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KINETICS OF GAS SYNTHESIS USING RECYCLE SYSTEMS

By J. F. Shultz, F. S. Karn, and R. B. Anderson

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KINETICS OF GAS SYNTHESIS USING RECYCLE SYSTEMS

by

J. F. Shultz,[1] F. S. Karn,[2] and R. B. Anderson[3]

ABSTRACT

The Bureau of Mines investigated the hydrogenation of carbon monoxide and carbon dioxide over Raney nickel catalyst and nitrided fused-iron catalyst using both a single-pass and a recycle system. Activation energy over Raney nickel catalyst is 29 to 32 kcal/mole for synthesis from either CO or CO_2. Pressure dependence of the gas conversion is to the 0.3 power for synthesis from CO and to the 0.5 power for synthesis from CO_2.

Nitrided fused-iron catalysts were tested using high recycle rates and $3H_2+1CO$, $2H_2+1CO$, and $1H_2+1CO$ feed gas at 21.4 atmospheres absolute pressure. The relative usage of hydrogen (moles H_2 consumed per moles H_2+CO consumed) was larger than in corresponding single-pass tests, and the relative usage of hydrogen approached the feed gas ratio monotonically as conversion increased. Activation energy was found to be 12 or 13 kcal/mole fresh feed gases of $3H_2+1CO$ or $2H_2+1CO$. For single-pass operation the activation energy under the same conditions was 19 to 21 kcal/mole.

INTRODUCTION

As a part of the Bureau of Mines investigations on conversion of coal to gaseous fuels, the hydrogenation of CO and CO_2 on Raney[4] nickel and the hydrogenation of CO on nitrided iron were studied. Commercial utilization of coal

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[4] Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

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as a source of high-Btu gas was brought closer by the bench-scale demonstrations of a tube-wall reactor coated with a catalyst of Raney nickel (7).[5] Catalyst life was sufficient to reduce catalyst cost to less than 1 cent per 1,000 ft[3] of high-Btu gas when it was made from $3H_2 + 1CO$ at 240° to 300° C and 28 atmospheres. In 1960 (6) this cost was estimated at 4 to 5 cents, using a Raney nickel catalyst adapted to a fluidized process. Likewise bench-scale tests using nitrided iron (5) in the oil circulation process demonstrated the feasibility of using this catalyst to produce relatively high-octane (92.9 rating) gasoline. The nitrided-iron catalyst produced high-octane gasoline containing up to 28 weight percent of alcohols which is equivalent to more than 3 milliliters of tetraethyl lead.

One of the more promising processes for supplementing natural supplies of methane and synthetic gasoline is based on coal gasified with steam to yield a mixture of H_2, CO, and CO_2. These have been the preliminary materials for much research on the product development of high-Btu gas and the reaction mechanism and kinetics in the Fischer-Tropsch reaction (1-2, 5-12, 15). Although the reactions and processes have been developed to a high degree of efficiency, there are no comprehensive data on the process variables. This is largely due to the exothermic nature of the reactions and to the economic necessity of complete gas conversion.

The first purpose of this study is to examine the reaction rates for synthesis of high-Btu gas at a variety of temperatures, pressures, and feed gas compositions, using both single-pass and gas-recycle systems. The second purpose is to examine the kinetics of the Fischer-Tropsch reaction over a nitrided fused-iron catalyst at 21.4 atmospheres pressure and several temperatures, using several feed gas compositions at a series of input rates. For each test the space-time yield (xS) was plotted as a function of reciprocal space velocity (1/S) and the curves were extrapolated to a reciprocal space velocity of zero; that is, to a conversion, x, of zero, where xS = r (r is the differential reaction rate). This rate could be related directly to the mole fraction of H_2 and CO in the feed gas. As an alternative, rates could be determined by graphical differentiation and related to mole fractions of H_2, CO, and water at any conversion. Since the first method gave a limited amount of data and the second method was subject to the inaccuracies of the technique, a recycle system was adopted.

