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Investigations on the Reaction-Velocity over "Brown oxide" Catalyst for the Shift Reaction

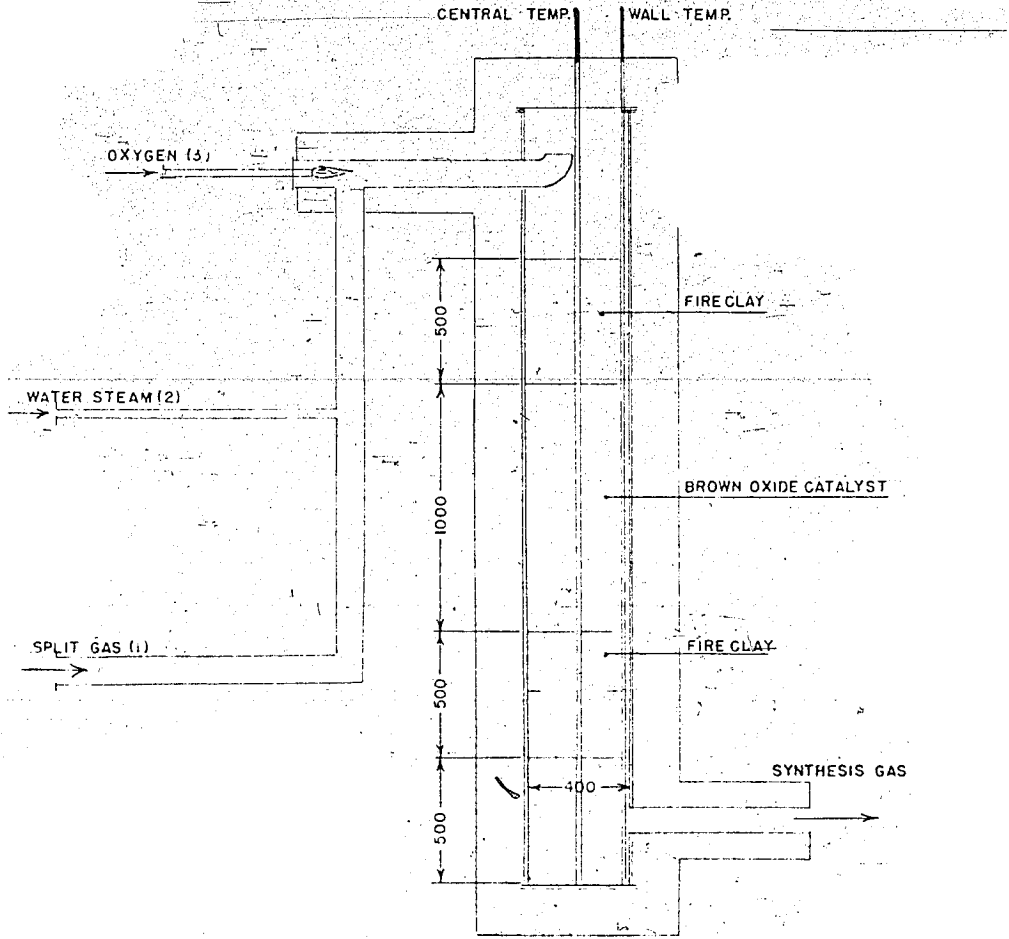
Summary

It is already known that the capacity of a "brown oxide" catalyst increases with an increasing pressure and it is also known that the increase of the capacity is not proportional to the pressure. As far as is known, systematic investigations of the efficiency of the catalyst depending on the total pressure have never been performed before.

The experimental station Op. 462 for two years dealt with the problem (in a scale of 50 to 200 cu. m. per-hour) of liberating under pressure from methane the letdown gas of the butyl-factory and by a following process to convert the CO over a brown oxide catalyst with intermediate cooling so that the gas without releasing the pressure can be fed to the ammonia synthesis installation just before the pressure water wash process. In connection with those experiments it was possible to study the question of the dependence of the activity of the brown oxide catalyst upon the pressure. With the experiments almost finished it is now possible to report the obtained results. The most important observation which could be made was that with an increase of the pressure from 1-11 atm the catalyst volume (applying the same temperature and obtaining the same efficiency) can be reduced to approx. 1/3. A further increase of the pressure is followed by almost no reduction of the catalyst volume.

Details of the apparatus and of the procedure applied for the performance of the experiments

The experiments were carried out with the letdown gas of the butyl factory which had been liberated from hydrocarbons by a preceding process. Unlike the gas which is fed to the gas factory (shift reaction) the gas which was used for the experiments was entirely free from sulphur. Its CO content is lower. The average composition was 32% CO, 6% CO₂, 54% H₂, 8% N₂. Since its composition changed very often, the tables contain the respective analysis of each experiment. Two different apparatuses were used for the experiments. The catalyst reactor the design of which is represented by picture 1 was employed for the experiments under atmospheric pressure. At first the let down gas was liberated from its methane content by adding air and oxygen and by passing it through a shifting apparatus. The split gas was cooled to its dew point by means of a condenser. Steam could be added to the split gas in order to obtain the desired proportion of H₂O to CO using pipe #2. With an orange gas flame the gas was heated to the proper temperature before it enters the brown oxide catalyst bed. The reactor consisted of a pipe (diameter 40 cm, height 3 meters), the outside of which was insulated by means of a 25 cm thick layer of bricks made of diatomaceous earth. Supported by a grate and counting from the bottom to the top the following material was filled into the tube: fire-clay-bricks 1/2 meter, brown oxide catalyst of normal granulation 1 meter, fire-clay-brick 1/2 meter. The reactor represented one layer of a shaft (sic) reactor which is usually employed in the gas factory. Two thermocouples were adjusted in the center and near the wall of the reactor in such a manner that they could be pulled through the entire length of the reactor. During the experiments it was observed that the thermocouple near the wall indicates a temperature which was 10°C. lower than that of the center. The insu-



REACTOR FOR ATMOSPHERIC PRESSURE TESTS

PICTURE 1

ation of the pipe was not efficient enough. The inlet temperature of the gas was indicated by the central thermocouple inside the upper brick layer. The outlet temperature was the highest temperature which was indicated if the central thermocouple was pulled through the reactor. Gas samples in order to determine the composition of the dry gas and of the water content could be drawn before and after the reactor.

