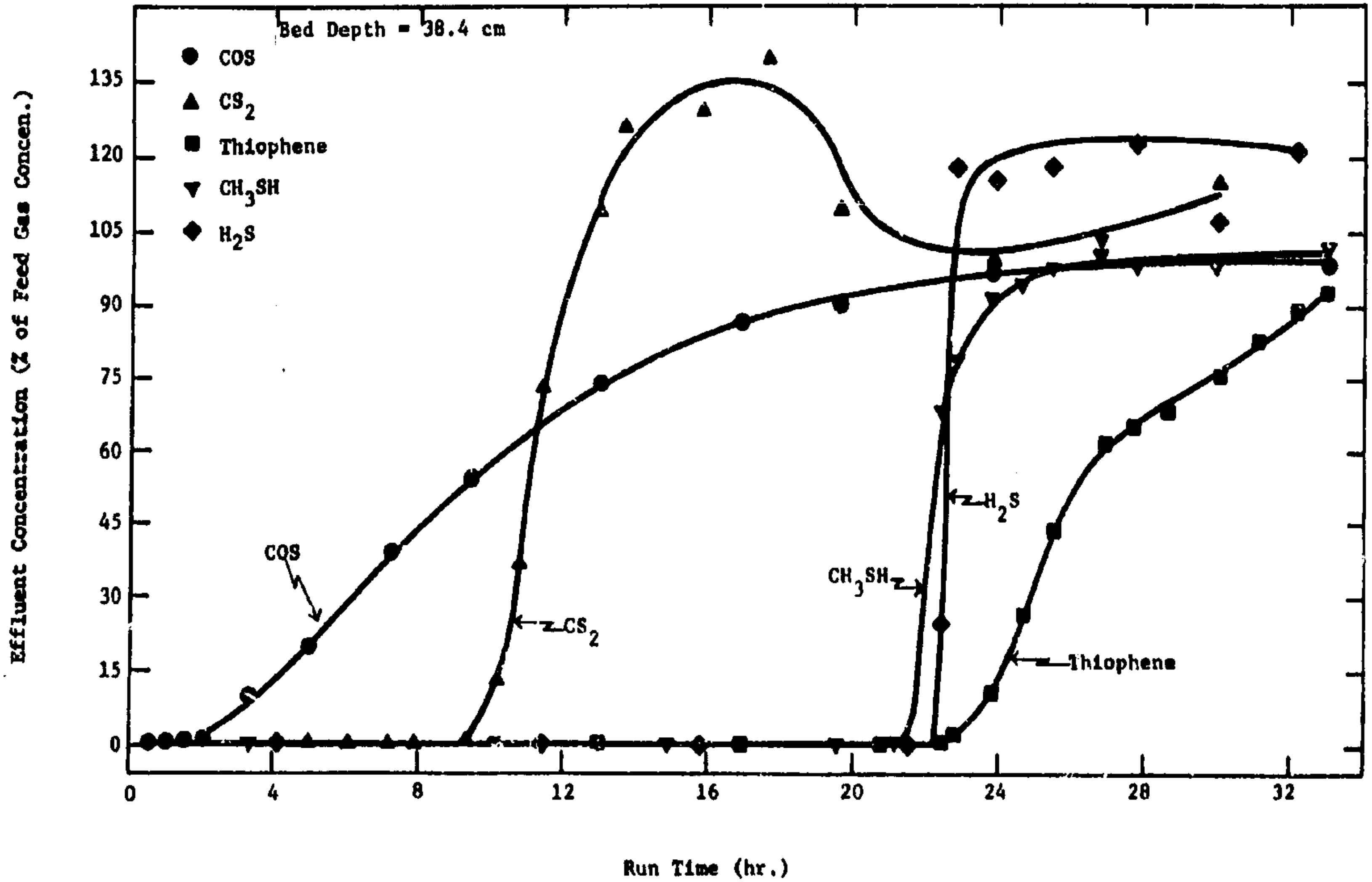


FIGURE 4.11

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		473,000 186,000	78,300 92,400	85,800 90,600	201,000 214,000	307,000 184,000	
	$\bar{x}$	329,500	85,350	88,200	207,500	245,500	
	s	202,900	9,970	3,400	9,192	86,973	
	$\frac{s}{\bar{x}} \times 100$	62%	11.7%	3.9%	4.4%	35.4%	Average precision for five component run 23.5%
Four		not present	145,000 151,000	120,000 109,000	257,000 242,000	no break-thru occurred	
	$\bar{x}$	-	148,000	114,500	249,500	-	
	s	-	4,243	7,778	10,607	-	
	$\frac{s}{\bar{x}} \times 100$	-	2.9%	6.8%	4.3%	-	Average precision for four component run 4.7%
Single		101,000 140,000 80,000	51,300 35,300 57,100	169,000 111,000 109,000 95,300	319,000 212,000 298,000	insuf-ficient data	
	$\bar{x}$	107,000	47,900	121,000	276,330		
	s	30,447	11,295	32,756	56,697		
	$\frac{s}{\bar{x}} \times 100$	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 multi-component 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.

