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Usefulness of a Slurry-Type Fischer-Tropsch Reactor for
Processing Synthesis Gas of
Low Hydrogen-Carbon Monoxide Ratios

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Abstract

One of the advantages claimed for the Fischer-Tropsch slurry-type reactor over the more conventional vapor-phase reactors is its ability to process satisfactorily synthesis gas of low H_2/CO ratios, without excessive formation of elemental carbon. We argue that this may be caused largely by the well-stirred mixing typical of slurry reactors combined with the use of catalysts, such as those containing iron, with which the water-gas-shift reaction proceeds rapidly.

Indirect liquefaction of coal to form transportation fuels involves gasification to carbon monoxide and hydrogen (synthesis gas), followed by catalytic conversion to hydrocarbon products. As coal gasification is the most costly step, it must be efficiently coupled to the synthesis stage. Shinnar⁽¹⁾, using thermal efficiency as a guideline to estimate process economics, concludes

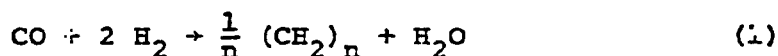
that the lowest cost synthesis gas can be produced from certain second generation gasifiers that use minimum amounts of oxygen and steam. The gas thus produced would have a H₂/CO ratio less than 1.0 and possibly as low as 0.5.

Conventional Fischer-Tropsch or methanol synthesis processes cannot, however, accept such low H₂/CO ratios. Conversion to methanol requires a H₂/CO ratio of 2.0 and the SASOL Fischer-Tropsch process uses a H₂/CO feed ratio of 1.8 or 6.0 for fixed- or entrained-bed reactors, respectively⁽²⁾. In general, H₂/CO ratios less than about one are considered to be incompatible with long-term, vapor-phase Fischer-Tropsch operation because of excessively rapid carbon deposition⁽³⁾. On the other hand, Kölbel et al.⁽⁴⁾ reported apparently satisfactory operation of a large slurry reactor using an iron catalyst with a H₂/CO ratio of 0.67. Detailed information on catalyst lifetime was not given but it appears to have been substantial.

We propose here that the capability of a slurry reactor to process low H₂/CO gases is probably caused by the mixing pattern characteristic of such systems, together with the use of catalysts that can cause the water-gas-shift reaction to occur simultaneously with the synthesis reaction.

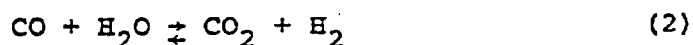
Chemistry of the Process

Although the products of carbon monoxide hydrogenation may be a complicated mixture of paraffins, olefins, other hydrocarbons and oxygenated species, the Fischer-Tropsch synthesis is approximately represented stoichiometrically by the overall equation:



Two important side reactions may occur concurrently with the synthesis.

Water, formed as a primary product, can react with carbon monoxide by the water-gas-shift reaction to generate hydrogen:



The extent to which this reaction proceeds markedly alters the ratio of hydrogen to carbon monoxide entering that is consumed by the reaction, termed the usage ratio.

Carbon monoxide can disproportionate by the Boudouard reaction to produce elemental carbon on the catalyst surface:



This results in rapid catalyst aging caused by fouling, and possibly mechanical disintegration. For the conditions of interest here, carbon deposition is thermodynamically favored. However, the amount of carbon formed is dictated by kinetic rather than equilibrium considerations. The main factors that influence carbon formation are catalyst composition, gas composition and temperature.

Carbon Formation

Of the two traditional Fischer-Tropsch catalysts, iron exhibits a greater activity for carbon deposition than cobalt under representative processing conditions. This is largely an inherent difference in catalytic properties, but a contributing factor may be the difference in operating temperatures. Processes using cobalt typically operate at only 175 or 200°C compared to 250 to 275°C for an iron catalyst.

Dry⁽⁵⁾ reports that the rate of the Boudouard reaction over an iron catalyst is given approximately by $r_C = kP_{\text{CO}}/P_{\text{H}_2}^2$

and that it is largely unaffected by the carbon dioxide concentration. The Fischer-Tropsch synthesis rate over a substantial concentration range and at temperatures below about 300°C is given approximately by $-r_{H_2+CO} = k'P_{H_2}$. There are secondary effects such as those caused by water vapor but in a gross sense it appears that decreasing the H_2/CO ratio causes an increased deposition rate of carbon but a decreased rate of hydrocarbon synthesis.