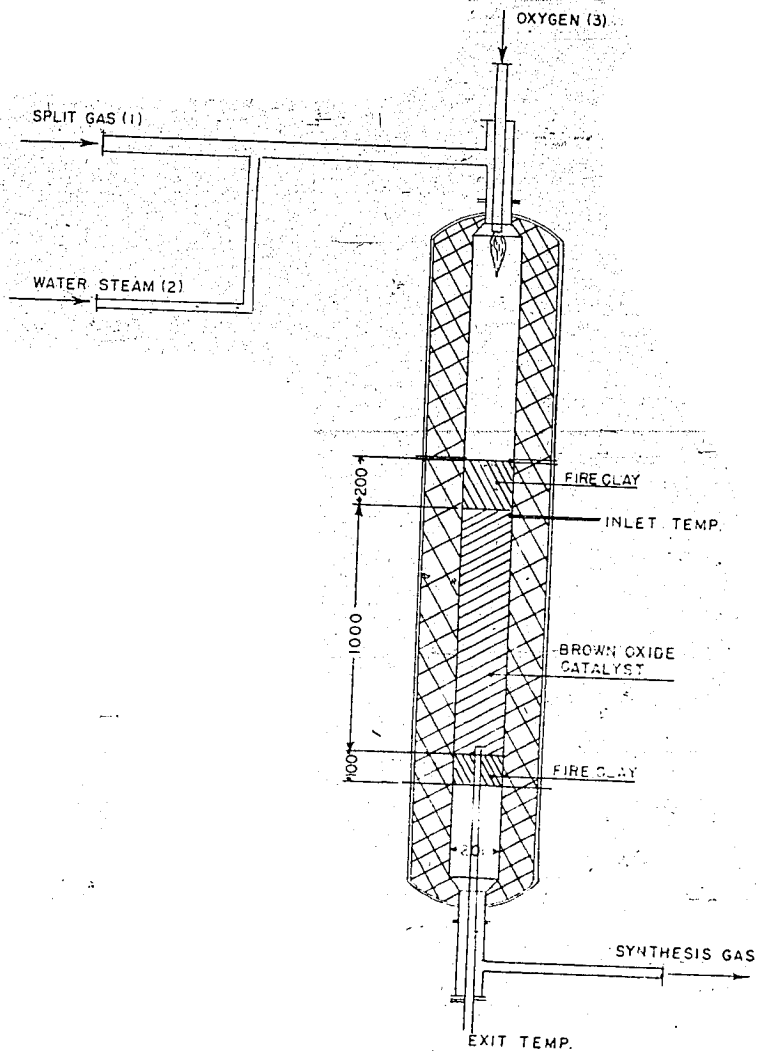
The apparatus shown in picture 2 was employed for the pressure experiments. The pipe system and the operating procedure were the same as for the low pressure tests. The reactor consisted of a pressure pipe which was 50 cm. wide and 2.75 m high. The insulation was fixed to the inner side of the wall. Since only a limited volume of let down gas was available, the inside diameter of the tube was varied between 10 and 20 cm depending on the operating pressure and the desired time passage. The height of the catalyst bed was 1 meter. The temperature at the entrance and outlet of the catalyst bed was determined by fixed thermocouples. Since the pressure of the high pressure steam (carried by line 2) was not higher than 8-10 atm the ratio $H_2O:CO$ could not be chosen at will if test-runs at higher pressures were carried out.

By a variation of the operating procedure of the preceding CH_4 -converter the ratio $H_2O:CO$ could be changed between 1.8 and 2.4, but it was impossible to obtain the usually employed ratio 3:1. The influence of an excess of steam was therefore investigated in a series of separate experiments.

