

Preparation of Catalysts

Four types of catalysts were used in the laboratory experiments - fused, precipitated, precipitated on a carrier, and simple mixed oxides. Following Huff, catalyst compositions were expressed as proportions of the pure metallic elements because of uncertainty as to the exact state of oxidation after heating. Thus, for example: 80:10:10 Cu:Cr:V represents a mixture of the oxides of copper, chromium, and vanadium which is equivalent to the proportions indicated of the pure metals.

The fused catalyst was prepared as follows: A weighed amount of ammonium dichromate was heated in an evaporating dish until transformation to the green oxide was effected. This active chromium oxide was then mixed with the calculated amounts of cuprous oxide and vanadium pentoxide. This mixture was then heated to approximately 1,600° C. in a graphite crucible, at which temperature the mixture reached a pasty consistency. The mixture was then cooled, crushed and sized to 10- to 14-mesh.

32/ See footnotes 29 and 30.

TABLE 7. - Tests with cobalt molybdate and platinized-alumina catalysts

Catalyst A - Cobalt molybdate
 Catalyst B - 0.5% platinum on alumina
 Gas used - Synthesis gas containing 30% steam

Catalyst	Catalyst temp., °C.	Sp. vel., hr.-1	H ₂ S in inlet gas, gr./100 cu. ft.	Total org. S in inlet gas, gr. S/100 cu. ft.	Approx. concentration of individual compounds in inlet gas, gr. S/100 cu. ft.			Total org. S in outlet gas, gr. S/100 cu. ft.
					CS ₂	C ₂ H ₅ SH	C ₄ H ₄ S	
A.....	400	500	0	35	10	16	9	3.5
B.....	400	500	0	35	10	16	9	5.8
A.....	500	700	0	35	10	16	9	.70
B.....	500	700	0	35	10	16	9	1.57
A.....	560	700	0	35	10	16	9	.69
B.....	560	700	0	35	10	16	9	1.58
A.....	500	700	0	38	15	23	9	.56
B.....	500	700	0	38	15	23	9	1.96
A.....	500	350	0	38	15	23	9	.43
B.....	500	350	0	38	15	23	9	1.53
A.....	500	700	340	30	9	12	9	6.02
B.....	500	700	340	30	9	12	9	8.94
A.....	600	700	250	29	14	15	25	4.86
A.....	600	700	250	25				4.95
A.....	500	700	250	0				.59
B.....	500	700	250	0				1.44

Precipitated catalyst was prepared as follows: The nitrates or chlorides of copper and vanadium (weighed amounts) were dissolved in water and precipitated with alkali. Some catalysts were prepared in which uranyl nitrate was used instead of the vanadium salt.

The alkali used was, at different times, ammonium, sodium, or potassium hydroxide. The precipitate was washed by decantation, then filtered and washed free of alkali. The precipitate was then added to a concentrated solution of ammonium dichromate; the resulting paste was then dried at 400° C.

To make precipitated catalyst on a carrier, the desired amount of carrier (clay or Porocel) is added to the aqueous solutions of the metallic salts. The catalysts containing carriers were baked at 815° C. for 2 hours.

Mixed-oxide catalysts were prepared by first mixing technical or C. P. cuprous oxide and vanadium pentoxide in the dry state. The oxide mixture was then added to a concentrated solution of ammonium dichromate and dried at 400° C.

All catalysts, except the fused catalysts, were made into 1/8-inch pellets in a Stokes Eureka tableting machine.

A large number of runs were first made to develop the technique of preparing and testing catalysts. From these runs, it was possible to select the most promising catalysts and conditions for further study. These first tests also revealed that thiophene was not removed; as a matter of fact, thiophene poisoned the catalyst so that, even when thiophene addition was stopped, the catalyst performed poorly for the removal of carbon disulfide and ethyl mercaptan. Such poisoning was largely eliminated after revivification by burning off sulfur with air.

Data in table 8 show the effect on removal of organic sulfur for one of these preliminary runs using a copper, chromium, uranium catalyst. No data for hydrogen sulfide removal are shown, since primary attention was being given during these runs to the effect of changing conditions on organic sulfur removal.

TABLE 8. - Run #1

Catalyst - 80% Cu, 10% U, 10% Cr (precipitated and pelleted)
Gas contains 3.0 mol percent steam

Catalyst temp., °C.	Sp. vel., hr.-1	H ₂ S in inlet gas, gr./100 cu. ft.	Org. S, gr. S/100 cu. ft.				Org. S in outlet gas, gr. S/100 cu. ft.
			Total	CS ₂	C ₂ H ₅ SH	C ₄ H ₄ S	
450.....	1,400	0	12	8	4	0	0.03
450.....	2,000	200	0.08				.01
450.....	2,000	200	10	10			.09
500.....	2,000	180	20	5		15	14.9
550.....	2,000	180	10	10			.30
450.....	2,000	200	5	5			1.20

Table 9 gives data for another series of preliminary runs, using three different catalyst compositions. Catalyst 1 was 80 percent Cu, 10 percent Cr, and 10 percent V, precipitated and pelleted, with no carrier. Catalyst 2 was a mixture of 70 percent Florida kaolin clay and 30 percent oxides (80 percent Cu, 10 percent Cr, and 10 percent V), precipitated, pelleted, and baked at 815° C. for 2 hours. Catalyst 3 was a mixture of 70 percent Porocel and 30 percent oxides (80 percent Cu, 10 percent Cr, and 10 percent V), precipitated, pelleted, and baked at 815° C. for 2 hours.

