

UNITED STATES
DEPARTMENT OF INTERIOR
BUREAU OF MINES
SYNTHETIC FUELS DEMONSTRATION PLANT
LOUISIANA, MISSOURI

T.O.M. Reel 132, Item 26

T-510
W. M. Sternberg

ON THE RATE OF CONVERSION OF CARBON MONOXIDE AT HIGHER
PRESSURES OVER A BROWN OXIDE CATALYST

11/26/41

Introduction

The brown oxide catalyst is known to permit higher throughput at higher pressures than at lower pressures, and this higher throughput is not proportional to the pressure increase. No systematic tests on the efficiency of the catalyst at different pressures have apparently as yet been made.

The Oppau Section 462 has worked on the problem for two years to eliminate methane under pressure from 50-200 m³ per hour pressure-release gas of the butyl factory, followed by conversion of CO on the brown oxide catalyst, permitting the ammonia synthesis gas to be supplied to pressure-scrubbing without pressure-release. In these tests the pressure relationship of the activity of the brown oxide and pressure were studied somewhat closer. These tests have come to a preliminary conclusion, and the results are reported below. The important results of these tests were that when pressure is increased from 1 to 11 atm., the catalyst volume can be reduced to about 1/3 for the same conversion and temperature. Further increase in pressures offers no possibility of additional reduction of the catalyst volume.

Details of Experiments

The pressure-release gas from the butyl factory was used in the test; hydrocarbons in it were recovered in a preceding stage. Unlike the gas used in gas manufacture, this gas was completely free from sulfur. Moreover, it contained appreciably less CO. Its composition was 32 percent CO, 6 percent CO₂, 54 percent H₂, 8 percent N₂. The composition of the inlet gases varied considerably, and its composition is given for each test.

The tests were run in two different units. The catalyst reactor shown in figure 1 was used for atmospheric pressure tests. The pressure-release gas was first freed from methane in CH₄ converter upon the addition of air and oxygen. The cracked gas was cooled to its dew point in a cooler. Outside steam could be supplied to the cracked gas through the line (2) and the required proportion of H₂O to CO could be established. The gas was next heated to the required temperature for the brown oxide catalyst conversion by burning it with a flame (3) with the addition of O₂. The reactor consisted of a tube 40 cm. in diameter and 3 meters high which was insulated on the outside with a 25 cm. layer of diatom insulation. Inside the tubing was a half meter-high firebrick insulation, 1 meter brown oxide catalyst of the usual fineness and finally 1/2 meter more of firebrick insulation. The reactor was, therefore, similar to one section of the shaft reactor used at the gas factory. Two thermocouples were arranged in the center of the reactor and immediately next to the wall in a way to

permit moving them through the whole length of the reactor. Tests showed that the reading of the outer thermocouple was about ten degrees lower than of the centrally located thermocouple. The insulation was, therefore, not entirely satisfactory. The inlet temperature of the gases was assumed to be that indicated by the central thermocouple in the upper firebrick layer, the temperature at the end of the catalysis the highest temperature found by lowering the central couple. Tests for determining the composition of the dry gas and the water contents were taken in front and behind the converter.

Pressure tests were run in the apparatus shown in figure 2. The leads and nature of operations were the same as in the low pressure tests. The reactors consisted of pressure tubing 50 cm. in diameter and 2.75 m. height. The tube was insulated on the inside. Only a limited amount of pressure-release gas was available and the inside diameter was varied between 20 and 10 cm. depending on the operating pressure and the desired residence time. The catalyst layer was 1 meter high. The temperature at the catalyst inlet and at the end of catalysis were measured by fixed thermocouples. The high pressure steam in line 2 was only 8 to 10 atm., and the proportion of $H_2O:CO$ at higher pressures could not be varied at will. Changing the operations of the CH_4 converter in front of the unit permitted changing the $H_2O:CO$ proportion between 1.0 and 2.4, but the usual proportion of 3:1 was not reached. The effect of steam excess upon the progress curve was not, therefore, studied in these special series of tests.

