Title

EFFECTS OF REACTOR DIAMETER ON THE PLUGGING OF FIXED-BED FISCHER-TROPSCH REACTORS

Authors

Bell, A.T.
Heinernann, H.
McKee, W.G.

Publication Date

1981-07-01

LBL-13047
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

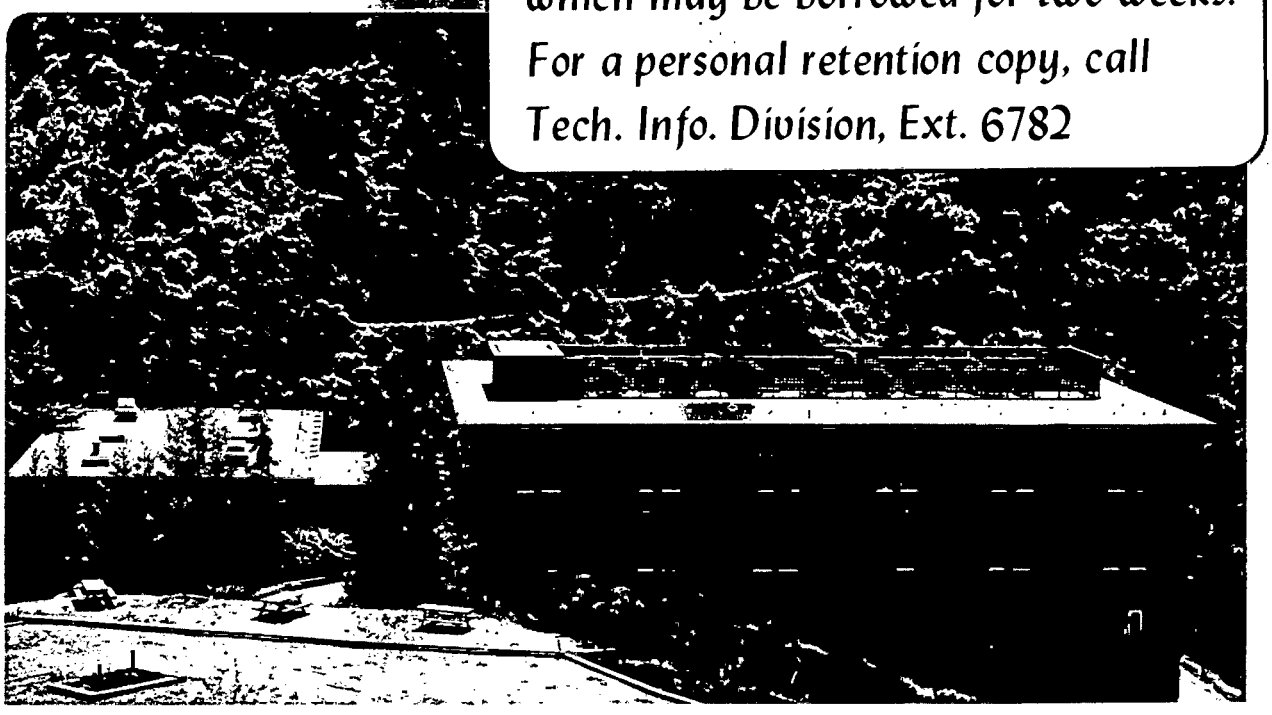
Materials & Molecular Research Division

Submitted to the Journal of Applied Catalysis

EFFECTS OF REACTOR DIAMETER ON THE PLUGGING OF FIXED-BED FISCHER-TROPSCH REACTORS

A.T. Bell, Heinz Heinemann, and W.G. McKee

July 1981



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

EFFECTS OF REACTOR DIAMETER ON THE PLUGGING OF FIXED-BED FISCHER-TROPSCH REACTORS

By

A. T. Bell, Heinz Heinemann, and W. G. Mc Kee

July, 1981

Materials and Molecular Research Division

Lawrence Berkeley Laboratory

and

Department of Chemical Engineering

University of California

Berkeley, CA 94720

This work was supported by the Assistant Secretary of Fossil Energy, Office of Coal Research, University Contracts Division of the U. S. Department of Energy under Contract Number W-7405-ENG-48.