Between successive runs, the catalysts were revived by means of air passed over the catalyst at bed temperatures of 450° C. and at a space velocity of 2,000 hours.⁻¹

Run 1 confirmed the previous observation that thiophene is not converted and also showed that the catalyst capacity for absorption of total sulfur - including hydrogen sulfide - is lessened by the poisoning action of thiophene.

Data from this table also show that changing the space velocity from 1,000 to 2,000 had practically no effect on the amount of sulfur absorbed to the "break point". In general, the break point is well-defined in all runs with the various Huff catalysts. During a typical run, the hydrogen sulfide in the outlet gas will be at an equilibrium value, depending on the catalyst temperature and the effectiveness of prior revivification for several hours. When the break point occurs, the value for hydrogen sulfide rapidly rises. Thus, in run 4, the hydrogen sulfide averaged approximately 0.1 grain per 100 cu. ft. for 12 hours. Between the twelfth and fourteenth hours, the hydrogen sulfide outlet concentration increased from 0.1 to 88 grains per 100 cu. ft. The hydrogen sulfide outlet concentration continued to increase, being 190 grains per 100 cu. ft. at 15 hours and 270 grains at 17 hours, reaching the inlet value at 18 hours.

In run 6, increasing the space velocity to 3,900 caused a marked decrease in the capacity for sulfur absorption of catalyst 1. Catalysts 2 and 3 reached the break point before data could be obtained.

Variations in hydrogen sulfide concentration of the inlet gas between 230 and 380 grains per 100 cu. ft. had little effect on the absorptive capacities of the catalysts, although lowering the concentration to 95 grains per 100 cu. ft. in run 2 improved the absorptive capacity appreciably.

Data from the series of runs in table 9 show that the solid catalysts - that is, the unsupported catalysts - absorb 2 to 2.5 times as much sulfur as do the catalysts to which clay or Porocel has been added. While the supported catalysts show a higher removal per gram of oxide content, the desirability of operating on longer cycles indicated that the solid catalysts were to be preferred. Consequently, in subsequent runs, solid Cu-Cr-V catalysts were used.

Table 10 gives data for three Cu-Cr-V catalysts prepared by different methods. Catalyst 1, in this table, was prepared by mixing C. P. oxides, catalyst 2 by mixing technical oxides, and catalyst 3 by precipitation. Methods of preparation have already been described.

TABLE 9. - Other preliminary runs

Catalyst 1 - 80% Cu, 10% Cr, 10% V (no carrier)
 Catalyst 2 - 70% kaolin clay, 30% oxides
 Catalyst 3 - 70% Porocel, 30% oxides
 Furnace temperature - 450° C.
 Gas contained 30% steam

Run No.	Cat. No.	Sp. vel., hr.-1	H ₂ S, gr./100 cu. ft.			Organic S, gr. S/100 cu. ft.			Operating hr. to brkpt.	Total S absorbed to brkpt., gr.
			Inlet	Outlet	Removal to brkpt., percent	Inlet	Outlet	Removal to brkpt., percent		
1	1	2,000	140	1.5	99.0	1/29.1	13.8	52.2	12	11.4
	2	2,000	140	2.0	98.6	29.1	11.2	61.5	5	3.3
	3	2,000	140	2.0	98.6	29.1	13.2	54.6	5	3.3
2	1	2,000	95	2.0	97.9	20.0	.4	98.0	29	24.6
	2	2,000	95	2.5	97.4	20.0	1.5	92.5	11	9.0
	3	2,000	95	2.3	97.6	20.0	3.7	81.5	11	8.7
3	1	2,000	230	2.3	99.0	8.5	.2	97.6	10	17.6
	2	2,000	230	2.8	98.8	8.5	.4	95.3	4	7.0
	3	2,000	230	1.2	99.5	8.5	.1	98.8	4	7.0
4	1	1,000	380	0.1	99.9	25.0	.2	99.2	13	18.9
	2	1,000	380	0.6	99.8	25.0	.1	99.6	5	7.3
	3	1,000	380	1.5	99.6	25.0	.1	99.6	5	7.3
5	1	1,000	300	2.0	99.3	25.0	.1	99.6	14	21.8
	2	1,000	300	2.4	99.2	25.0	.5	98.0	6	6.9
	3	1,000	300	2.4	99.2	25.0	.4	98.4	6	6.9
6	1	3,900	350	0.5	99.9	16.4	.3	98.2	3.5	14.4
	2	3,900	350	2.2	99.4	16.4				
	3	3,900	350			16.4				

1/ Gas used in run 1 contained 14 grains of sulfur as thiophene; gas for remaining runs contained equal amounts of CS₂ and C₂H₅SH, no thiophene.

TABLE 10. - Data for three catalysts prepared by different methods

(Furnace temp., 450° C.; gas contains 30% steam)

Catalyst 1 80% Cu - 10% Cr - 10% V (C.P. oxides) 18.7 grams
 Catalyst 2 80% Cu - 10% Cr - 10% V (tech. oxides) 20.4 grams
 Catalyst 3 80% Cu - 10% Cr - 10% V (ppt. oxides) 11.5 grams