In recycle experiments the differential reaction rate equals xS at any conversion. The fraction of gas converted per pass can be kept so small that gas composition is essentially constant throughout the catalyst bed. Thus, the space-time yield, xS, can be related directly to recycle-gas composition.

EXPERIMENTAL PROCEDURE AND APPARATUS

The apparatus (fig. 1), and procedure are essentially the same as those described previously (3, 17). The reactor was a ½-inch, schedule 80, 347 stainless steel pipe, which had an inside diameter of 1.38 cm by 60 cm, a 30-cm catalyst zone, and a 39-cm preheat zone filled with aluminum wire.

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[5]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

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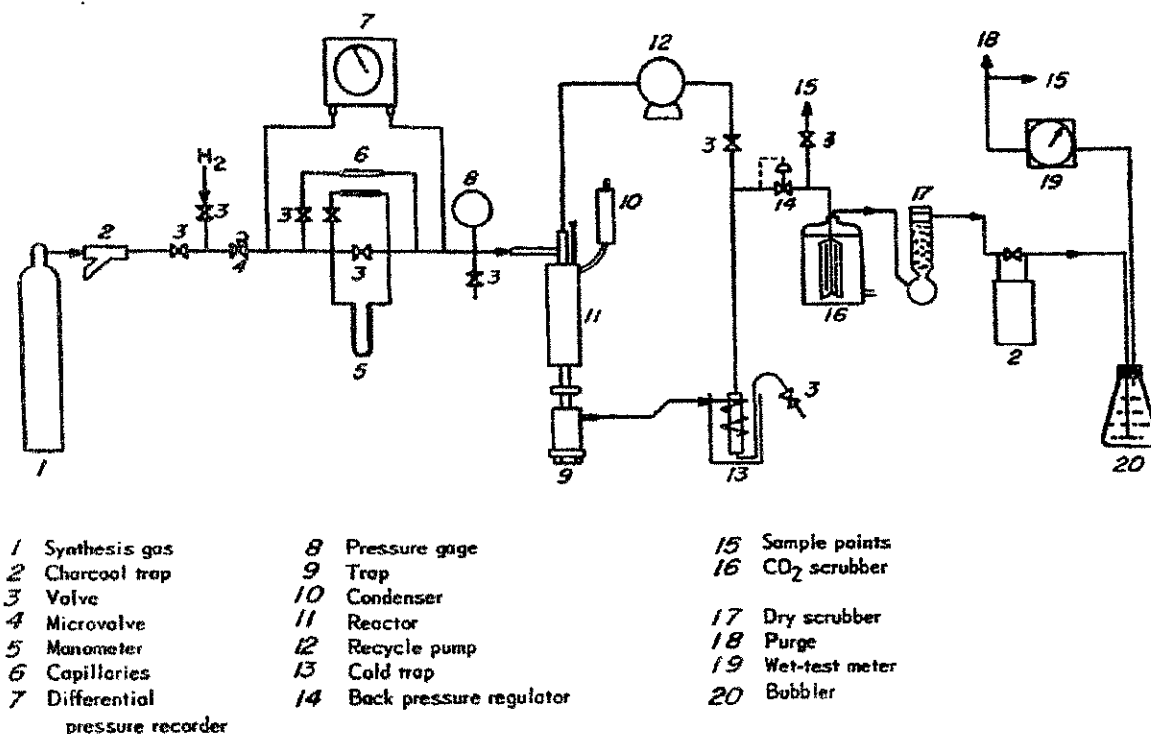|					
1	Synthesis gas	8	Pressure gage	15	Sample points
2	Charcool trap	9	Trap	16	CO$_2$ scrubber
3	Valve	10	Condenser		
4	Microvalve	11	Reactor	17	Dry scrubber
5	Manometer	12	Recycle pump	18	Purge
6	Capillaries	13	Cold trap	19	Wet-test meter
7	Differential pressure recorder	14	Back pressure regulator	20	Bubbler

FIGURE 1. - Flow Diagram of Catalyst-Testing Apparatus.