The utilization of fixed bed reactors for Fischer-Tropsch synthesis, while commercially practiced (1-3), presents some inherent difficulties. Among them are: the need for rapid heat removal in a highly exothermic reaction, which has led to the installation of fluid bed reactors and of specifications for length/diameter ratios at various space velocities for fixed bed reactors (4); and the requirement for relatively high H_2/CO ratios (>2:1) in the synthesis gas to prevent catalyst deactivation and reactor plugging. The advent of second and third generation gasifiers, all of which produce relatively low H_2/CO ratio synthesis gas (5) has emphasized the desirability to operate Fischer-Tropsch reactors with such low H_2/CO ratio gas without having to go through extensive and energy inefficient external water/gas shift steps. There has consequently been renewed interest in the slurry-type, three-phase Fischer-Tropsch reactor, first proposed by Kolbel (6-8). Among the advantages claimed for the slurry reactor are: uniformity of reactor temperature; catalyst tolerance of H_2/CO feed ratios as low as 0.6; high conversion without external gas recycle. The disadvantages of slurry reactors are: the need for relatively large reactor volumes, because of low catalyst loadings; and the separation of high-boiling reaction products from the liquid phase needed to suspend the catalyst.

In the present study, we have investigated the extent to which better reactor isothermicity and the suppression of reactor plugging can be achieved by reducing the diameter of a fixed bed reactor, containing an iron catalyst. Conclusions on the relationship between isothermicity and tolerance for low H_2/CO ratio synthesis gas in fixed bed reactors assist in the explanation of differences previously observed in the tolerance level for such gas between fixed bed and slurry bed reactors.

A. Equipment

Equipment was designed to permit operation at high conversion with single pass fixed bed reactors of different diameters. The reactors consisted of replaceable stainless steel tubes ranging from one quarter inch O.D. (U-tube, approximately 13" long) to 1" O.D. (lengths of 5") with a wall thickness of .028." The reactors were heated by means of a Techne Sandbath (model SBL-2D) which provided a working volume 12" deep by 9" in diameter. Bath

temperature was uniform to within 1/2°C and varied by no more than 3°C at 300°C during the course of the reaction. The flow rate of the reactant mixture was monitored during the reaction using both a rotometer and a bubble flow meter and typically set at 20 to 150 cc per minute. Products consisted of carbon dioxide and hydrocarbons ranging from methane to components with molecular weights in excess of C_{30}. Liquid products in the effluent from the reactor were collected by means of an ice trap, and less condensable products were either vented or analyzed by gas chromatography. For short runs, a small volume trap was used to minimize lag time and to make it possible to follow the rapid initial deactivation during carbiding.

Gas samples could be taken at any time during a run by means of a Carle six port gas sampling valve, while liquid samples could only be analyzed as an integrated product at the conclusion of the run. A Varian model 3760 gas chromatograph equipped with two columns was used to analyze product composition and determine over-all carbon monoxide conversion.

B. Experimental Procedure

For all runs in this investigation, an equal amount of ammonia synthesis catalyst (United Catalyst Incorporated, Girdler Catalyst C73-1) was utilized. This catalyst is a low surface area (0.24 m^2/gm) unsupported iron catalyst, singly promoted with 0.8% potassium. Fresh catalyst was used in each run with the same catalyst pretreatment to insure a consistent starting point for each experiment. The catalyst was ground to between 30 and 60 mesh and reduced in flowing hydrogen at a GHSV of 1500 cc per gram per hour at 300°C and 2 atmospheres for a period of 16 hours.