Run No.	Cat. No.	Sp. vel., hr.-1	H ₂ S, gr. 100 cu. ft.		Org. S, gr. S as CS ₂ 100 cu. ft.		Removal to brkpt., percent	Operating hr. to brkpt.	Total S absorbed to brkpt. (calc.), gr.	S, absorbed per gram catalyst, gr.	S as SO ₂ from revivification, gr.	S as SO ₂ during 1st hr. of succeeding run, gr.
			In	Out	In	Out						
27	1	2,000	350	1.5	56	0.01	99.99	8.5	22.6	1.2	16.7	
	2	2,000	350	3.0	56	.10	99.80	8.5	22.6	1.1	10.4	
	3	2,000	350	2.5	56	.01	99.99	8.5	22.6	2.0	13.8	
28	1	1,000	350	2.5	35	.05	99.86	24.75	32.1	1.7	14.3	
	2	1,000	350	2.5	35	.05	99.86	18.25	23.5	1.2	13.6	
	3	1,000	350	2.0	35	.02	99.94	18.25	23.5	2.0	9.8	
29 ^{1/}	1	2,000	530	2.5	60	.10	99.83	7.25	29.2	1.6	11.2	
	2	2,400	530	2.5	60	.00	100.00	6.25	25.2	1.2	10.0	
	3	2,000	530	2.0	60	.05	99.92	5.25	21.2	1.9	4.9	
30	1	2,000	400	2.5	40	.05	99.88	9.5	30.1	1.6		
	2	2,000	400	2.0	40	.10	99.75	7.0	22.2	1.1		
	3	2,000	400	2.0	40	.06	99.85	5.5	17.4	1.5		
31	1	2,250	250	2.5	30	.05	99.83	13.5	32.4	1.7	12.6	
	2	2,000	250	2.5	30	.00	100.0	13.5	29.1	1.4	14.2	
	3	2,400	250	2.5	30	.10	99.67	6.0	15.3	1.3	4.6	
32	1	2,200	280	2.5	30	.03	99.90	13.75	31.7	1.75	15.1	12.1
	2	2,400	280	2.5	30	1.5	95.0	12.25	30.9	1.5	-	11.4
	3	2,000	280	2.0	30	.10	99.67	4.25	10.9	.95	3.9	6.6

^{1/} Gas used in run 29 contained no steam.

TABLE 10. - Data for three catalysts prepared by different methods (Cont'd.)

Run No.	Cat. No.	Sp. vel., hr.-1	H ₂ S, gr. 100 cu. ft.			Org. S, gr. S as CS ₂ 100 cu. ft.			Operating hr. to brkpt.	Total S absorbed to brkpt. (calc.), gr.	S, absorbed per gram catalyst, gr.	S as SO ₂ from revivification, gr.	S as SO ₂ during 1st hr. of succeeding run, gr.
			In	Out	Removal to brkpt., percent	In	Out	Removal to brkpt., percent					
33	1	2,200	450	3.0	99.3	25	0.07	99.72	9.25	34.2	1.8	13.5	9.8
	2	2,000	450	2.5	99.4	25	4.0	84.0	11.0	37.6	1.8	21.8	4.9
	3	2,000	450	3.0	99.3	25	.01	99.60	5.25	17.9	1.6	4.9	8.6
34	1	2,000	300	2.5	99.2	50	.10	99.80	9.5	22.9	1.25		
	2	2,000	300	2.0	99.3	50	.01	99.98	14.0	33.5	1.6		
	3	2,000	300	1.5	99.5	50	.00	100.0	6.0	14.1	1.3		
35	1	1,500	350	3.0	99.2	63	.08	99.9	10.75	22.6	1.2	13.3	9.0
	2	2,000	350	2.0	99.4	63	.15	99.7	13.75	38.6	1.9	18.0	13.3
	3	2,000	350	2.0	99.4	63	.00	100.0	5.75	14.1	1.3	6.9	5.5
36	1	1,850	250	2.5	99.0	40	.00	100.0	13.25	24.5	1.3	8.5	12.1
	2	1,000	250	2.0	99.2	40	.00	100.0	40.0	39.4	1.9	19.7	12.2
	3	1,700	250	2.5	99.1	40	.08	99.8	6.25	10.9	.95	2.9	6.7

The results show that catalyst prepared from technical grades of oxides is equal, and in some cases superior, to catalyst prepared from C.P. oxides, or prepared by precipitation from C. P. chemicals. This is important from cost considerations.

Up to the hydrogen sulfide break point, the sulfur absorbed by the catalysts amounted to from 6.1 to 13.5 percent of the catalyst weight. This variation is undoubtedly due to variation in the effectiveness of revivification.

Data from run 29 show that the presence of steam in the gas is not necessary to obtain good removal of both hydrogen sulfide and organic sulfur. Steam was added to the gas in most of the runs, however, to simulate plant practice, where excess steam from the gasification process would be present in the gas.

Organic sulfur removal in virtually all runs was excellent; except for runs 32 and 33, the organic sulfur in the outlet gas was not over 0.10 grain per 100 cu. ft. Catalyst 2 of runs 32 and 33 showed poor removal of organic sulfur, but it was later found that the high result for organic sulfur was undoubtedly due to the presence of sulfur dioxide in the gas which escaped removal because the caustic scrubbing bottle had become spent.

Beginning with run 33, provision was made for determining sulfur dioxide in the purified gas during the first hour of operation after revivification.

As previously stated in this report, the catalysts were revivified at a furnace temperature of 450° C. Figure 14 shows a typical curve for revivifying a fouled, unsupported copper-chromium-vanadium catalyst at this temperature. More rapid revivification can be effected at 550° C.; but at this temperature, difficulty was sometimes experienced with fusion of the catalyst. With proper temperature control within the catalyst bed and careful operation, this higher temperature could be used.

Although most of the sulfur is burned off during the first hour of revivification, it has been the practice of this laboratory to continue revivification until the sulfur dioxide concentration in the outlet gas reaches a somewhat constant value. Therefore, a revivification may take as long as 4 hours.