1. Results

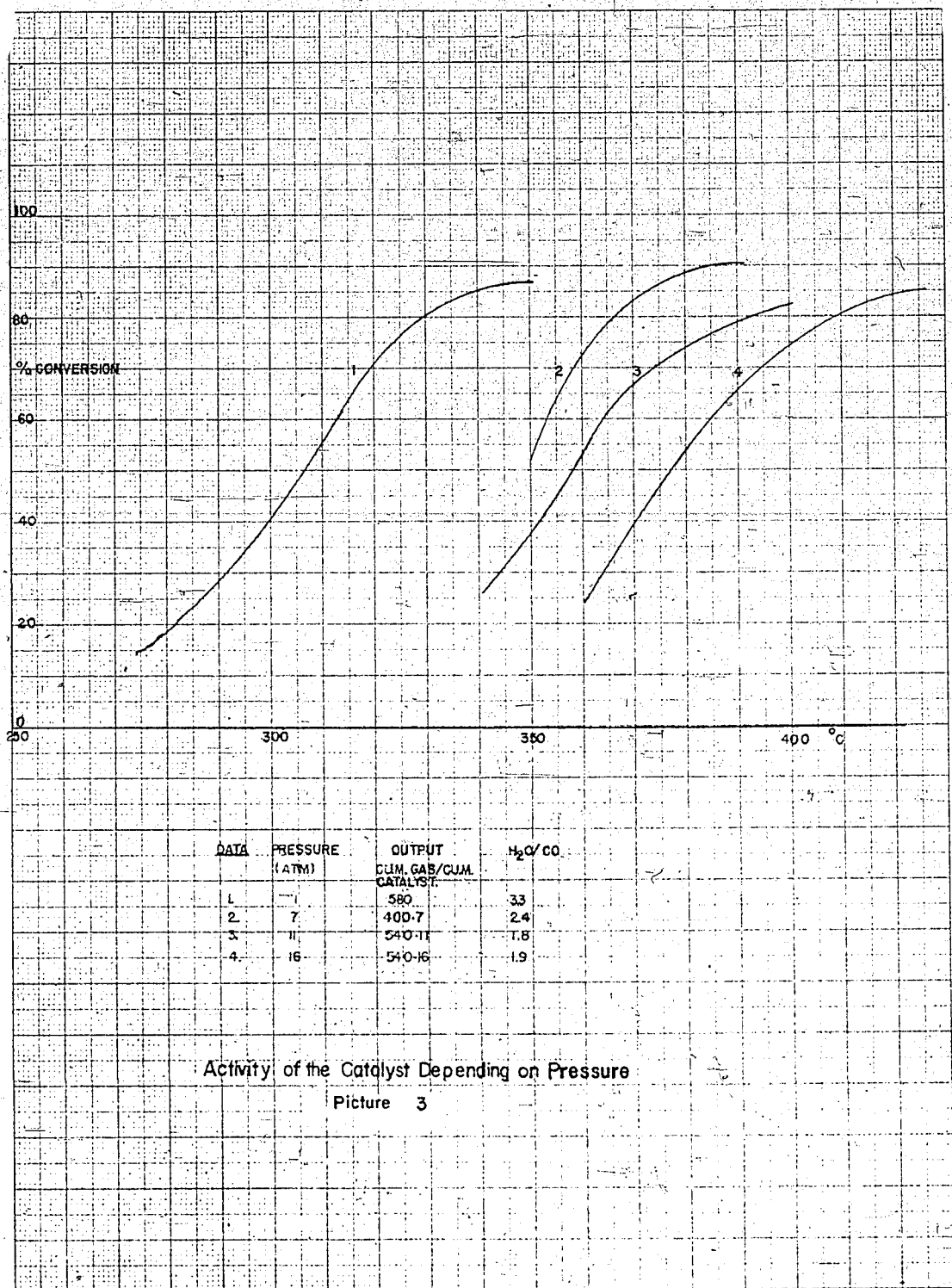
a) The CO conversion depending on the pressure but employing equal time passages.

The atmospheric pressure shift reaction is mostly carried out with a catalyst output of approx. 550 m^3 gas (15°C ., 735 mm Hg) per m^3 catalyst. A series of experiments was therefore performed in such a manner that with increasing pressures ranging from 1-16 abs-atm the activity of the catalyst was determined at an output of 540 P m^3 gas per m^3 catalyst. At each pressure the entrance temperature was altered and the CO-content of the finished gas was determined. As a criterion for the activity of the catalyst the obtained CO-conversion in percent of the possible conversion at the measured temperature and considering the composition of the fed in gas was chosen. By the application of this procedure the changes in the constant of equilibrium with temperature was eliminated. The attached table 1 represents the results of the experiments. Picture three shows the obtained CO-conversion in percent of the possible conversion at the actual outlet temperature depending on the inlet temperature and on the employed pressure. The curves show very clearly the remarkable result, that the absolute volume of the converted CO maintaining equal temperatures and time passage does not increase in proportion to the applied pressure indicating that under equal conditions it is impossible to operate the pressure conversion with an output P-times as high as it is usually employed under atmospheric pressure. Should this be actually true, all curves should coincide, but diagram #3 shows very clearly that this does not happen. Should it be desirable to convert 16 times as much CO applying a pressure of 16 abs. ata. and an equal time passage as it is possible under atmospheric pressure the inlet temperature of the gas, and consequently the operating temperature must be raised about 70°C . Such a raise of 70°C . will increase the activity of the catalyst to such an extent that it is now possible to operate the reactor with $540 \times 16 = 8,600 \text{ m}^3$ (15°C ., 735 mm Hg) per 1 m^3 catalyst.



REACTOR FOR EXPERIMENTS UNDER PRESSURE

PICTURE 2



Activity of the Catalyst Depending on Pressure

Picture 3

b) Dependence of the CO-conversion upon the operating temperature and the time passage employing a constant pressure

The necessity to raise the temperatures a considerable amount makes it necessary to investigate how far under a constant pressure the time passage can be decreased by increasing the operating temperature. At 7 abs. atm. and 16 abs. atm. experiments were therefore made with time passages varied in the ratio 1:2. The results are represented by table 2 and by the pictures 4 and 5 for the operating pressures of 7 and 16 abs. atm. respectively.

Although the obtained results vary because of a considerable variation of the composition of the fed in gas and because a proper water content was difficult to maintain, from the curves it is clearly seen that the activity of the catalyst is twice as high as before if the temperature is raised for about 30°C. Assuming an increase of the temperature of 10°C. the velocity of the reaction will be increased for the factor $\frac{16}{7} = 1.26$. Similar results were obtained by Laupichler, (Ind. Eng. Chem. 30, 578, 1938) who found with an increase in temperature of 10°C., a factor of 1.23 for increase of the velocity constant. The experiments were performed under atmospheric pressure with an unspecified catalyst and applying a gas of considerably different composition. Applying the obtained results to the experiments at 1 and 16 abs. atm. which have been described in the preceding paragraph, it is obvious that an increase of the reacting temperature for 70°C. will be accompanied by an increase of the velocity of the conversion by the factor $(1.26)^7 = 5$. Another increase by the factor $\frac{16}{5} = 3.2$ is due to the increase of the pressure from 1 to 16 abs. atm.