Following reduction, the reactor was purged with helium for approximately 0.5 hours prior to introduction of the reaction mixture. During this time, the reactor was adjusted to operating conditions in the general range of 275°C to 325°C and 132-150 psig pressure. Premixed cylinders of carbon monoxide and hydrogen were used in order to provide uniformity of the H_2/CO ratio in similar runs. After purging, the reaction mixture was charged and two process variables were observed: reactor plugging and catalyst deactivation. Gas samples were used to follow the deactivation of the catalyst by monitoring both the concentration of carbon monoxide in the exit gas as well as the exit gas flow rate. The onset of plugging could be observed directly by measuring the pressure differential across the reactor.

C. Results

A major concern of this investigation was the effect of reactor diameter and reaction conditions on long-term deactivation of the catalyst. As the bed diameter increases, there is relatively less wall area per unit of catalyst volume for heat transfer from the reactor to the environment. Local instabilities can therefore occur, resulting in high surface temperatures on the catalyst or "hot spots." These hot spots may cause catalyst deactivation and reactor plugging.

Conditions chosen for operation with the different diameter reactors were intended to yield an over-all conversion of about 50% (temperature 300°C; pressure 10 atmospheres; GHSV equal to 80 cc per gram per hour and variable H_2/CO ratio) and the run was allowed to proceed for approximately 100 hours or until plugging was observed, whichever occurred first. Figure 1 shows runs for the two reactors of 1/4" and 1" diameter at a H_2/CO ratio of 1. Although there seems to be a minor difference in the rate of deactivation in the first half of the run, the plateau phase is the same in each case, and there is no plugging or sudden loss of activity for the remainder of either run. An internal thermocouple showed no temperature rise in the smaller reactor and a temperature rise of about 10°C in the 1" reactor. The initial loss of CO conversion shown in this figure is attributed to carbiding of the catalyst.

Runs in the smaller 1/4" reactor at different lower gas space velocities and lower H_2/CO ratios of 0.6 and 0.8 resp. (Fig. 2) demonstrate development of pressure drop after certain periods of time, such pressure drop occurring earlier at lower H_2/CO and lower space velocity. When the temperature was raised from 300 to 325° in the small diameter reactor pressure drop developed and increased rapidly already after about 40 hours on stream even at a H_2/CO ratio of 1 and realtively high space velocity (Fig. 3). The importance of temperature on plugging is evident.

Reduction of the H_2/CO ratio from 1 to 0.8 resulted in a pressure drop developing in both reactors but developing in the larger diameter reactor at a shorter time on stream than in the smaller diameter as shown in Figure 4.

An attempt was then made to determine the effect of temperature at a H_2/CO ratio of 1 for both reactors by determining the pressure drop after 90 hours on stream at different sand bath temperatures. This is shown in Figure 5. It is apparent that there is a critical temperature of about 275°C above which the 1" diameter reactor begins to show plugging after about 90 hours on stream at a hydrogen/CO ratio of 1 and a gas hourly space velocity of 80cc per gram per hour. The 1/4" reactor shows the plugging phenomena at a temperature about 20°C higher than that of the 1" reactor.

D. Conclusions

The findings of this study indicate that the diameter of a fixed-bed Fischer-Tropsch reactor critically affects the resistance of the reactor to plugging caused by the build up of carbonaceous or waxy deposits. At a fixed temperature and space velocity, plugging occurs at a shorter time on stream the larger the reactor diameter. Plugging is also accelerated by operation at high temperatures and low H_2/CO ratios. While the cause of plugging has not been established, it is very likely due to local nonuniformity in the catalyst temperature. Hot spots in the reactor are expected to occur since the heat release associated with Fischer-Tropsch synthesis is very high and the catalyst thermal conductivity is low. Decreasing the reactor diameter at a fixed gas space velocity, should improve temperature uniformity by decreasing the length of the thermal conduction path and increasing the extent of convective heat transfer from each catalyst particle. The latter effect can be ascribed to the higher gas velocity in a smaller diameter reactor. The suppression of plugging at higher H_2/CO ratios is likely due to a reduction in the product average molecular weight and the reaction with hydrogen of carbon deposited via the Boudouard reaction. A slurry bed reactor with its much greater isothermicity can be expected to behave similarly to very small diameter fixed bed reactors and therefore have a higher tolerance of lower H_2/CO ratio feed gas.