Temperature was controlled by an electrically heated bath of boiling Dowtherm, surrounding the catalyst and preheater, with a pressure control system. A recycle pump (16) was installed between the cold trap and the top of the reactor. It consisted of a 1/40-hp motor and a rotary pump designed to operate at pressures up to 500 psig. Recycle rates as high as 60 volumes of recycle to 1 volume of fresh feed gas were used. The flow of synthesis gas from premixed cylinders was controlled by a geared needle valve and measured by a calibrated capillary flowmeter. The synthesis gas passed down through the catalyst bed to a room-temperature trap and from there to a 4° C refrigerated trap. The gas was then either recycled or allowed to exit through a back pressure regulator. In the recycle stream the preheater restored the gas to operating temperature before reaching the catalyst. High recycle prevented excessive temperature variations due to heat of reaction. When recycle was not used overheating was minimized by limiting the amount of gas reacted per hour. After exiting through the back pressure regulator, the gas was scrubbed with potassium hydroxide solution (13) to remove carbon dioxide. For the tests on the nickel catalyst the exit gas was sampled by both proportionator and spot sampler, and the surplus gas was measured by a wet-test meter. For the tests on the nitrided catalyst the exit gas was passed through a charcoal trap to remove gaseous hydrocarbons and thence to a proportionator, and the surplus gas was measured on a wet-test meter. Samples of the exit gas were analyzed for carbon dioxide by the Haldane method and by gas chromatography or mass spectrometer for H$_2$, CO, and hydrocarbons.

Since the operational procedure was different for the two catalysts, the testing will be described separately.

Raney Nickel Catalyst

The catalyst was 6 to 8 mesh granules of Raney nickel (58 percent aluminum-42 percent nickel) which was extracted with alkali to remove half of the aluminum as evidenced by hydrogen evolution. The experimental procedure consisted of fixing the composition of the fresh feed gas and the temperature and pressure of the catalyst bed. Then a series of reaction rates and exit gas analyses were obtained by varying the fresh feed gas rate. Fresh feed rate, indicated by the symbol S, is the volume of fresh feed (STP) per volume of catalyst space per hour. The symbol x is the fraction of H_2+CO or H_2+CO_2 reacted; xS is the volume (STP) of H_2+CO or H_2+CO_2 reacted per volume of catalyst space per hour.

Nitrided Fused-Iron Catalyst

The catalyst was 6-to-8 mesh granules of fused-iron ammonia synthesis catalyst D3001. The raw catalyst contained the following: 67.42 weight-percent iron, 0.71 weight-percent SiO_2, 0.65 weight-percent Cr_2O_3, 4.61 weight-percent MgO, and 0.57 weight-percent K_2O, and 26.04 weight-percent oxygen combined with iron. The catalyst was reduced in hydrogen at an hourly space velocity of 2,500 at 450° C for 40 hours and at 500° C for 8 hours in a metal block reactor (14). Nearly complete reduction was achieved.

The reduced catalyst was then nitrided because it had been found (4) that a nitrided-iron catalyst produced lower molecular weight hydrocarbons than the reduced iron catalyst. The nitriding was accomplished by treating the reduced catalyst with ammonia at an hourly space velocity of 1,000 at 350° C for 12 hours. The nitrogen-to-iron ratio was found to be 0.47. Twenty-five cubic centimeters of this catalyst were installed in the reactor at the center of the boiling liquid Dowtherm. Above the catalyst 25 cu cm of aluminum wire pellets were placed to serve as a preheater.

The nitrided catalyst was tested at 21.4 absolute atmospheres pressure using H_2-to-CO feed gas ratios of 1 to 1, 2 to 1, and 3 to 1. Temperatures were held constant at 274° or 284° C and 218° or 228° C. The flow rates were varied to produce the desired CO_2-free contractions. Sufficient time was allowed for the apparatus to attain equilibrium for each condition before samples were taken for analysis. The time required for reaching steady state conditions varied inversely with the space velocity. The recycle pump was operated at approximately constant flow of 450 liters per hour or 18,000 volumes (STP) per volume of catalyst space per hour. The fresh feed gas input was 180 to 2,000 volumes per hour.