7. REFERENCES

1. Abel, W. T., Shultz, F. G., and Langdon, P. F., "Removal of Hydrogen Sulfide from Hot Producer Gas by Solid Sorbents," Bu. Mines RI 7974, (1974).

2. Anonymous, "SNG Process Description: Benfield Corporation CO_2 Removal Process for SNG Plants," Pipeline and Gas J. (Oct. 1972).

3. Clines et. al., Paper No. 111F, 68th Annual AIChE meeting, Los Angeles, Nov. 16-20, 1975.

4. Conviser, S. A., "Molecular Sieves Used to Remove Mercaptans from Natural Gas," Oil and Gas J. (Dec. 6, 1965).

5. Estep, J. W., et. al., "The Recovery of Sulfur from Sour Natural and Refinery Gases," from "Advances in Petroleum and Chemistry and Refining," J. J. McKetta, Jr. Ed., Interscience 1962.

6. Forney, A. J., Haynes, W. P., Gasior, S. J., Kornosky, R. M., Schmidt, C. E., and Sharkey, A. G., "Trace Element and Major Component Balances Around the Synthane PDU Gasifier," PERC/TPR-75/1 (August 1975).

7. Forney, A. J., Haynes, W. P., Gasior, S. J., Johnson. G. E., and Strakey, J. P., Jr., "Analysis of Tars, Chars, Gases, and Water Found in Effluents from the Synthane Process," PERC Bu. Mines AITPCE Program TPR 76 (January 1974).

8. Grant, R. J., Manes, M., and Smith, S. B., "Adsorption of Normal Paraffins and Sulfur Compounds on Activated Carbon," A.I.Ch.E.J., 8, No. 3, 403 (1962).

9. Grant, R. J., "The Adsorption of Sulfur Gases and Vapors by BPL Activated Carbon," Pittsburgh Coke & Chemical Company, Project No. 4-1141, Report No. 2 (Sept. 1, 1960).

10. Greyson, M., Demeter, J. J., Schlesinger, M. D., Johnson, G. E., Jonakin, J., and Myers, J. W., "Synthesis of Methane," Bu. Mines RI 5137 (July, 1955).

11. Haynes, W. P., Elliott, J. J., and Forney, A. J., "Experience with Methanation Catalysts," Preprints, 163rd National ACS Meeting, Boston, April 10-14, 1972, 16, No. 2, 47-63.

12. Riesz, C. H., Dirksen, H. A., Kirkpatrick, W. J., "Sulfur Poisoning of Nickel Catalysts," IGT Res. Bul. No. 10, Inst. of Gas Technol. (September 1951).

13. Kalfadelis, C. D., and Magee, E. M., "Evaluation of Pollution Control in Fossil Fuel Conversion Processes; Gasification: Section 1, SYNTHANE Process," EPA-650/2-74-009b, June 1974.

14. Lukchis, G. M., Chemical Engineering, p. 111, June 11, 1973.

15. Mason, D. Mc A., and Hakewill, H., Jr., "Identification and Determination of Organic Sulfur in Utility Gases," IGT Res. Bul. No. 5 (A.E.S. Newmann, Ed.), Inst. of Gas Technol. (Jan. 1959).

16. Mills, G. A., and Steffgen, F. W., "Catalytic Methanation," Catalysis Reviews, 8 (2), 159 (1973).

17. Parrish, R. W., and Neilson, H. B., "Synthesis Gas Purification Including Removal of Trace Contaminants by the BENFIELD Process", 167th ACS Nat'l Meeting, Div. of Ind. and Eng'g. Chem., Los Angeles (Mar. 31-Apr. 5, 1974).

18. Risenfeld, F. C., and Kahl, A. L., "Gas Purification," 2nd Edition, Gulf Publishing Co., 1974.

19. Johnson, G. E., Field, J. H., Decker, W. A., and Jimeson, R. M., "Removing Hydrogen Sulfide Synthesis Gas with Iron Oxide at Elevated Pressure," Bu. Mines RI 6023 (1962).

20. Rostrup-Nielson, J. R., "Some Principles Relating to the Regeneration of Sulfur-Poisoned Nickel Catalyst," J. Catalysis, 21, 171 (1971).

21. Turnock, P. H., and Gustafson, K. J., "Advances in Molecular Sieve Technology for Natural Gas Sweetening," 22nd Annual Gas Cond. Conf., U. of Okla. (April, 1972).

22. Satterfield, C. N., et. al., AIChE J., 21, No. 6, 1100, Nov. 1975.

23. Satterfield and Roberts, AIChE J., 14, No. 1, 159 (1968).

24. Ranke, G., "Advantages of the Rectisol-Wash Process", Chem. Eng. World, Vol. IX, No. 8, August 1974.

25. Sweny, J. W., "The Selexol Process for Acid Gas Removal", Bulletin #273, Allied Chemical Corp.

26. Bonnifray, P. et al., "Partial and Total Sulfur Recovery," Chemical Engineering Progress, Vol. 68, No. 8, pp. 51-52, August 1972.