Activation energies for carbon deposition have been reported by several authors. The carbon deposition rate is increased by alkali promoters⁽⁶⁾ and the activation energy may vary moderately with the nature and amount of the alkali promoter, but a typical value is about 100 kJ/mol⁽⁷⁾. The activation energy for the synthesis reaction is about the same, so an increase in temperature to increase the synthesis rate can be expected to be accompanied by an approximately equal increase in carbon deposition rate.

Water-Gas-Shift Reaction

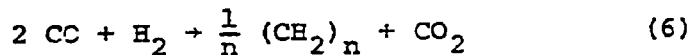
While carbon monoxide disproportionation is a deleterious side reaction, the water-gas-shift reaction is very beneficial for carbon monoxide-rich feeds, since hydrogen is produced from water by Equations (1) and (2). Karn et al.⁽⁸⁾ report that the rate of the shift reaction on a nitrated iron catalyst is much greater than the synthesis reaction at 230 to 240°C. If this reaction, then, proceeds to equilibrium the product composition should correspond to that predicted by Equation (4):

$$K = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} \quad (4)$$

The equilibrium constant K as a function of temperature T (in °K) is⁽⁹⁾:

$$K = 0.0102 \exp [4730/T] \quad (5)$$

For example, at 250°C the equilibrium constant is 86 and, therefore, the reaction proceeds nearly to completion. Overall, Equations (1) and (2) then become:



The H₂/CO usage ratio for this reaction is 0.5 compared to 2.0 when water is the final product of the Fischer-Tropsch synthesis, as in Equation (1), in both cases taking the product composition to average (CH₂)_n. The in-situ occurrence of this secondary reaction is particularly helpful in using a hydrogen-deficient feed gas. Whenever the H₂/CO usage ratio is less than that of the feed, the H₂/CO ratio present in the reactor will increase with extent of conversion. This is illustrated in Figure 1 which shows the results of calculations utilizing the synthesis stoichiometry given by Equation (6), i.e. with K = ∞. The H₂/CO ratio in the exit gas is presented as a function of the percent conversion of H₂ plus CO in the feed, for various feed composition ratios. When the feed ratio exceeds 0.5, the exit ratio increases greatly at high percent conversions, as the consumption of CO approaches completion.

Liquid-Phase Backmixing in a Slurry Reactor

While the effluent gas of a conventional, fixed-bed Fischer-Tropsch reactor operated with a low H₂/CO feed may be enriched with hydrogen by the shift reaction, as shown above, the entrance of the catalyst bed is still exposed to a hydrogen-lean gas, and carbon deposition would be most likely there. Similarly, in an

entrained-bed reactor, the gas and solids travel in approximately plug flow and the catalyst at the inlet is exposed to the lowest H_2/CO ratio composition. The use of a H_2/CO ratio of 6.0 in the SASOL entrained bed reactor is probably this high to minimize carbon monoxide disproportionation and catalyst disintegration.

The slurry reactor configuration for the Fischer-Tropsch synthesis that has been generally considered applicable to commercial operation is a bubble-column in which synthesis gas is passed upward through a slurry of finely divided catalyst suspended in non-volatile liquid, most of the product being removed overhead. Deckwer et al. ⁽¹⁰⁾ have reported axial dispersion coefficients for bubble columns for Fischer-Tropsch synthesis which show that a high degree of liquid mixing occurs. This results from an upward entrainment of liquid and solid in the vortex tail of the sparged gas bubbles. Since the catalyst is quite fine, it moves essentially with the liquid. A high degree of back-mixing was also shown in the bubble-column study of Schlesinger et al. ⁽¹¹⁾ who reported that the suspension was uniform over the bed height, by taking catalyst samples at different locations. At high gas velocities and column diameters of 0.6 to 2m, K"olbel and Ralek ⁽¹²⁾ state that with viscous liquids, mixing in the gas phase is of the same order of magnitude as that in the liquid phase.