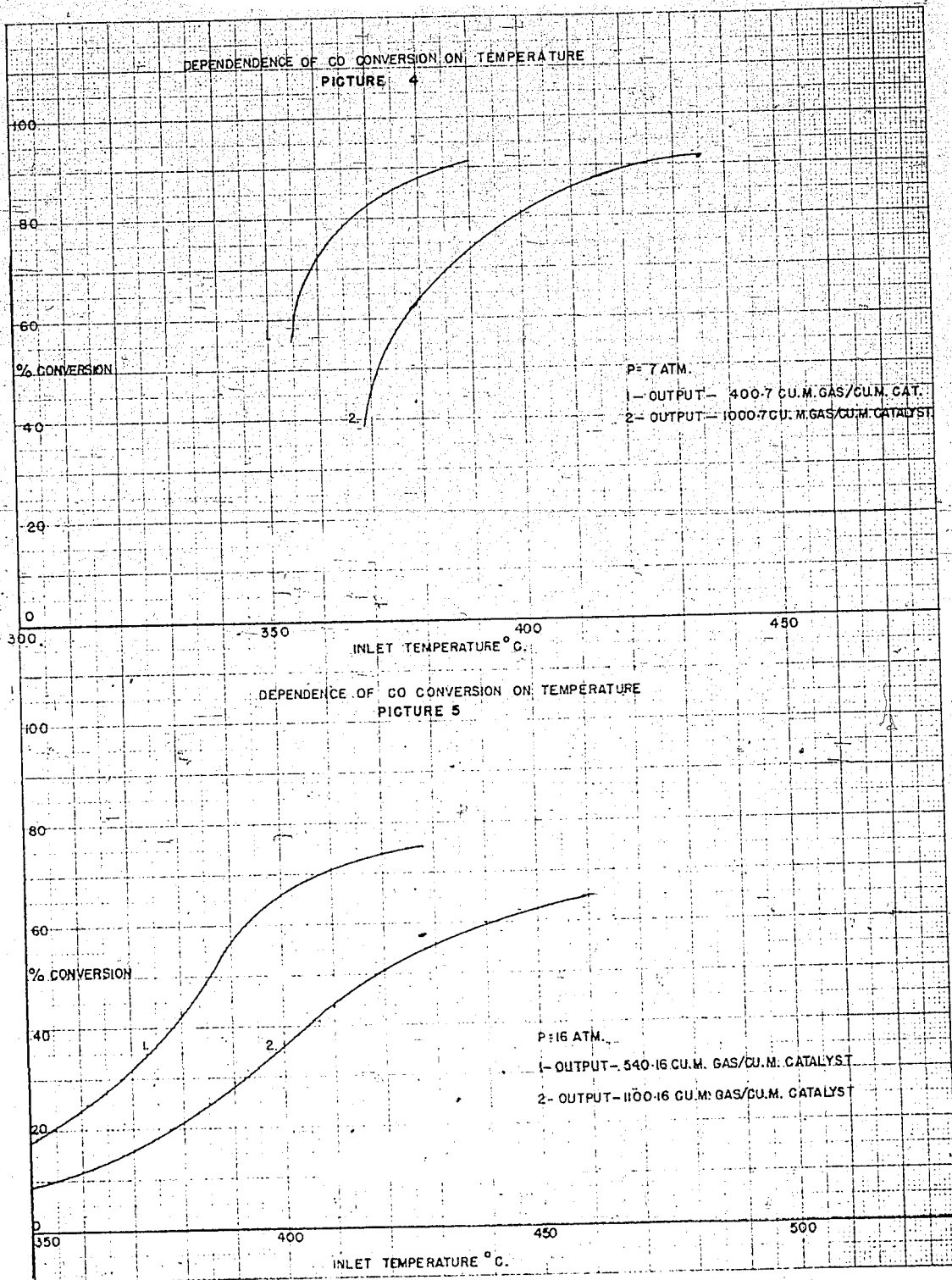
Comparing the curves of picture 3 which represent the obtained results of the 11 and 16 atm. experiments it is obvious that in order to get an increase of the reaction velocity for the factor $\frac{16}{11} = 1.46$

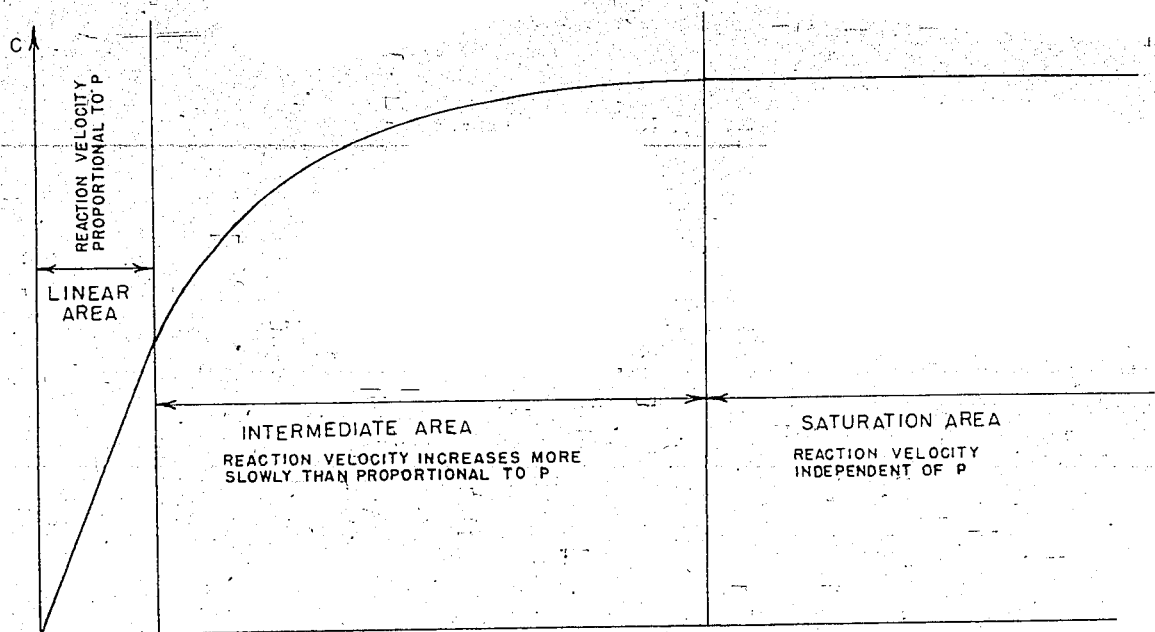
besides an increase of the pressure an increase of the temperature for about 15°C. will be required. Resulting from this temperature increase alone, the reaction velocity is increased by the factor $(1.26)^{1.5} = 1.5$. Considering the accuracy of the experiments an increase of the pressure from 11 to 16 atm. gives almost no increase in the reaction velocity. Generally speaking the effect of increased pressure on the reaction velocity of CO over brown oxide catalysts may now be stated. The reaction velocity on the surface of the catalyst itself does not depend on the partial pressure of the CO in the gaseous phase, but on the concentration of the CO on the surface of the catalyst. The connection between partial pressure and concentration is indicated by an adsorption isotherm, the slope of which is very well represented by Langmuir's