This work was supported by the Assistant Secretary of Fossil Energy, Office of Coal Research, University Contracts Division of the U. S. Department of Energy under Contract Number W-7405-ENG-48.

References

1. Pichler, H., Advances in Catalysis 4, (1952).

2. Dry, M. E. Ind. Eng. Chem, Prod. Res. Dev., 15, 282, (1976).

3. Weitkamp, A. W., Seehj, H. S., Bouman, N. J., Cody, W. E., Ind. Eng. Chem. 45, 363, (1953).

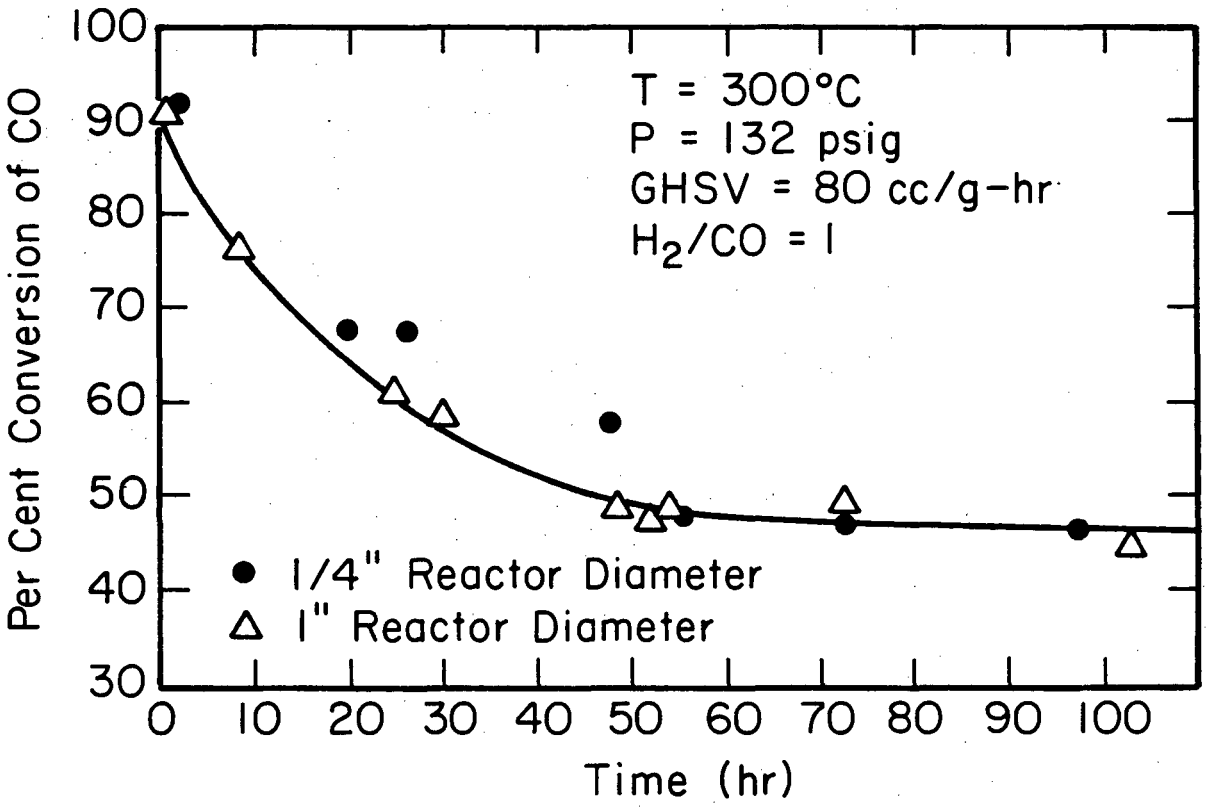
4. "Chemierohstoffe Kohle" ed. J. Falbe, Georg Thieme Verlag, Stuttgart, 1977, p. 237-239.