The total sulfur given up during a revivification is determined by passing the outlet gas through a 20 percent solution of KOH, and the sulfur absorbed is determined gravimetrically. Spot tests used to determine the completion of revivification are taken with a Tutwiler.

The following data show how rapidly the sulfur is burned off. This is an important factor in sulfur recovery.

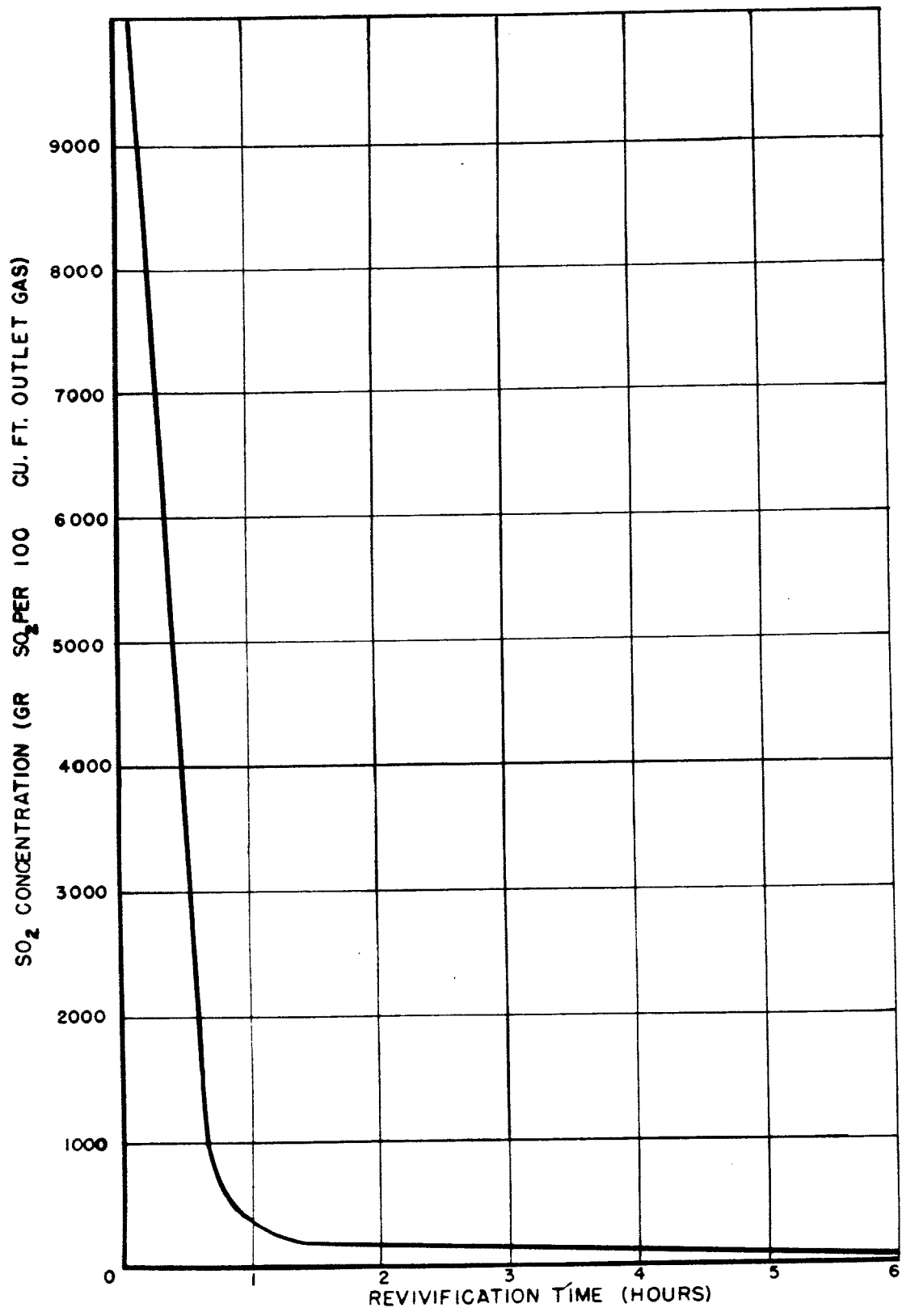


Figure 14. - Curve showing a typical revivification of a fouled Cu-Cr-V catalyst, space velocity, 2,000 hr.⁻¹, air flow: 0.72 c. f. h.

<u>Minutes after air is started</u>	<u>SO₂/100 cu. ft. of outlet gas, gr.</u>
5	10,000
15	8,800
45	500
75	180
195	116
255	76
315	76

After revivification, the catalyst is reduced using raw synthesis gas, thereby effecting purification along with reduction. Using a space velocity of 2,000 hr.⁻¹, the reduction is substantially complete at the end of 1 hour.

Figure 15 shows curves representing the consumption of carbon monoxide and hydrogen during the reduction of a solid Cu-Cr-V catalyst.

The following gas analyses give the composition of the gas during the reduction period of run 30:

	Time after synthesis gas is started			
	Inlet	6 min.	30 min.	60 min.
CO ₂	0.6	44.1	5.9	3.4
O ₂6	.9	.7	.8
Illuminants.....	.9	.7	1.9	.9
H ₂	49.3	3.9	39.7	50.2
CO.....	44.2	40.7	47.3	42.3
CH ₄9	.6	.9	.7
N ₂	3.5	9.1	3.6	1.7

From table 10 it can be noted that only about 40 to 60 percent of the calculated amount of sulfur absorbed during a run is burned off during a revivification. In spite of this low sulfur recovery, subsequent runs show good catalyst activity and adsorptive capacity.