$$C = C_0 \times \frac{p}{p+b}$$

- C = surface concentration at pressure p
- C₀ = " " " " " "
- b = individual constant

The slope of an adsorption isotherm indicated by the above mentioned equation is represented in picture 6 whereby C₀ and b are arbitrary values. In presence of low pressures, when p is small compared with b, the surface concentration will increase in proportion to the partial pressure which is present in the gas phase with the result that the velocity of the catalyst reaction will increase in proportion to the partial pressure in the gas phase. Operating, therefore, in the linear branch of the adsorption isotherm, by increasing the pressure to p atm., the output will be p-times as high as before





ADSORPTION ISOTHERM

DEPENDENCE OF THE CONCENTRATION C ON THE SURFACE ON THE PARTIAL PRESSURE P IN THE GAS PHASE

applying the same volume of catalyst. But operating under high pressures, when p is large compared with b , the surface concentration C becomes independent of the pressure and attains the saturation value C_s . It is evident that operating in that branch of the curve, an increased pressure will be without influence on the conversion velocity followed by a smaller catalyst volume. Operating in the intermediate branch of the curve which is situated between the linear branch and the branch which indicates saturation, the surface concentration and consequently the velocity of the heterogeneous reaction increases more slowly than in proportion to the pressure.

Viewing picture 3 it is quite evident that in the case of CO-conversion applying a brown oxide catalyst we are no longer in the linear branch of the curve because in that event the curves of all pressures must coincide. Under the most usually employed operating conditions we are in the intermediate branch of the curve.