If there are no mass or heat transfer limitations in a Fischer-Tropsch slurry reactor and the gas and liquid phases are well mixed, then the liquid concentration corresponds to saturation at the effluent hydrogen and carbon monoxide partial pressures. In other words, even though the H_2/CO feed ratio may be low, the concentration in the liquid and consequently

that to which the catalyst is exposed will be higher whenever the usage ratio is lower than the feed ratio. Even if the gas phase is not well mixed, but the liquid phase is, the same behaviour will be observed.

In slurry-phase experimental studies reported to date with an iron catalyst, the usage ratio has been less than the feed ratio. Even in the early work of Kölbel and co-workers, reviewed by Kölbel and Ralek⁽¹²⁾, in which a H₂/CO feed ratio of 0.67 was used in a commercial reactor of 10,000 L, we estimate that the usage ratio was about 0.63 for their reported 89% conversion of H₂ plus CO. Figure 1 suggests that the H₂/CO ratio in their exit gas would have been considerably higher than in the feed gas and therefore it is not surprising that they apparently obtained substantial catalyst lifetimes.

Experimental

Experimental verification of the above model was obtained in our laboratory from studies of the Fischer-Tropsch synthesis carried out in a 1-liter, mechanically-stirred autoclave operated in a semi-batch fashion. The autoclave diameter was 7.6 cm and was agitated by a six flat-bladed disk turbine impeller 5.1 cm in diameter. Synthesis gas was introduced into the wide-conical bottom of the reactor through a 0.32-cm i.d. blow tube and volatile products were removed overhead. Further details of the apparatus and analytical procedures will be published elsewhere. The catalyst (crushed to particle sizes between 170 to 270 mesh) and liquid carrier (normal-octacosane of +99% purity) remained in the reactor for the duration of a run (about 20 days). The catalyst (from United Catalysts, Inc. and designated C-73) was fused-iron and normally employed for ammonia synthesis. On an unreduced basis it contained 2.0-3.0% Al₂O₃, 0.5-0.8% K₂O, 0.7-1.2% CaO and < 0.4% SiO₂. It was pre-reduced in a separate

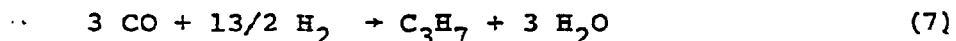
vessel using hydrogen at 400°C for 72 hours at a space velocity of 5000 cm³ gas/cm³ catalyst-hr and atmospheric pressure. It was then slurried with about 0.5 L of n-octacosane to produce a 15-weight percent suspension.

Conversion was varied by changing the space velocity from 50 to 430 cm³ gas (at S.T.P.)/cm³ liquid-hr. No heat or mass transfer limitations were present, as evidenced by a negligible change in conversion at faster stirring speeds. After an initial period steady-state operation was obtained over the entire run. The entire organic product spectrum from gases through waxes was collected. Gas chromatographic analyses showed the average net atomic H/C ratio (expressing oxygenated species as hydrocarbon plus water) in the entire organic product was about 2.3 in contrast to the value of 2.0 taken for construction of Figure 1.

Representative exit ratios of H₂/CO observed experimentally are shown by the data points in Figures 2 and 3 for runs with H₂/CO feed ratios of 1.3 and 0.71, respectively. The solid curves are those predicted theoretically for each of three temperatures assuming that the water-gas-shift reaction proceeds to equilibrium as calculated by Equations (4) and (5), instead of taking a value of $K = \infty$ as in Figure 1; and the product composition is taken to have a H/C atomic ratio of 2.3.