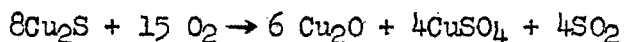
As stated previously, sulfur dioxide was found to be present in the gas when, in run 32, the caustic preceding the platinum spiral became spent and sulfur dioxide was being determined as organic sulfur. A study of this problem revealed that much of the sulfur absorbed in a run escaped burn-off during revivification and was expelled during the beginning of the succeeding run. This formation of sulfur dioxide would not be too serious if the synthesis gas, after the first hour of the run, were free of sulfur dioxide, inasmuch as the gas during the reduction period of the catalyst is worthless for synthesis. However, there is as much as 2 grains of sulfur dioxide per 100 cu. ft. of outlet gas 4 hours after the beginning of the run. The following data show the sulfur dioxide given up by a freshly revivified Cu-Cr-V catalyst whenever synthesis gas flow is begun:

Space velocity - 2,000 hr.⁻¹
 Furnace temperature - 450° C.

<u>Time after synthesis gas is started, hr.</u>	<u>SO₂/100 cu. ft., gr.</u>
1/4	12,160
1/2	310
3/4	28
1	25
1-1/4	9
1-1/2	9
2	2

Data given in table 10 also show the approximate amount of sulfur given up by revived catalysts during the first hour after synthesis gas is started. The amounts shown for runs 32, 33, 35, and 36 are, of course, the sulfur given up during the first hour of the succeeding runs. The total of the sulfur from revivification and reduction never equals the calculated amount which has been absorbed during the run inasmuch as a revivification is never continued until the outlet gas is free of sulfur dioxide. There is also a loss of sulfur dioxide due to sampling, as well as a loss in the steam condensate trap bottle after the catalyst tubes.

It is believed that during revivification, cupric sulfate is formed according to the following equation:



Various methods of revivification were tried in an attempt to prevent this formation of cupric sulfate - operation with and without steam in the air, variation of furnace temperatures during burn-off between 300 and 550° C., dilution of the air with nitrogen to give an oxygen content as low as 6 per cent, and various air space velocities. All experiments were unsuccessful in eliminating or even lessening the formation of cupric sulfate.

Since the formation of cupric sulfate could not be eliminated, tests were made in an effort to decompose the cupric sulfate as quickly as possible. The decomposition temperature of cupric sulfate is 650° C. Data from decomposition tests made on C. P. cupric sulfate showed that decomposition begins at a lower temperature in a reducing atmosphere (synthesis gas) and proceeds at a faster rate than in an inert (nitrogen) or oxidizing (air) atmosphere. It had been hoped that after revivification and during an inert gas purge, the catalyst temperature could be raised to 650° C. and the sulfur dioxide completely driven off in a short time. However, clean synthesis gas when passed over freshly revived catalyst at 650° C. for 3 hours contained 20 grains of sulfur dioxide per 100 cu. ft. The literature states that, in air, cupric sulfate begins losing sulfur dioxide at 341° C. and exists as 8 CuO.3SO₂ between 341° and 621° C. and as 2 CuO.SO₂ between 621° and 670° C. This latter compound does not begin to decompose until 704° C.