5. Shinnar, R. and Kuo, J. C. W., DOE report FE-2766-13, Dist. Category UC-90D, (1978).

6. Kölbel, H. and Ackermann, P., Chem. - Ing. - Tech. 28, 381, (1956).

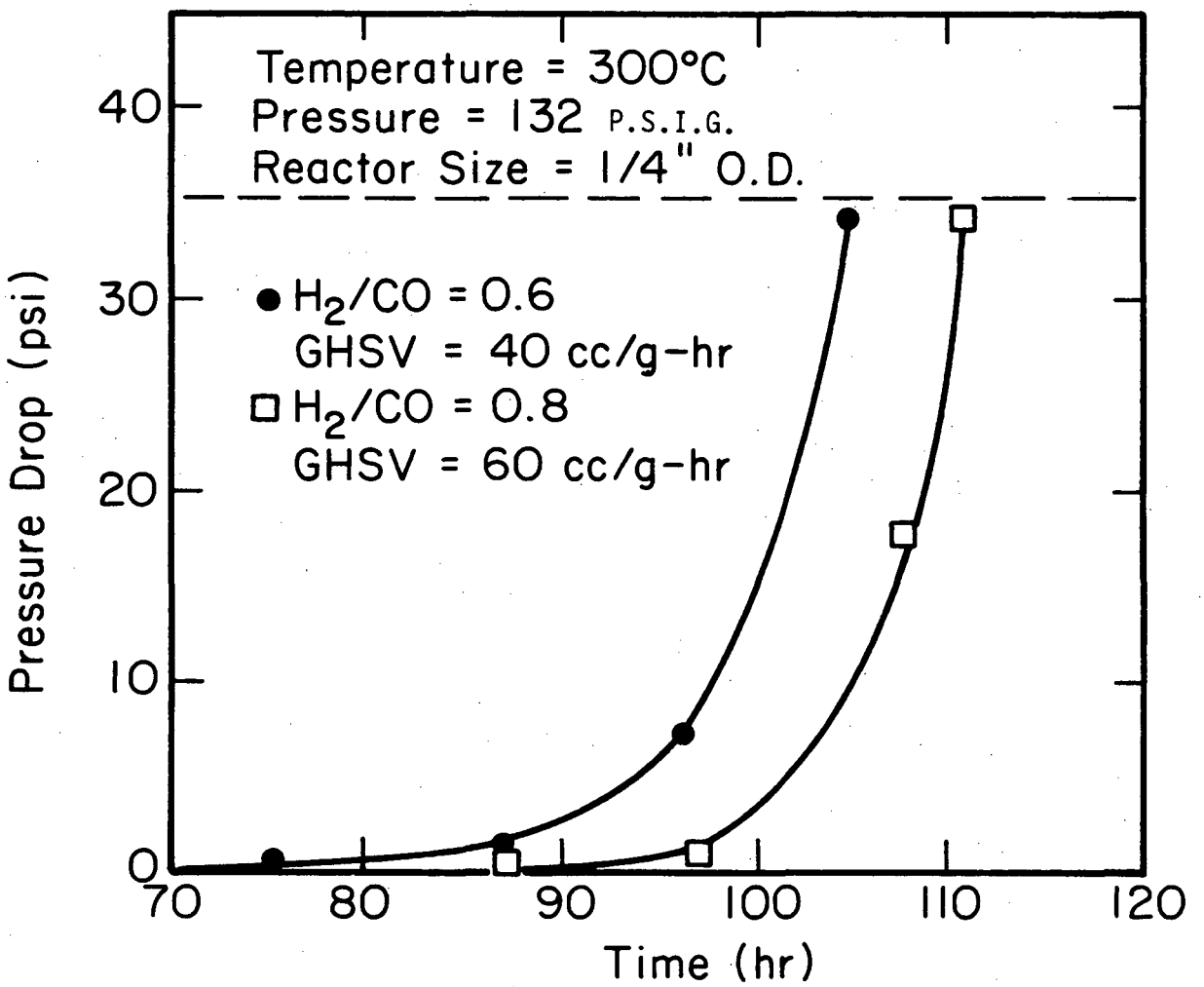
7. Kölbel, H., Ackermann, P., and Engelhardt, F., Erdoel und Kohle 9, 153, 225, 303 (1956).