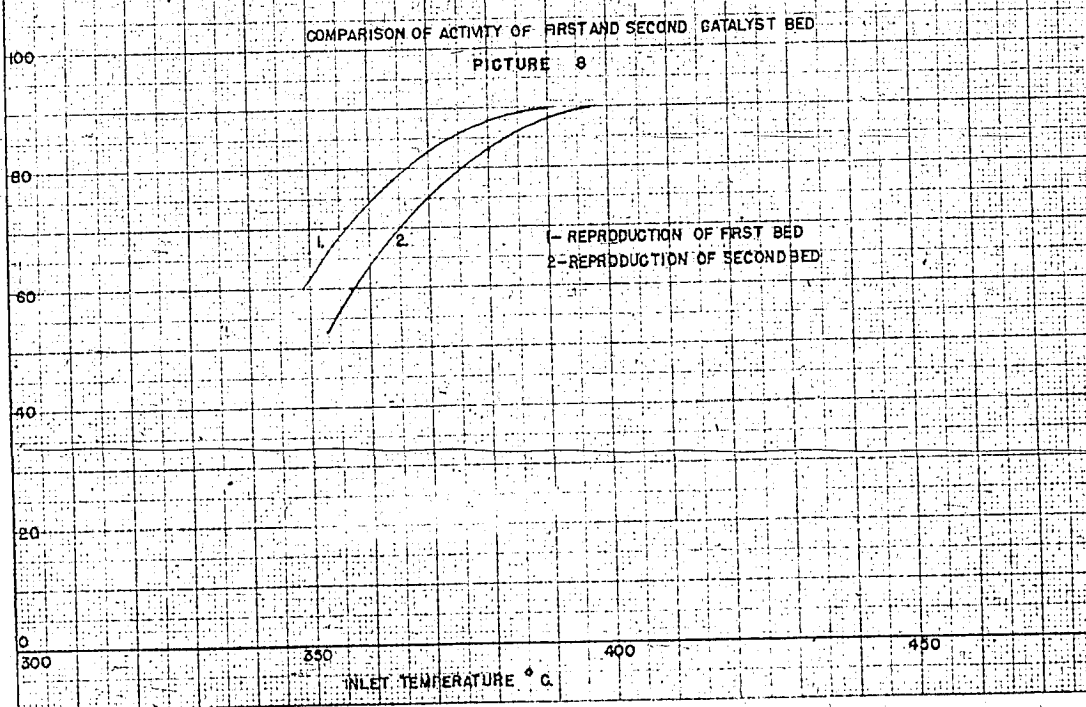
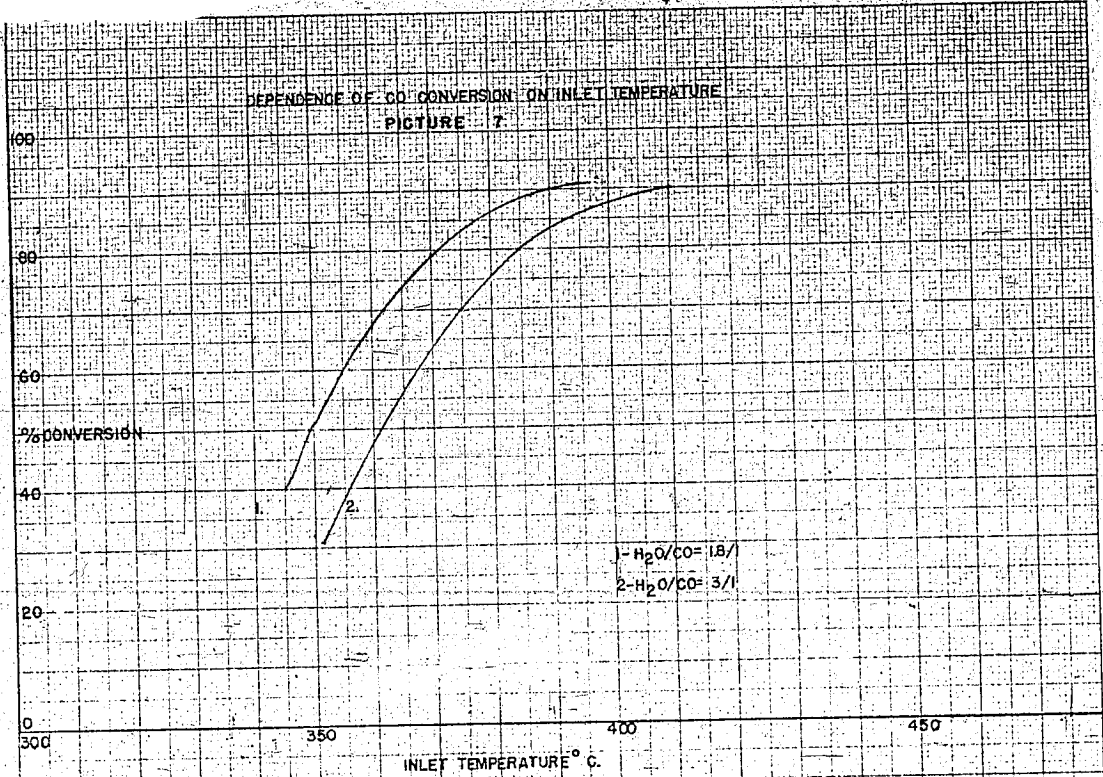
Since the evaluation of the experiments proved that a pressure increase from 11 to 16 atm resulted in almost no increase in conversion velocity, we may draw the conclusion that operating under 11 atm. the saturation branch of the adsorption isotherm which is responsible for the reaction on the catalyst surface has almost been reached already. Operating under higher pressures than 11 atm., the absolute volume of the converted CO is governed only by the time passage and by the temperature, but not by the pressure. We are now in that branch of the adsorption isotherm where by an increased pressure no further decrease of the catalyst volume can be obtained.

Summary

By the application of pressure it is possible to reduce the catalyst volume to approx. 1/3 of that volume which is required if atmospheric pressure is employed, provided that equal operating conditions are maintained. Such a reduction can be carried out by increasing the operating pressure to 11 atm. Still higher pressures do not result in further substantial reductions.

c) The dependence of the CO-conversion on the excess of steam

As mentioned before, high pressure steam was sometimes available with a pressure of but 7 atm. Those experiments which were carried out applying higher pressures must be performed without an admixture of controlling steam. It was therefore impossible to maintain the usual applied proportion of $H_2O:CO = 3:1$. The experiments had therefore to be carried out with a substantially lower excess of steam. In order to get a general view of the influence of the variation of an excess of steam on the conversion velocity, a series of experiments were carried out at a pressure of 11 atm applying the usual proportion of 3:1 and another series of experiments without any admixture of steam at a time when steam at a high pressure was available. Table 3 and picture 7 show the results. With an increase of the proportion of $H_2O:CO$ from 1.0 to 3 the inlet temperature, which is required to put in the same approximation to the equilibrium expressed in per cent., must be raised about 15°C. Such a result is easy to understand, considering the results of the preceding experiments. As shown by table 3, with an increased excess of steam based on the same volume of dry gas, the total volume of gas and steam will increase in the proportion 1.95:1. equals 1.23. Such an increase of the gas velocity however requires an increase of the temperature of approx. 10°C.



The remaining 5°C. are due to the fact that in applying a larger excess of steam, more parts CO must be converted provided an equal approach to the equilibrium expressed in percent has to be maintained. Furthermore with a larger excess of steam applied and provided an equal CO conversion is maintained, the catalyst temperature is not raised to the same extent as when smaller volumes of steam are employed. By the application of a larger excess of steam, the partial pressure of the CO, which is present in the gas phase, is lowered. According to the results which have been reported in the preceding paragraph, the concentration of the CO on the surface of the catalyst shows practically no decrease if a pressure of 11 atm. is employed. Applying higher pressures the reduction of the partial pressure in the gas phase is without influence on the velocity of the conversion.

d) Comparison between the first and second catalyst beds

The previously described experiments have been carried out employing a gas which had the composition of the gas mixture just before the entrance into the CO-converter. The experimental reactor is but a reproduction of the first catalyst bed of the usual commercial shaft kilns. Since the temperature rise of the second catalyst bed, due to the smaller amount of the converted volumes of CO is substantially smaller than in the first bed, it is not to be expected that with an equal entrance temperature into both of the catalyst beds, the same approach to the equilibrium can be reached. It was therefore necessary to perform experiments employing a gas which represented the composition of the gas mixture before the entrance into the second catalyst bed. Such a gas was not available in the experimental station. Experiments were therefore carried out using a gas which had been obtained by diluting the usually employed gas with hydrogen. It was now possible to operate with such a CO content as is usually present in the gas before the entrance into the first catalyst bed. The only difference was that the gas contained substantially less CO₂ but a correspondingly higher percentage of hydrogen. It must therefore be borne in mind that the obtained results do not reproduce exactly the operating conditions of a commercial plant. The conclusion can be drawn however that, applying equal inlet temperatures, there is almost no difference in the activity of the first and second catalyst beds.