0.3

CONVERSION, x

30

SPACE - TIME YIELD, xS

□ x

○ xS

20

.2

.1

0

0

EXIT GAS, mole fraction

1.0

○ H_2

Ô CO

△ CH_4

▽ CO_2

□ H_2O

.8

.6

.4

.2

0

0   2   4   6   8   10   12   14   16   18   20

RECIPROCAL SPACE VELOCITY, hr X 10^3
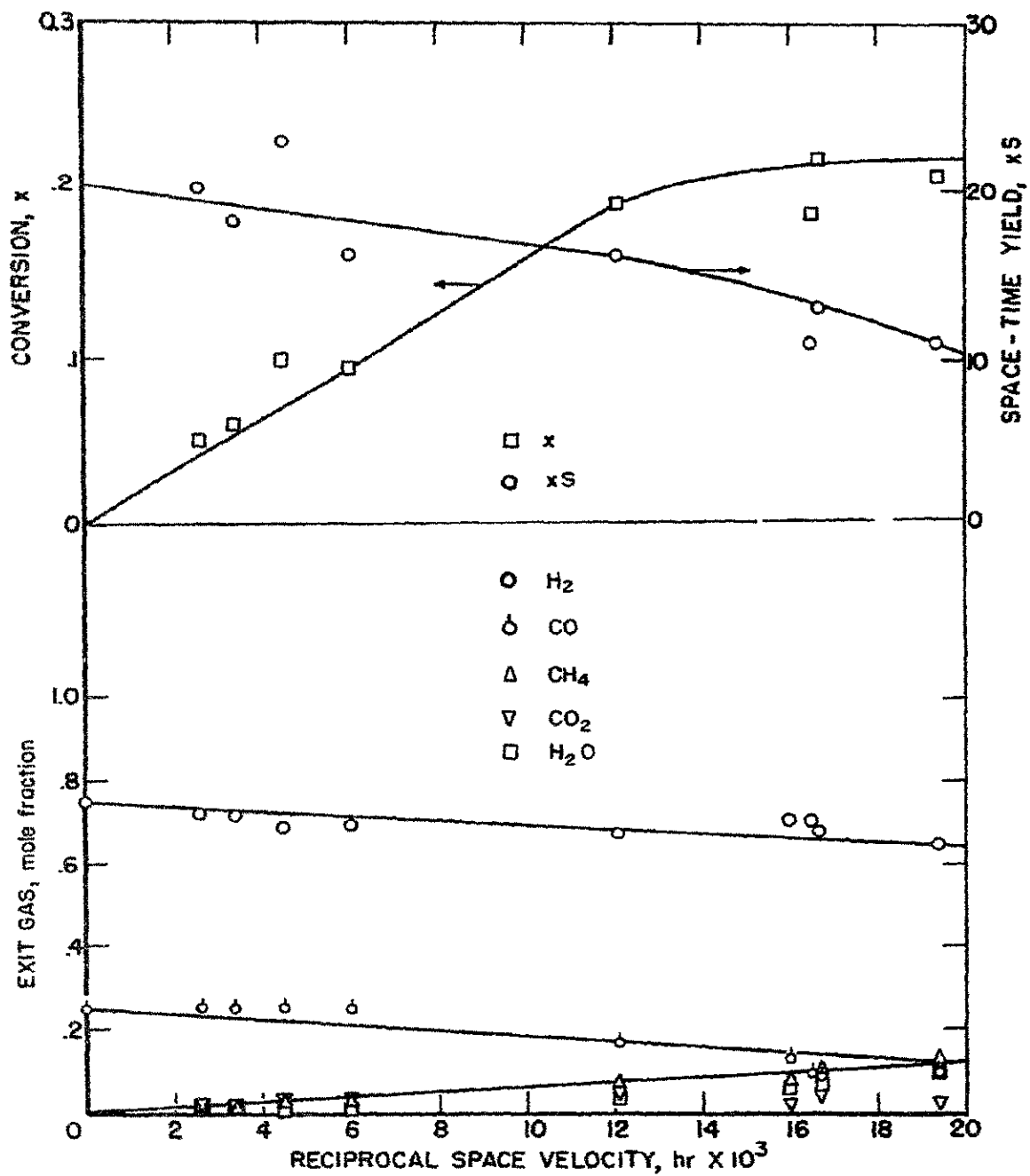