8. Kölbel, H. and Ralek, M., Catal. Rev. - Scie. Eng. 21 (2), 225 (1980).



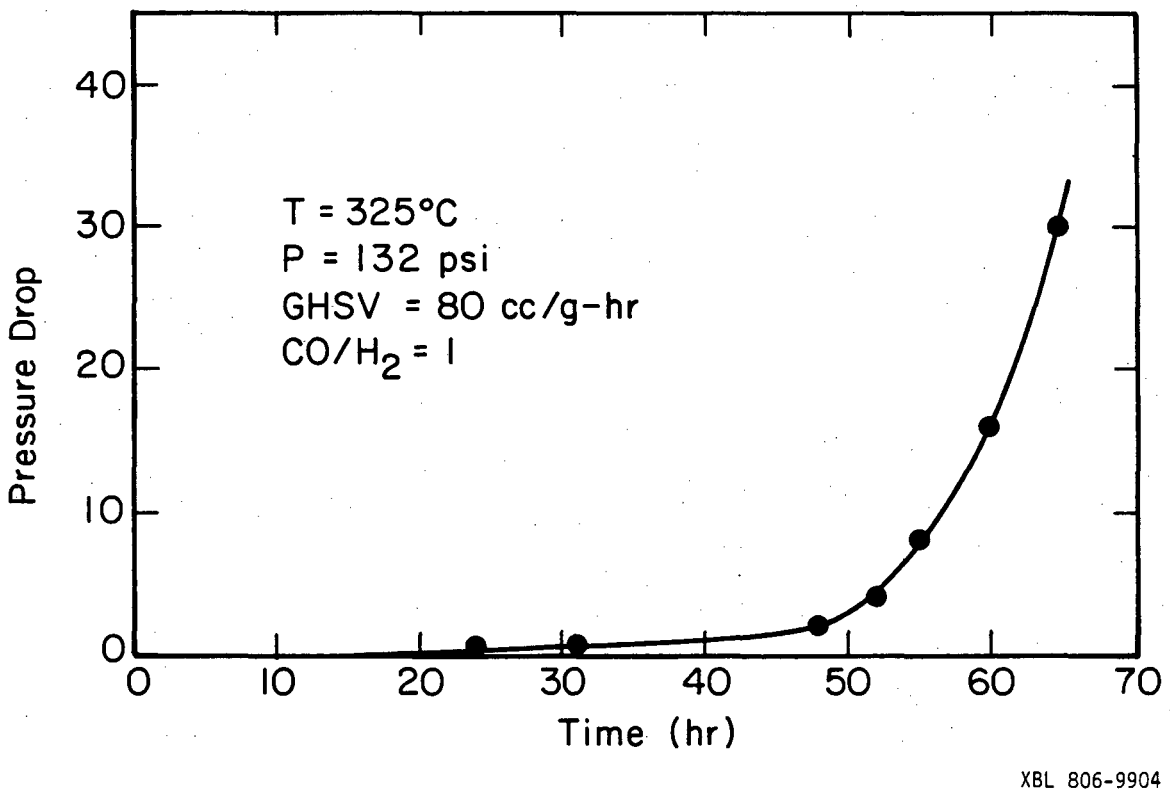
XBL 806-9911

Figure 1



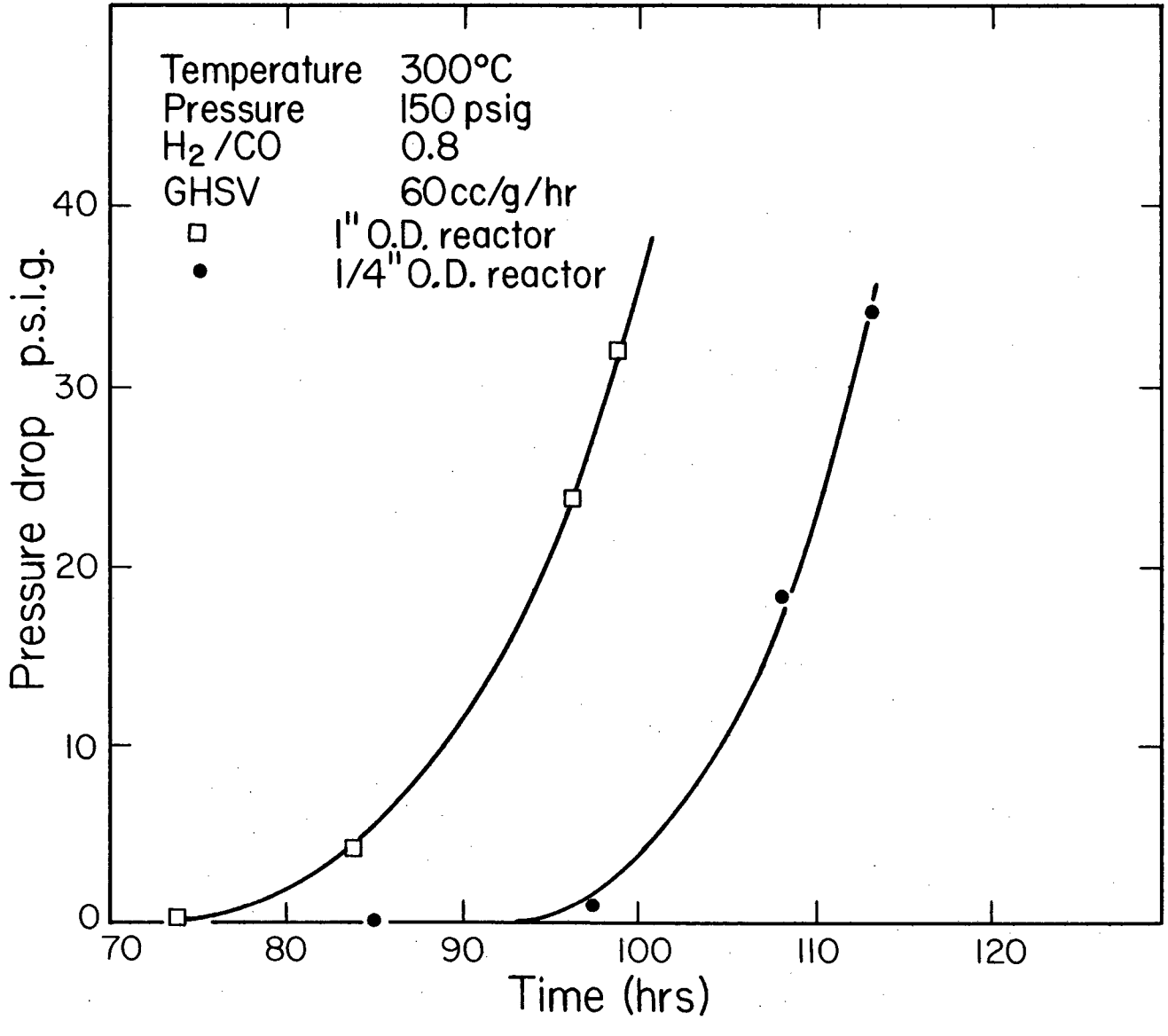