Table 4 and picture 8 contain the results of the experiments. It is obvious that both of the curves have the same slope, even if the temperatures of the curve for the second bed are about 10°C. higher. But the difference, as shown in table 4, is due to the fact that the gas output has been increased in the proportion $500 \times 1.7 = 1.18$. The results which are applicable for the first $400 = 1.8$ catalyst bed can be transferred to the second bed.

e) The formation of methane on the brown-oxide catalyst

In connection with the conversion, working under pressure, the brown oxide catalyst is sometimes blamed for favoring a certain amount of methane formation. Although the experiments hitherto performed at Oppau never indicated a methane formation employing the pressure conversion process, special attention was paid to a possible methane formation because, with H₂S completely absent in the gas, most favorable conditions for the formation of methane were present. The methane content of the gas mixture before and after the reactor was carefully recorded by means of an infra red recorder which is especially suitable for a quick and exact determination of the methane content. No increase of the methane content has been observed.

Summary

Experiments were carried out with the aim of investigating the CO-conversion-process applying pressures of 1, 7, 11 and 16 abs. atm. The efficiency of the catalyst was determined employing the above mentioned pressures and various temperatures, outputs, and content of steam. The efficiency was indicated by the converted volume of CO expressed in percent of the maximum possible conversion governed by the equilibrium.

Results:

- 1) The output can be tripled by increasing the pressure from 1 to 11 abs. atm. No substantial increase of the output can be obtained by a further increase of the pressure.
- 2) The temperature dependence of the reaction velocity at 7 and 16 abs. atm. is represented by the factor 1.26 which indicates the increase of the reaction velocity for a rise in temperature of 10°C.
- 3) The influence of added steam can be explained by the variation of the time passage depending on the volume of the added steam.
- 4) There is no difference in the activity of the brown oxide catalyst between the first and second catalyst beds.
- 5) Even if a sulfur-free gas is employed, no methane formation could be observed.

Table 1

Exp. No.	Press. atm.	Output m ³ Gas/m catalyst	CO	CO ₂	H ₂	Analysis of the ingoing gas (%)	H ₂	H ₂ O	m ³ H ₂ O/m ³ CO	Inlet Temp. °C.	Outlet Temp. °C.	% finished gas	conv. in % of the max. possible
1	1	580.1	30.1	7.4	50.7	96.6	3.3	276	296	24.9	14.5		
2	1	580.1	28.6	8.4	50.5	94.9	3.3	291	346	20.0	27.4		
3	1	580.1	28.6	9.0	52.0	96.1	3.3	308	380	14.8	47.		
4	1	580.1	28.7	8.7	49.5	97.9	3.4	316	419	10.4	66.		
5	1	580.1	28.0	9.4	48.3	98.5	3.5	336	424	5.9	86.4		
6	1	580.1	28.0	8.8	48.7	99.5	3.5	351	456	5.9	86.5		
12	7	400.7	32.4	4.6	54.0	81.2	2.4	356	466	15.0	59.		
13	7	400.7	34.8	4.6	54.6	80.0	2.5	362	485	10.8	78.		
14	7	400.7	31.6	5.2	53.8	80.7	2.6	375	510	9.4	87.		
15	7	400.7	32.4	5.2	52.5	78.8	2.3	390	515	9.0	90.		
43	11	540.11	32.9	6.0	49.0	58.8	1.8	343	413	24.6	29.		
44	11	540.11	33.7	6.2	50.0	58.9	1.8	363	471	16.9	59.		
45	11	540.11	31.4	6.3	45.9	64.4	1.9	383	501	13.5	76.		
46	11	540.11	34.4	6.2	48.1	61.5	2.0	403	515	11.6	81.		
52	16	540.16	34.4	5.2	48.9	59.1	1.7	385	479	17.1	62.		
53	16	540.16	34.0	4.8	49.0	59.5	1.8	389	503	14.6	74.		
54	16	540.16	34.1	5.0	49.4	59.5	1.7	390	495	16.7	65.		
55	16	540.16	33.9	5.1	49.1	55.4	1.6	405	515	14.3	82.		
56	16	540.16	35.2	6.1	48.4	70.1	2.0	366	440	22.0	39.		
57	16	540.16	34.9	5.8	49.6	64.7	1.8	370	409	24.0	29.		
58	16	540.16	32.8	5.6	52.0	65.5	2.0	386	484	16.7	59.		
59	16	540.16	34.1	5.9	54.9	63.2	2.0	406	484	15.8	64.		
60	16	540.16	33.9	5.5	49.3	69.5	2.0	406	522	11.4	87.		
61	16	540.16	33.9	5.8	50.5	69.2	2.0	406	525	13.4	80.		
62	16	540.16	34.3	5.3	49.2	70.1	2.0	423	549	13.0	84.		