FIGURE 2. - Rate Data for the Reaction $3H_2+1CO \rightarrow CH_4+H_2O$ Over Raney Nickel at 240° C
Single Pass.
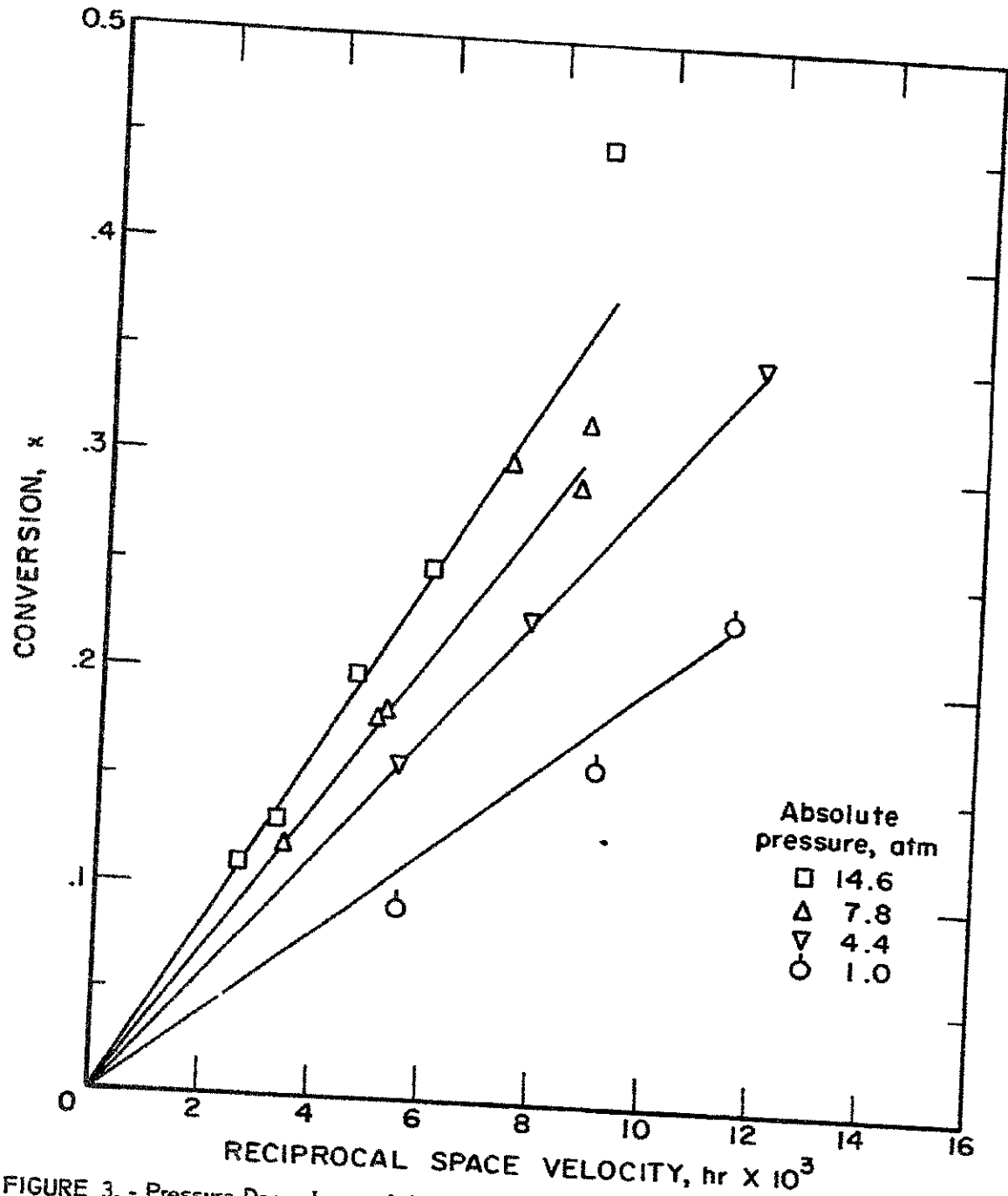
FIGURE 3. - Pressure Dependence of the Reaction $3H_2 + 1CO \rightarrow CH_4 + H_2O$ Over Raney Nickel at 282° C Single Pass.