Results

a) Conversion of CO during the same residence time at different pressures

As a rule, the catalyst load is approximately 550 m³ of gas (15° C., 735 mm. Hg.) per cubic meter catalyst per hour during low pressure conversion. A series of tests was run first at which the catalyst activity was tested with a throughput of approximately 540 m³/m³ catalyst, hr. while the pressure was raised from 1 to 16 atm. The CO conversion in percentage of CO at the conclusion of the test and at the start was used as a measure of catalyst activity. The change of the equilibrium constants with the temperature was in that way eliminated. The results obtained in this series of tests are shown in table 1. Figure 3 shows the CO conversion in percent of the maximum conversion possible at the outlet temperature in relation to the inlet temperature at the different pressures used in the tests. This figure shows clearly the important point that the absolute amount of CO conversion does not increase proportionately to the pressure at any given temperature and time of residence, and that pressure conversion cannot be operated with a throughput proportional to the pressure, with other conditions used in low pressure conversion unchanged. Should this have been the case, all curves would coincide at all pressures. Figure 3 shows clearly that such is not the case. Should it be desired to convert 16 times greater amount of CO at 16 atm. as at 1 atm., the inlet temperature and, therefore, also the operating temperature must be increased by

around 70° C. Only by an increase by these 70 degrees will the catalyst activity be raised sufficiently for a $540 \times 16 = 8600 \text{ m}^3$ (15°, 735 mm.)/ m^3 catalyst.

b) The relation of CO conversion and operating temperature to the residence time at a constant pressure

The necessity of such considerable temperature rise creates immediately the question, to what extent the catalyst load can be increased at a constant pressure by increasing the operating temperature. Tests were accordingly run at 7 and 16 atm. pressure, in which the time of residence was varied in proportion of 1:2. The results are summarized in table 2 which is arranged similarly to table 1. They are moreover shown graphically in figure 4 for an operating pressure of 7 atm. and in figure 5 for an operating pressure of 16 atm. The different points are scattered because the inlet gas composition varied considerably and chiefly because the steam concentration was difficult to maintain; the two figures show, nevertheless clearly that at 7 atm. and at 10 atm. the conversion can be doubled by raising the temperature by around 30° C. The temperature increase of 10 degrees represents a rise in the reaction rate by the factor $\sqrt[3]{2} = 1.26$. Laupichler (Ind. Eng. Chem. vol. 30, 1930, p. 578) has arrived at similar results. In atmospheric pressure tests with a catalyst not identified any closer and a considerably different gas composition, the velocity constants increased by a factor of 1.23 for a 10 degree temperature rise. When these results are applied to the tests

made at 1 atm. and 16 atm. described in the preceding section, the rise in the operating temperature of 70 degrees should result in an increase of the conversion velocity by a factor of $1.26^7 = 5$. The factor should be further increased by $\frac{16}{5} = 3.2$ by increasing the operating pressure from 1 atm. to 16 atm. (Table 1). A comparison of the curves at 11 atm. and 16 atm. in figure 3 shows that an increase in the conversion rate by the factor $\frac{16}{11} = 1.46$ requires a temperature increase by 15 degrees in addition to the pressure rise. The temperature rise alone increases the reaction velocity by the factor $1.26^{1.5} = 1.41$. An increase in pressure from 11 to 16 atm. results therefore in practically no increase in the conversion velocity within the limits of accuracy of the tests. This result tells in a general way to what extent the conversion velocity of CO on the brown oxide catalyst can be increased by raising the pressure. The reaction velocity on the catalyst does not depend on the partial pressure of CO in the gas phase, but on the density of adsorption on the catalyst surface. The connection between partial pressure and the adsorption density is given by the adsorption isotherm which is expressed by the Langmuir formula

$$c = c_p \times \frac{p}{p+b}$$

c in this formula represents the surface concentration at the pressure p . c_p is the surface concentration at the pressure p , and b is a constant. The adsorption isotherm in agreement with this equation is shown in figure 6 in arbitrarily selected values of c_p and b . At low pressures, when p is small in comparison with

b, the surface concentration increases proportionately to the partial pressure in the gas space. The velocity of the catalysis reaction also rises in this region proportionately to the pressure. When working within the linear region of the adsorption isotherm, an increase in pressure to p atm. will increase by p the value of the low pressure throughput for the same catalyst volume. At high pressure, when p is large in comparison with b , the surface concentration is independent from pressure and reaches the saturation value c_p . In this range, pressure increase will result in no increase in the conversion velocity, and therefore, the catalyst volume could be reduced. In the intermediate area between the linear part and the saturation range, the surface concentration increases slower than the pressure and, therefore, also the velocity of the heterogeneous reaction. Figure 3 shows that the CO conversion upon the brown oxide catalyst is no longer in the linear range, because otherwise the curves for all pressures should coincide. Such is, however, not the case. In the usual operating conditions, operations are carried under conditions in the transition range. Closer computation of the tests shows that a rise in pressure from 11 to 16 atm. will no longer increase the conversion rate, which means that even at 11 atm. the saturation pressure of the adsorption isotherm for the catalyst surface is already practically reached. At higher pressure than about 11 atm., the absolute amount of converted CO_2 depends, therefore, only on the residence time and the temperature, and no longer upon the pressure. In

this region, pressure increase alone will no longer permit any reduction of the catalyst volume.