The theoretical curves in Figs. 2 and 3 were calculated by the following procedure:

Take as a basis 1 mole of CO and F moles of H₂ entering. F is then the inlet feed ratio of H₂/CO. Assume that the water-gas-shift reaction proceeds to equilibrium. For the observed product composition, the stoichiometry for the Fischer-Tropsch reaction is:



Let z be the number of " C_3H_7 " moles formed by Equation (7) and y be the number of CO_2 moles formed by Equation (2). Material balances result in the following:

$$U = (-y + 13z/2)/(3z + y) \quad (8)$$

$$X_{CO+H_2} = (19/2)z/(F + 1) \quad (9)$$

and
$$M = (F + y - 13z/2)/(1 - 3z - y) \quad (10)$$

where U is the H_2/CO usage ratio, X_{H_2+CO} is the fractional conversion of hydrogen plus carbon monoxide, and M is the H_2/CO ratio out of the reactor. The equilibrium relationship given by Equation (4) becomes:

$$K = y(F + y - 13z/2)/[(1 - 3z - y)(3z - y)] \quad (11)$$

Given the fractional conversion of carbon monoxide plus hydrogen and the feed ratio, z can be calculated from Equation (9).

Substitution of z into Equation (11) allows y to be calculated.

Equation (10) is then solved for M .

Unlike Fig. 1 where a constant usage ratio of 0.5 was assumed as given by Equation (6), the usage ratio varies slightly with conversion in Figs. 2 and 3 since it is affected by the equilibrium of the water-gas-shift reaction. At 269°C, for the conditions in Fig. 2 the usage ratio increases from 0.60 to 0.71 as conversion of H_2 plus CO is increased from 10 to 70 percent. With lower feed ratios, the change in usage ratio with conversion is less marked. At 251°C, for the conditions in Fig. 3, in which the feed ratio was 0.71, the usage ratio ranges from 0.59 at 10 percent conversion of $H_2 + CO$ to only 0.60 at 80 percent conversion.

The effect of temperature is shown by the curves for 200 and 300°C. The marked difference in predicted behavior in the presence and the absence of the shift reaction is also shown. The close agreement

of theory and experiment, over a wide range of conversion and exit H_2/CO ratios, shows that equilibrium with respect to the water gas shift was closely attained.

Conclusions and Summary

We conclude that the ability of a slurry-type Fischer-Tropsch reactor to process satisfactorily a feed synthesis gas of low H_2/CO ratio is intimately associated with a high degree of mixing in the reactor and the use of a catalyst active for the water-gas shift reaction. It is noteworthy that when the feed ratio exceeds the usage ratio in such a reactor, the highest degree of conversion results in the highest ratio of dissolved H_2 to CO in the liquid. This should minimize the extent of carbon formation and catalyst disintegration caused by disproportionation of CO . Thus high conversion is desired not only for economic performance but also to help maintain catalytic activity.

References

- (1) Shinnar, R., Chem. Tech. 8, 686 (1978).
- (2) Henrici-Olivé, G. and Olivé, S., Angew. Chem. (Engl. Ed.) 15, 136 (1976).
- (3) Poutsma, M.L. Oak Ridge National Laboratory Report ORNL-5635 (1980).
- (4) Kölbel, H., Ackermann, P., and Engelhardt, F., Erdöl und Kohle 9, 153, 225, 303 (1956).
- (5) Dry, M.E., Hydrocarbon Processing 59 (2), 92 (1980).
- (6) Dry, M.E., Shingles, T., and Botha, C.S. van H., J. Catal. 17, 341 (1970).
- (7) Dry, M.E., Shingles, T., Boshoff, L.J. and Botha, C.S. van H., J. Catal. 17, 347 (1970).
- (8) Karn, F.S., Shultz, J.F., and Anderson, R.B., Actes du Deuxième Congrès International de Catalyse, Paris, Tome 2, 2439 (1960).
- (9) Rossini, F.D., Pitzer, K.S., Taylor, W.J., Ebert, J.P., Kilpatrick, J.E., Beckett, C.W., Williams, M.G., and Werner, H.G., A.P.I. Research Project 44.
- (10) Deckwer, W.-D., Louisi, Y., Zaidi, A., and Ralek, M., Ind. Eng. Chem. Process Des. Dev. 19, 699 (1980).
- (11) Schliesinger, M.D., Benson, H.E., Murphy, E.M. and Storch, H.H., Ind. Eng. Chem. 46, 1322 (1954).
- (12) Kölbel, H. and Ralek, M., Catal. Rev. - Sci. Eng. 21, 225 (1980).