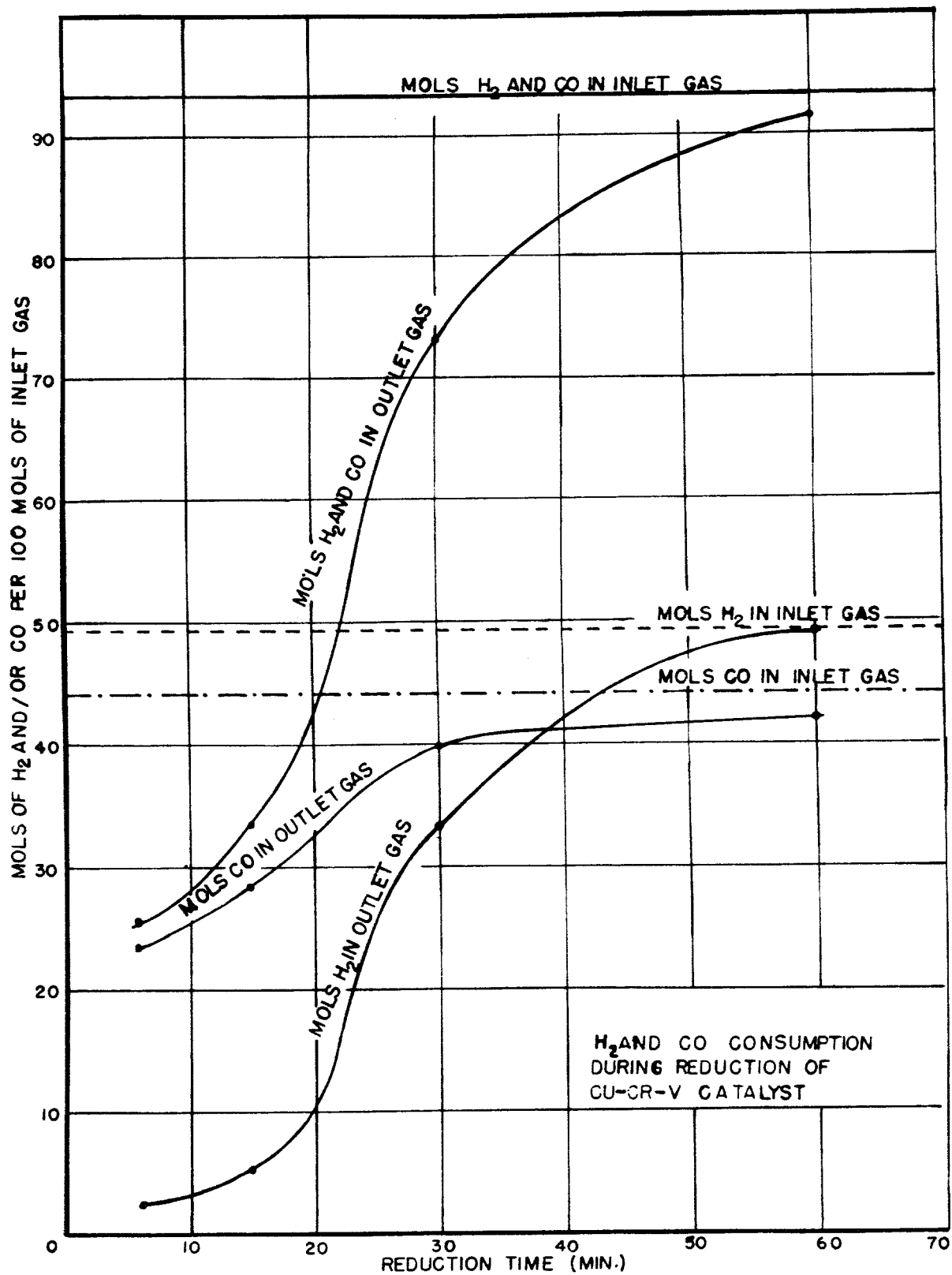


Figure 15. - H₂ and CO consumption during reduction of Cu-Cr-V catalyst.

The presence of sulfur dioxide in the gas, of course, created another purification problem, since the total sulfur content of purified synthesis gas must not exceed 0.1 grain of sulfur per 100 cu. ft. Additional equipment for sulfur dioxide removal would make the Huff catalysts less attractive. However, experiments showed that by following a freshly revived catalyst with a fouled one the sulfur dioxide could be completely removed from the gas.

Table 11 summarizes data from experiments run to determine the effectiveness of sulfur dioxide removal by a fouled Huff catalyst. The experimental method was as follows:

Two catalyst tubes were converted in series; the first contained a freshly revived Cu-Cr-V catalyst, the second a sulfided Cu-Cr-V catalyst (that is, one that had been operated to the break point). Synthesis gas containing hydrogen sulfide and carbon disulfide was passed over the revived catalyst at space velocities up to 2,850. During reduction, the gas leaving the first tube was vented to the atmosphere, since this gas is unsuitable for synthesis. This gas has a high sulfur dioxide content. At the end of the first hour, with reduction substantially completed, the synthesis gas was diverted to the catalyst tube second in the series and containing the fouled catalyst. The sulfur dioxide content of the gas at this time was as high as 1,550 grains per 100 cu. ft. As can be noted in table 11, there was no sulfur dioxide in the gas leaving the fouled catalyst bed. Whenever the revived catalyst reached the break-point, it was placed second in the series. The initially fouled catalyst was then revived and placed first in the series.

The synthesis gas feed to the freshly revived catalyst contained from 300 to 650 grains of hydrogen sulfide per 100 cu. ft. and 35 to 65 grains of organic sulfur as CS₂ per 100 cu. ft. The value given in table 11 for hydrogen sulfide and organic sulfur are the inlet and outlet concentrations for the fouled catalyst; the inlet values are, of course, the outlet concentrations in the gas leaving the revived catalyst. In most of the runs, the fouled catalyst further reduced the hydrogen sulfide and organic sulfur content of the gas; but, in a few runs, there were slight increases.

This manner of operation to prevent loss of sulfur dioxide into the purified gas stream did not adversely affect the catalyst life. There is no trend showing a decrease in the amount of sulfur removed per run, as measured by the total grains of sulfur (as sulfur dioxide) removed during revivification and the first hour (reduction period) of the subsequent run.

Table 12 shows the effect of temperature on the removal of hydrogen sulfide and organic sulfur by the Huff catalyst. These data show that the optimum temperature for hydrogen sulfide removal is lower than that for organic sulfur removal. This indicates that, to meet purification specifications for synthesis gas, two separate catalyst beds would be required, operated at different temperatures.

TABLE 11. - Removal of SO from gas with a sulfided Cu-Cr-V catalyst

Catalyst 2 - 80% Cu - 10% Cr - 10% V

Catalyst 3 - 80% Cu - 10% Cr - 10% V

Furnace temperature - 450° C.

Gas contains 30% steam.

Run No.	Sulfided catalyst No.	Sp. vel., hr. ⁻¹	SO ₂ , gr./100 cu. ft.		H ₂ S, gr./100 cu. ft.		Org. S, gr.S/100 cu. ft.		Total S from revivification and 1st hr. of run, gr.
			In	Out	In	Out	In	Out	
49	2	1,950	2	0.0	2.0	4.0	0.11	0.01	Sample lost.
50	3	2,000	22	.0	3.0	1.5	.40	.10	21.0
51	2	2,350	20	.0	2.3	1.4	.00	.04	21.4
52	3	2,000	130	.0	3.5	2.0	.10	.24	21.2
53	2	2,250	34	.0	2.6	3.4	.08	.13	Sample lost.
54	3	2,000	100	.0	2.5	1.4	.07	.01	20.6
55	2	1,700	70	.0	2.2	3.3	.20	.08	22.2
56	3	1,850	200	.0	2.5	1.9	.15	.20	Sample lost.
57	2	672	1,080	.0	4.0	5.5	.20	.10	Do.
58	3	2,000	500	.0	2.5	2.0	.67	.10	Do.
59	2	900	5	.0	2.0	2.5	.10	.15	29.9
60	3	2,000	120	.0	2.9	2.5	.13	.05	21.8
61	2	2,000	1,550	.0	1.6	1.2	.10	.10	24.9
62	3	2,850	140	.0	2.5	1.8	.00	.00	23.6
63	2	2,000	550	.0	1.8	2.9	.34	.00	Sample lost.
64	3	2,000	1,100	.0	2.3	2.0	.00	.00	20.1
65	2	2,000	260	.0	1.3	2.0	.00	.00	31.3
66	3	672	1,300	.0	1.5	1.1	.00	.00	21.5