XBL 806-9905

FIGURE 2



XBL 806-9904

Figure 3



XBL 814-762

Figure 4

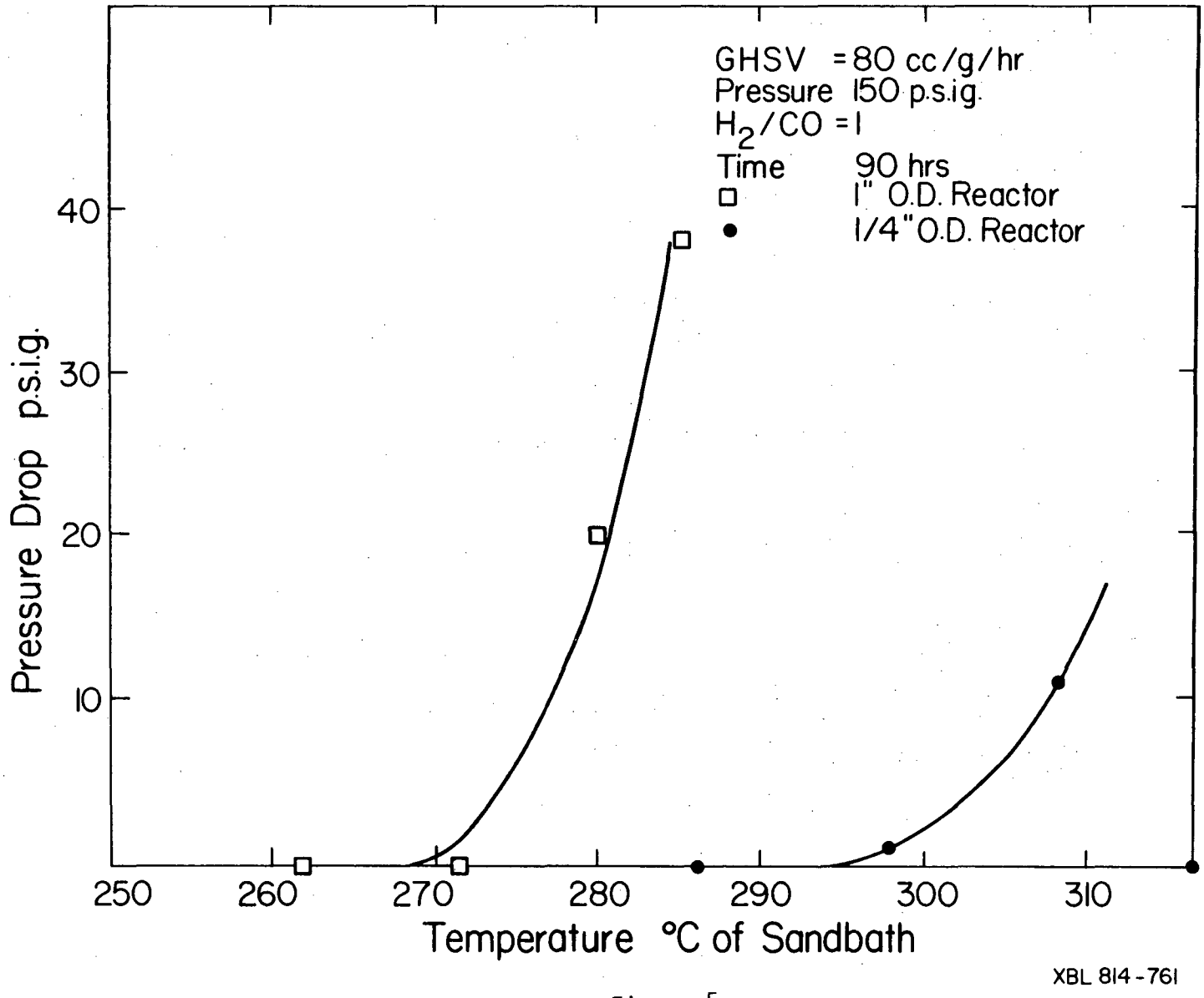

GHSV = 80 cc/g/hr
Pressure 150 p.s.i.g.
$H_2/CO = 1$
Time 90 hrs
1" O.D. Reactor
1/4" O.D. Reactor
Pressure Drop p.s.i.g.
40
30
20
10
250
260
270
280
290
300
310
Temperature °C of Sandbath
XBL 814-761

Figure 5

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720