Acknowledgement

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Figure Captions

Figure 1. Calculated Effect of Percent Conversion on Exit H_2/CO Ratio for Selected Values of H_2/CO Feed Ratio. Product composition taken as having an H/C atomic ratio of 2.0, and water gas shift assumed to go to completion ($K = \infty$). Usage ratio is thus 0.5.

Figure 2. Comparison of Calculated and Experimental Results. 269°C, 0.79 MPa, 600 RPM stirrer speed, H_2/CO feed ratio = 1.3. Net H/C ratio in organic product = 2.3.

Figure 3. Comparison of Calculated and Experimental Results. 251°C, 0.79 MPa, 500 RPM stirrer speed, H_2/CO feed ratio = 0.71. Net H/C ratio in organic product = 2.3.

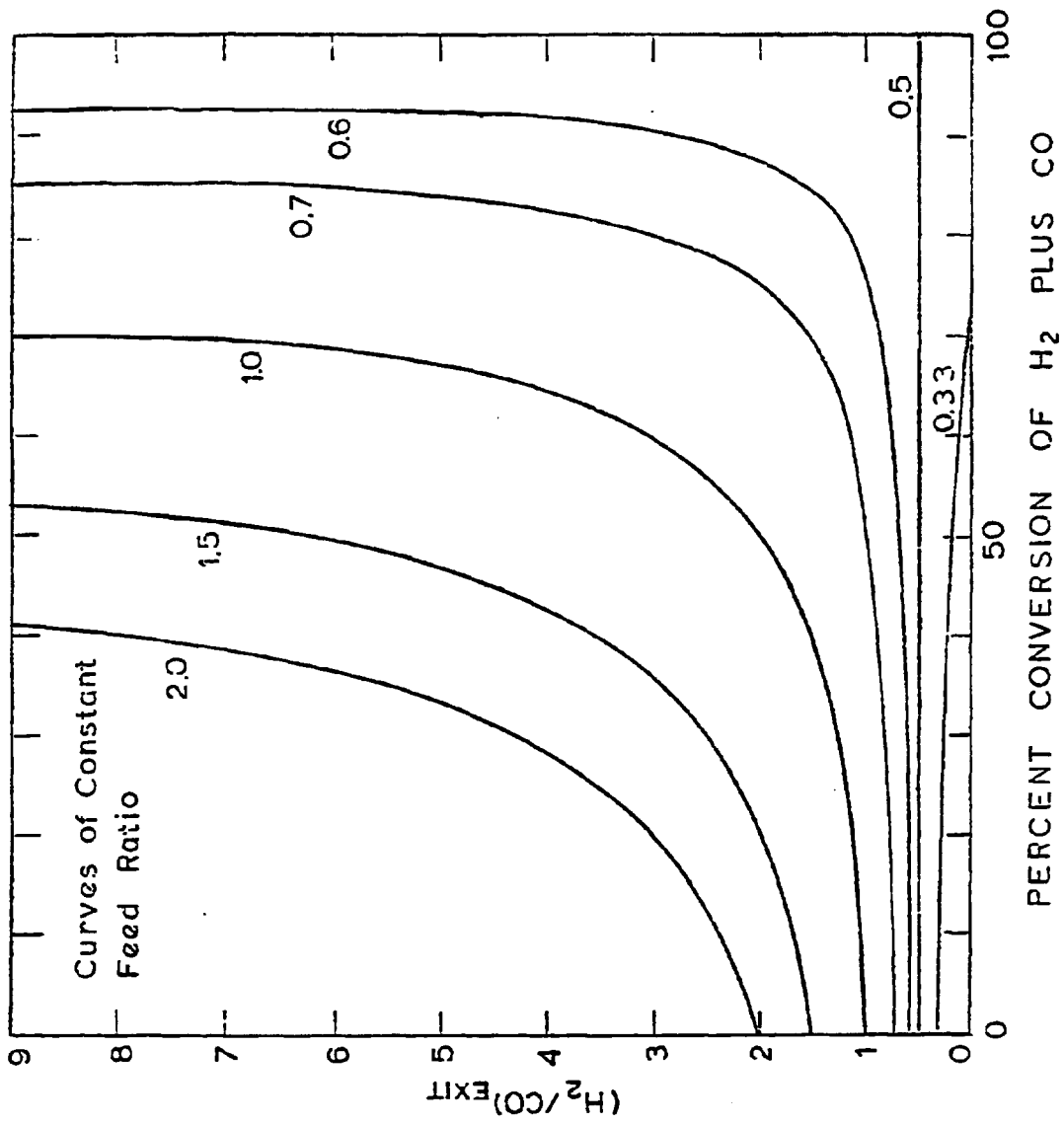


Figure 1

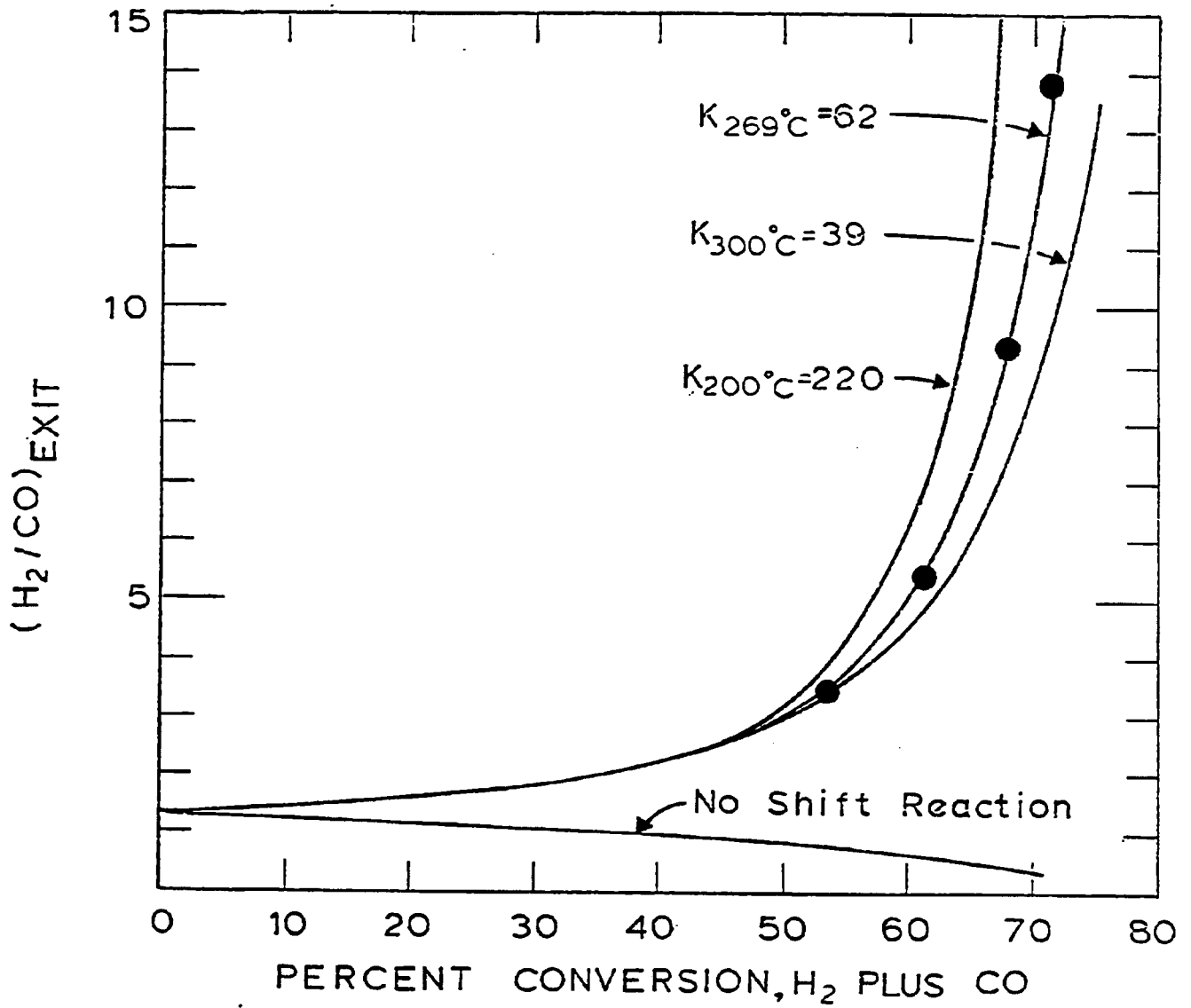


Figure 2

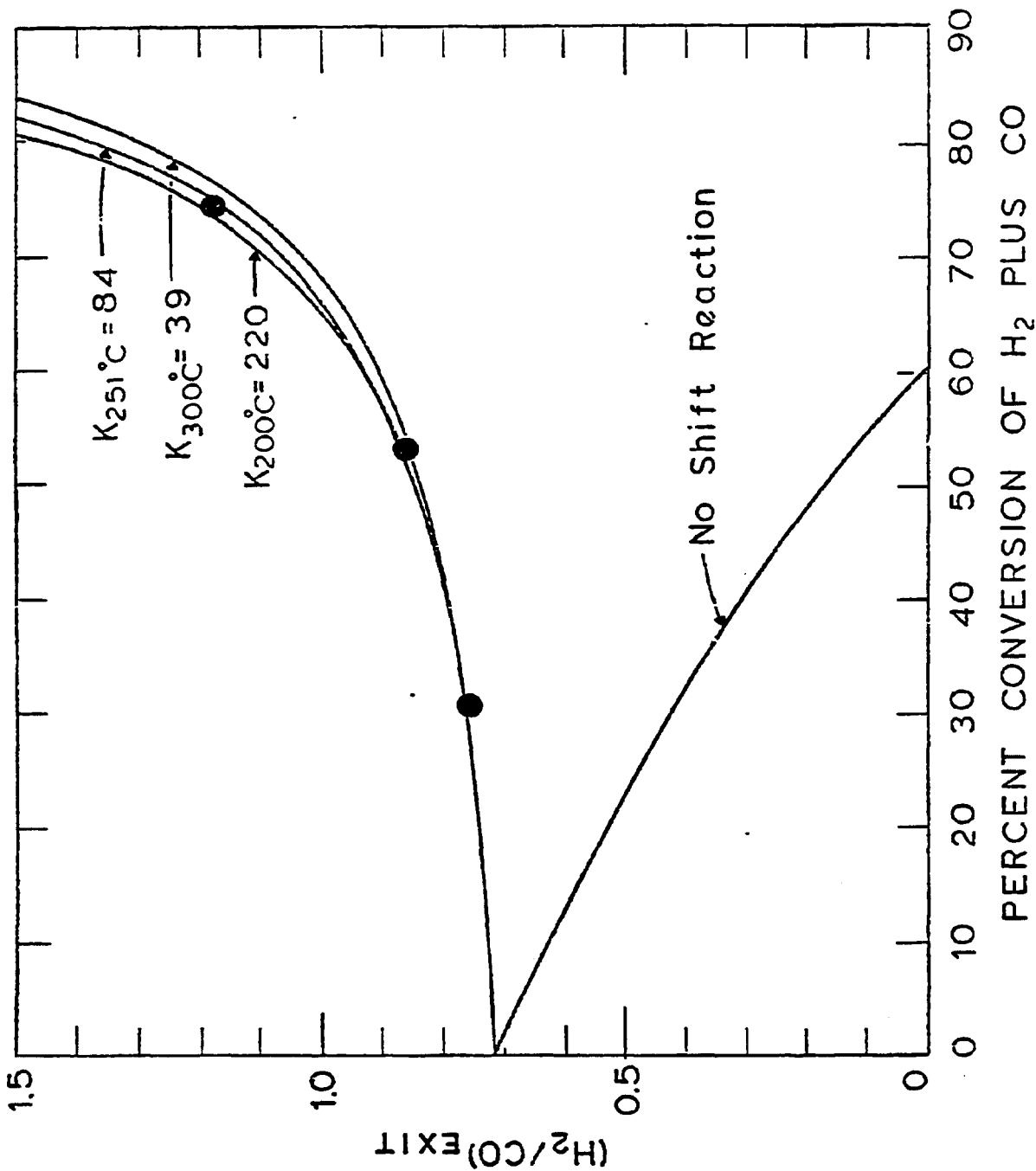


Figure 3