TABLE 12. - Effect of catalyst temperature on removal of hydrogen sulfide and organic sulfur by Cu-Cr-V catalyst

Catalyst - 80% Cu - 10% Cr - 10% V (tech. oxides)

Gas contained 30% steam

Run No.	Sp. vel., hr. ⁻¹	Furnace temp., °C.	H ₂ S, gr./100 cu. ft.		Org. S, gr. S/100 cu. ft.	
			In	Out	In	Out
12.....	2,000	250	200	0.22	22	12
11.....	2,000	300	180	.00	11	.16
10.....	2,000	300	160	.00	13	.19
31.....	2,000	450	250	2.5	30	.00
37.....	1,500	550	300	5.0	30	.00

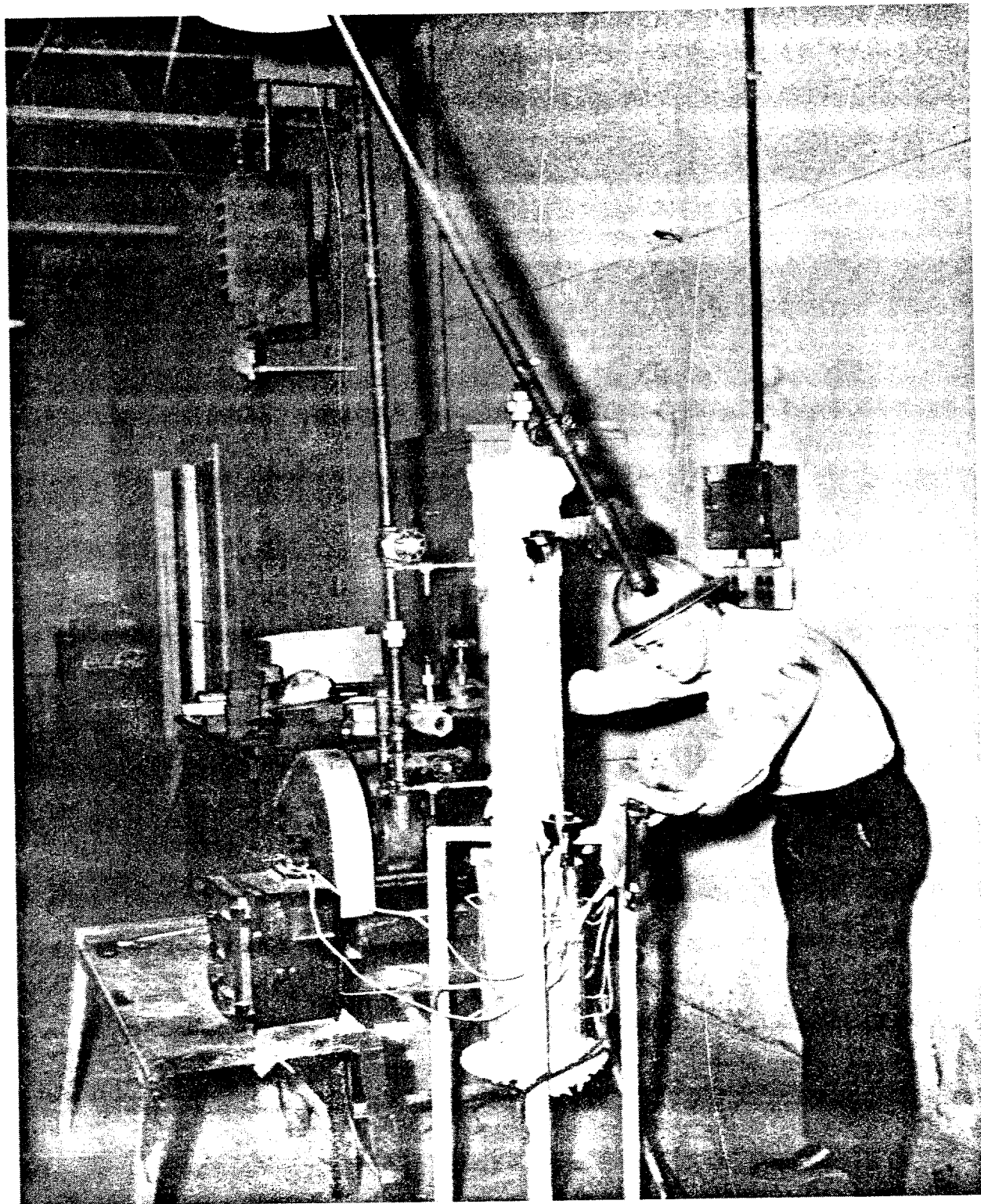


Figure 16. - Apparatus for testing Huff catalysts in a fluidized state.