To summarize, a $1/3$ reduction of the catalyst volume is the maximum that can be reached at higher pressures, when other operating conditions are unchanged. This reduction can be reached at an operating pressure of 11 atm., and cannot be appreciably increased at pressures exceeding 11 atm.

c) Relation between CO conversion and excess steam

It was already mentioned that only 7 atm. high-pressure steam was available for tests. Higher pressure tests could, therefore, be run generally only without the addition of the regulating steam. The usual proportion of $H_2O:CO = 3:1$ could not, therefore, be used in these tests. The tests had to be run with the considerably lower steam excess. The study of the effects of reduction of steam excess upon the conversion velocity had to be postponed until steam at sufficient pressure would become available in one series of tests for the usual proportion of 3:1 at 11 atm. without the addition of steam. The results are shown in table 3 and in figure 7. When the proportion of $H_2O:CO = 1.0$ was raised to 3, the inlet temperature required for the same percent approach to equilibrium had to be raised by about 15 degrees. This result is readily understood in the light of the earlier results. Increasing the steam excess with the same amount of dry gas raises the amount of gas + steam in the proportion of

1.95:1.58 = 1.23, as may be seen in table 3. Such increase in gas velocity is required to compensate for a temperature increase of 10 degrees. The remaining five degrees are explained by the greater amount of CO converted for the same percent approximation of the equilibrium conversion with the steam excess. Moreover, a larger steam excess for the same CO conversion increases the catalyst temperature by less than smaller steam additions, so that for the same inlet temperature the average operating temperature of the catalyst must be different under the two conditions. Finally, with larger steam excess, the CO partial pressure in the gas space is reduced. According to the results shown in the preceding section, this will result at 11 atm. in a very small reduction of the CO density upon the catalyst surface. A reduction of the CO partial pressure in the gas phase does not, therefore, affect the conversion velocity.

d) Comparison between the first and second catalyst sections

The tests so far described were all run with the gas of the usual composition of the mixed gas at the inlet to the CO converter. The experimental converter was, therefore, a model for the first section of the usual shaft converter. The temperature rise in the second section is considerably lower because of less CO converted than in the first layer, and one may expect that at the same inlet temperature in both sections similar approximation to the equilibrium values will be reached. Tests had, therefore, to be run with the gas of a composition of the mixed gas before

the inlet to the second layer of the CO converter. Such gas was not available for experimental operations. Tests were, therefore, made with a gas diluted with hydrogen. In this manner, the CO content usually found at the outlet from the first catalyst section was obtained. Such a gas contained, however, considerably less CO_2 and correspondingly higher proportion of hydrogen. For these reasons no more than very general quantitative conclusions can be reached from the experimental results. The important question is whether with the same inlet temperature any considerable difference in activity exists in the first and second catalyst layers. The experimental results are shown in table 4 and in figure 8. The progress curve for the second section may be seen to proceed as for the first layer. The points measured for the second layer were obtained at 10 degrees higher temperatures than for the first layer in table 4 and this difference was principally due to the gas throughput being in proportion of $500 \times 1.7 \div 400 \times 1.8 = 1.18$. Results obtained for the first section can, therefore, be applied to the second section of the converter.

e) Methane formation upon brown oxide catalyst

A connection between pressure conversion with methane re-formation is frequently mentioned in the literature. Tests made so far in Oppau have never indicated any CH_4 -formation in the pressure conversion, but this point was, nevertheless carefully watched because the absence of H_2S produces especially favorable

conditions for CH_4 -formation. The methane content of the mixed gas was determined before and after the conversion with an infrared spectrograph at Oppau which is particularly well adapted for a rapid and accurate indication of the CH_4 -contents. No increase in the CH_4 -content was observed during conversion.

Summary

Pressure conversion of brown oxide was tested at 1, 7, 11, and 16 atm. The catalyst efficiency at these pressures and different temperatures, throughputs, and steam excess was investigated. Efficiency was expressed by the percent of unconverted CO to the maximum conversion given by equilibrium conditions.

The results indicated:

- 1) The load could be increased threefold when pressure was raised from 1 to 11 atm. No further appreciable increase in the load resulted from additional rise in pressure.
- 2) A factor of 1.26 for an increase in the reaction rate with a temperature rise of 10 degrees was found for the temperature relationship of the reaction velocities between 7 and 16 atm. pressure.
- 3) The effect of steam upon conversion can be explained by the different residence time with different steam content.
- 4) No difference in activity of the brown oxide catalyst has been found for operating conditions in the first and second catalyst layers.

5) No methane is formed with the sulfur-free gas by brown oxide catalyst.

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W. M. Sternberg
2/20/53