RESULTS AND DISCUSSION

Hydrogenation of CO Over Raney Nickel Catalyst

Single Pass

The rate of a reaction may be expressed in terms of $H_2 + CO$ and $H_2 + CO_2$ consumed. Thus for single-pass experiments the data have been plotted in figure 2 as the fraction of feed gas consumed, x, as a function of reciprocal space velocity or time. To determine the pressure dependence of the reaction of hydrogen with carbon monoxide, the conversion is plotted as a function of reciprocal space velocity at several pressures in figure 3. The rate or conversion, xS, is plotted against the absolute pressure for conversions of 10, 20, and 40 percent in figure 4. Deviation from linearity occurs above 40-percent conversion. This is due to the heat of reaction being inadequately removed.

$\triangle$ 10 pct conversion
$\square$ 20 pct conversion
$\bigcirc$ 40 pct conversion
Rate $= k P^{0.29}$
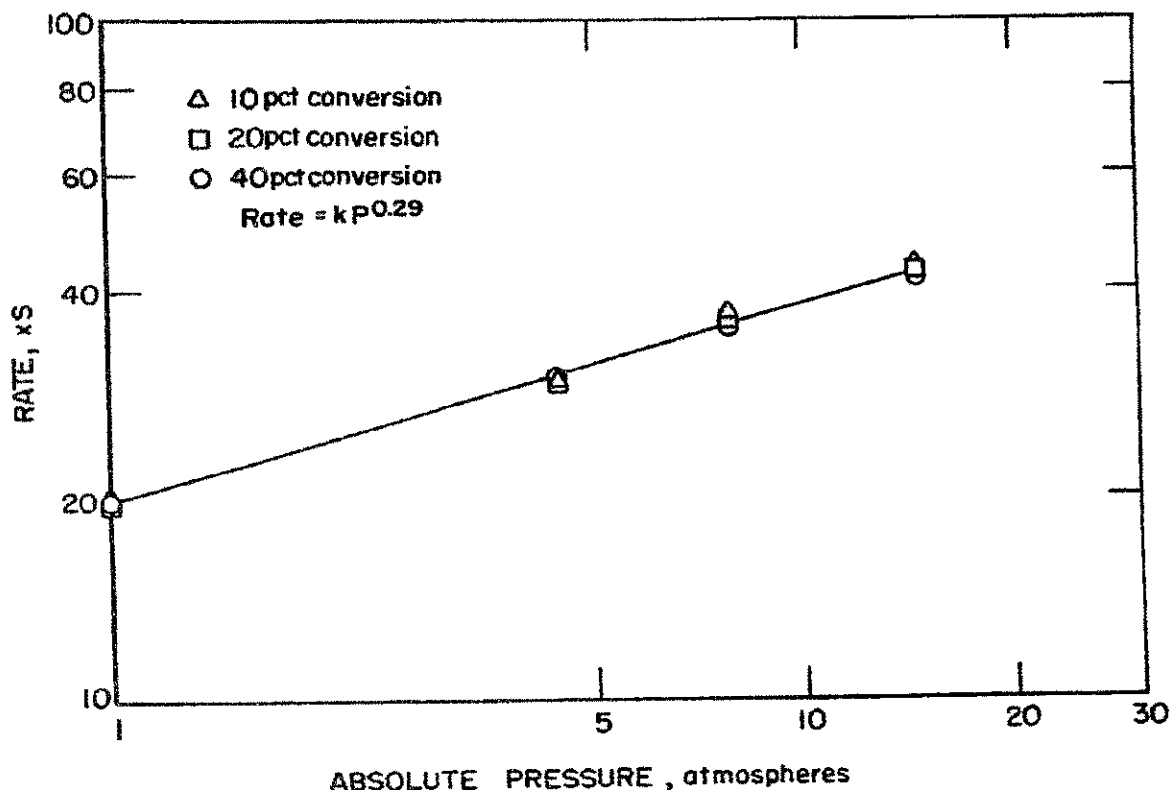
RATE, xS