Table 13 shows the removal of hydrogen sulfide and organic sulfur obtained during complete absorption periods when operated at optimum temperatures. Note that, in these runs, the catalyst beds were not in series; the inlet gas contained a high concentration of hydrogen sulfide and organic sulfur. In an actual purification process, the first catalyst bed would be operated at about 450° C. and should remove all of the organic sulfur and most of the hydrogen sulfide. The second bed in series, operated at 300° C., would remove the residual hydrogen sulfide, yielding a purified gas containing well below 0.1 grain of total sulfur per 100 cu. ft. The second bed in series presumably would also be removing sulfur dioxide evolved from the first bed, although it might well be that a third fouled, or partly fouled, bed would be required for this purpose.

TABLE 13. - Hourly data for runs 10 and 31

Furnace temp. for run 10 - 300° C.

Furnace temp. for run 31 - 450° C.

Space velocities - 2,000 hr.⁻¹

Catalysts: Cu-Cr-V (tech. oxides)

Run No.	Operation, hr.	H ₂ S, gr./100 cu. ft.		Org. S, gr. s/100 cu. ft.	
		In	Out	In	Out
10.....	1	130	0.00	13.5	0.16
	2.5	160	.00	13.2	.19
	3.5	160	.00		
	4	160	.00		
	5.5	160	.00	13.0	.12
	6	160	.00		
	7	160	.00		
	8.5	160	.00		
	9.5	160	6.95	12.6	.17
	10	160	9.90		
31.....	1	290	2.76	35.4	.00
	2	250	2.52		
	4	270	2.56	31.8	.00
	6	250	2.32	30.8	.00
	7	250	2.60		
	10	250	2.86	29.2	.00
	11.5	250	2.73		
	12	260	3.87	28.1	.00
13.5	250	9.12			

Because of the cyclic nature of the process when using fixed beds, it is believed that use of a fluidized catalyst might be advantageous, since the catalyst could be transferred continuously from one vessel to another. Very little work using the fluidized technique with these catalysts has been done; a preliminary test using the apparatus shown in figure 16 reduced an inlet concentration of 400 grains of hydrogen sulfide and 23 grains of organic sulfur per 100 cu. ft. to 0.08 grain of hydrogen sulfide and 0.8 grain of organic sulfur per 100 cu. ft.

Work on fluidized revivification and continuous transfer of fouled catalyst to the regenerator and of the revivified catalyst from the regenerator to the absorber remains to be done. It will also be necessary to determine the number of beds required in series and to solve the problem of removing sulfur dioxide evolved from the freshly actified catalyst. It is hoped that, since fluidized catalyst will be a mixture of fresh and fouled, or partly fouled, catalyst the sulfur dioxide will be removed by the fouled material, as in the fixed beds.

It is hoped that, by the use of fluidization, the amount of catalyst in use at any time will be less than that required for fixed beds and that the investment in catalyst will be reduced thereby.

In addition to work with fluidized catalyst, more work is planned with the catalyst in fixed beds at atmospheric pressure and at 300 p.s.i.g. Experiments with catalyst beds in series, at optimum temperatures, and including a partly fouled bed for sulfur dioxide removal are to be carried out. It is also desired to study other catalyst combinations, especially catalysts that will eliminate vanadium, or to find a cheaper substitute for that element.

More work needs to be done on the recovery of sulfur dioxide; studies should be made of revivification of catalyst by means of oxygen mixed with recycled sulfur dioxide. This should make it possible to produce an off-gas containing 90 to 100 percent sulfur dioxide which should be more valuable for sulfuric acid manufacture, or for recovery of pure sulfur dioxide which could presumably be liquefied and shipped in cylinders. When enough information is obtained from bench-scale operations, pilot-plant work will be carried out.

Under terms of a cooperative agreement with the Southern Natural Gas Co., it is planned to carry out gas-purification experiments with the object of purifying gas to a total sulfur content below 0.002 grain per 100 cu. ft. Use of the Huff catalyst is believed to be one method of accomplishing this.

When pilot-plant data are available, cost estimates for the process in a commercial plant will be prepared. Rough preliminary cost estimates were prepared before laboratory experiments to determine whether the process had sufficient potentialities to warrant experimentation. It is not intended at this time - with only laboratory data at hand - to present cost estimates.

One charge against the process that should not be overlooked is the value of the synthesis gas consumed by reduction of the catalyst. The relation between the amount of gas purified and amount of gas used during reduction depends on the hydrogen sulfide content of the gas. At a space velocity of 2,000 l hour is required for reduction; during this period, gas leaving the catalyst will be discarded. When the gas contained 250 grains of hydrogen sulfide per 100 cu. ft., the total period of gas flow through the catalyst was 13.5 hours in one run. In this case, 7.5 percent of the total gas was consumed during reduction. If, for example, synthesis gas were to cost 15 cents per 1,000 cu. ft., reduction-gas cost would represent about 1.1 cents per 1,000 cu. ft. of synthesis gas.

Cost of raw materials for the catalyst, at current market price, is approximately 55 cents per pound of reduced catalyst (less than 45 cents per pound of catalyst in the oxidized state).

For synthesis-gas purification, it is assumed that the gas leaving the waste-heat boiler of the gasifier will contain enough heat to effect the removal of sulfur. If dust can be removed to a sufficiently complete degree without cooling the gas, no charge for heating the gas for catalytic purification need be assumed. Indeed, the ability to remove sulfur completely without cooling the gas (as is necessitated in liquid purification or dry box methods) constitutes a credit to the process, since the heat remaining in the purified gas will preclude the necessity of preheating the gas for synthesis. Both the Fischer-Tropsch process for synthesis liquid fuels and processes for methane synthesis utilize synthesis gas at 250° to 300° C. Saving in this preheat might logically be credited to the purification process which makes this saving possible.