Table 2

Exp. no.	Press. abs. atm.	Output catalyst	CO	Comp. entering	CO ₂	H ₂	gas (%)	m ³ H ₂ O/m ³ CO	Entrance Temp. °C.	Outlet Temp. °C.	% CO finished gas	Converted parts of the max. possible conv.
12	7	400.7	32.4	4.8	54.0	51.2	2.4	356	466	15.0	59	
13	7	400.7	31.8	4.6	54.6	50.0	2.5	362	485	10.8	78	
14	7	400.7	31.6	5.2	53.8	50.7	2.6	375	510	29.4	87	
15	7	400.7	32.4	5.2	52.5	78.6	2.3	390	515	9.0	90	
16	7	1000.7	31.8	5.2	55.0	92.9	2.9	371	473	16.6	49	
17	7	1000.7	31.0	5.0	57.0	77.9	2.6	389	505	12.6	73	
18	7	1000.7	31.7	4.7	56.3	97.2	3.1	396	504	9.8	80	
19	7	1000.7	31.3	4.7	56.5	83.5	2.7	490	526	10.5	81	
20	7	1000.7	31.4	4.6	56.8	81.0	2.6	418	526	9.4	89	
52	16	1540.16	34.3	5.2	49.9	59.1	1.7	385	479	17.1	62	
53	16	540.16	34.0	4.8	49.0	59.5	1.8	339	503	14.6	74	
54	16	540.16	34.1	5.0	49.4	59.3	1.7	390	495	16.7	65	
55	16	540.16	33.9	5.1	49.1	53.4	1.6	405	515	14.3	82	
56	16	540.16	35.2	6.1	45.4	70.1	2.0	366	440	22.0	39	
57	16	540.16	34.9	5.8	49.6	64.7	1.6	370	409	24.9	29	
58	16	540.16	32.8	5.6	52.0	65.5	2.0	386	484	16.7	59	
59	16	540.16	34.1	5.9	54.9	63.2	2.0	386	484	15.8	64	
60	16	540.16	33.9	5.5	49.3	69.5	2.0	406	522	11.4	87	
61	16	540.16	34.3	5.3	50.5	69.2	2.0	406	525	13.4	80	
62	16	1100.16	33.8	6.1	47.2	70.1	2.0	423	549	18.0	84	
63	16	1100.16	34.0	5.8	47.9	83.5	2.5	358	392	26.5	19.0	
64	16	1100.16	33.7	5.8	47.9	82.1	2.4	360	400	26.5	20	
65	16	1100.16	33.8	5.4	48.1	60.8	1.8	398	478	19.5	50	
66	16	1100.16	33.9	5.6	49.0	71.2	2.1	400	468	19.7	44	
67	16	1100.16	33.9	5.6	48.9	65.2	2.0	400	490	20.7	42	
68	16	1100.16	33.8	5.8	48.9	66.3	2.0	418	510	17.4	60	
69	16	1100.16	32.9	5.5	43.7	70.3	2.1	419	517	16.9	68	
70	16	1100.16	32.0	6.0	43.3	68.7	2.1	447	524	14.6	68	
71	16	1100.16	32.5	5.8	46.8	61.6	1.9	451	545	15.2	73	

Exp. No.	press. atm.	Output m^3/m^3 catalyst	Comp. of entering gas (%)	$\text{m}^3 \text{H}_2$	$\text{m}^3 \text{H}_2/\text{m}^3 \text{CO}$	Inlet temp. $^{\circ}\text{C}$.	Outlet temp. $^{\circ}\text{C}$.	% CO in finished gas	Converted parts CO in % of the max. possible conversion
30	11	460.11	32.0 5.2	55.5 56.5	1.8	347	424	21.4	36
31	11	460.11	32.4 5.6	53.3 60.3	1.8	360	482	13.8	73
32	11	460.11	34.0 6.0	52.0 62.8	1.8	366	498	13.6	78
33	11	460.11	31.3 5.0	55.4 53.2	1.7	367	484	12.1	83
34	11	460.11	33.3 5.3	53.2 59.5	1.8	369	475	12.6	79
35	11	460.11	31.4 5.4	55.2 55.7	1.8	373	490	12.0	84
36	11	460.11	31.7 5.5	54.9 56.2	1.8	394	506	11.0	92
37	11	460.11	32.4 5.6	53.0 96.0	3.0	350	408	21.4	32
38	11	460.11	32.4 5.3	53.4 95.0	2.9	365	467	15.5	56
39	11	460.11	33.2 5.6	51.8 101.4	3.1	368	468	13.6	63
40	11	460.11	35.5 5.1	50.6 98.0	2.9	384	492	10.0	80
41	11	460.11	32.8 5.4	50.8 93.0	2.8	398	511	8.8	87
42	11	460.11	33.4 5.6	50.2 93.9	2.8	413	515	8.6	89

Table 4
m³ H₂O/m³ CO

Exp. No.	Press. atm.	Output 3-gas/m ³ catalyst	comp. of inlet gas (%)	m ³ H ₂ O	m ³ CO	Inlet temp. OC.	Outlet Temp. OC.	% CO in finished gas	Converted parts CO in max. possible conversion
12	7	400.7	CO ₂ 32.4 CO 4.8	54.0	81.2	356	466	15.0	59
13	7	400.7	CO ₂ 51.8 CO 4.6	54.6	80.0	362	435	10.8	78
14	7	400.7	CO ₂ 31.6 CO 5.2	53.8	80.7	375	510	9.4	87
15	7	400.7	CO ₂ 32.4 CO 5.2	52.5	78.8	390	515	9.0	90
21	7	500.7	CO ₂ 8.8 CO 1.2	83.2	67.0	350	380	4.4	54
22	7	500.7	CO ₂ 9.0 CO 1.0	82.5	78.5	365	400	3.4	66
23	7	500.7	CO ₂ 8.4 CO 1.2	83.7	67.9	380	425	2.3	85
24	7	500.7	CO ₂ 9.4 CO 0.4	82.5	73.1	395	437	1.9	92