ABSOLUTE PRESSURE, atmospheres

FIGURE 4. - Pressure Dependence of the Reaction $3H_2 + 1CO \rightarrow CH_4 + H_2O$ Over Raney Nickel at 282° C Single Pass.
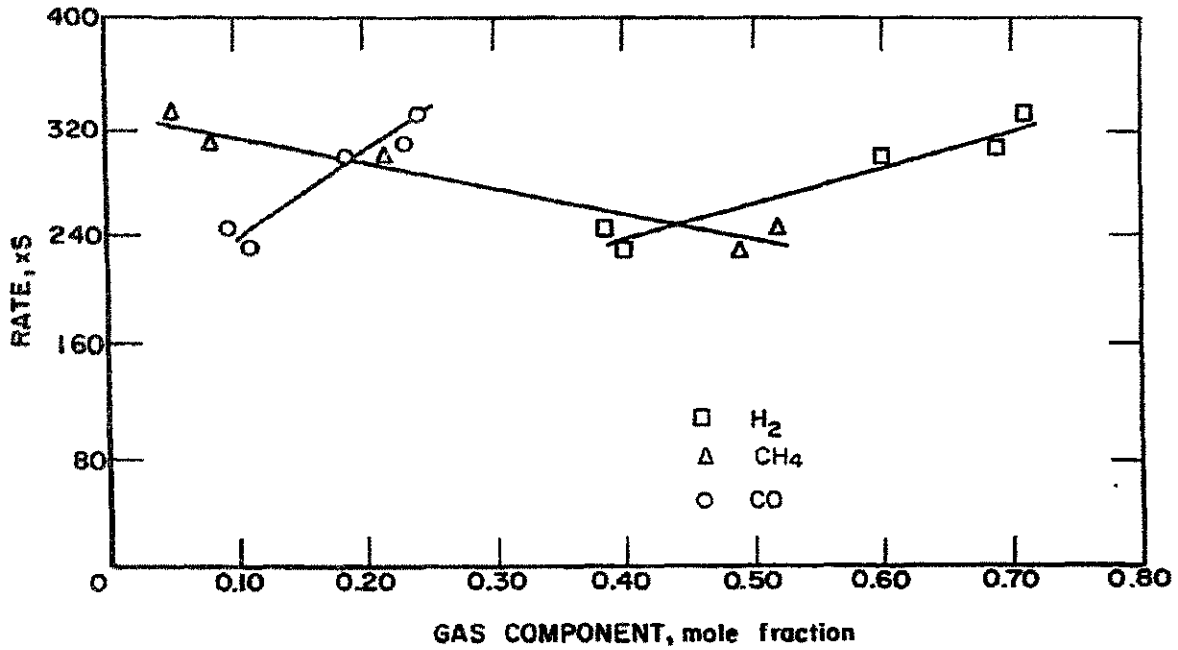
8

FIGURE 5. - Kinetic Data for Methanation of $3H_2+1CO$ on Raney Nickel at 292° C With Recycle.
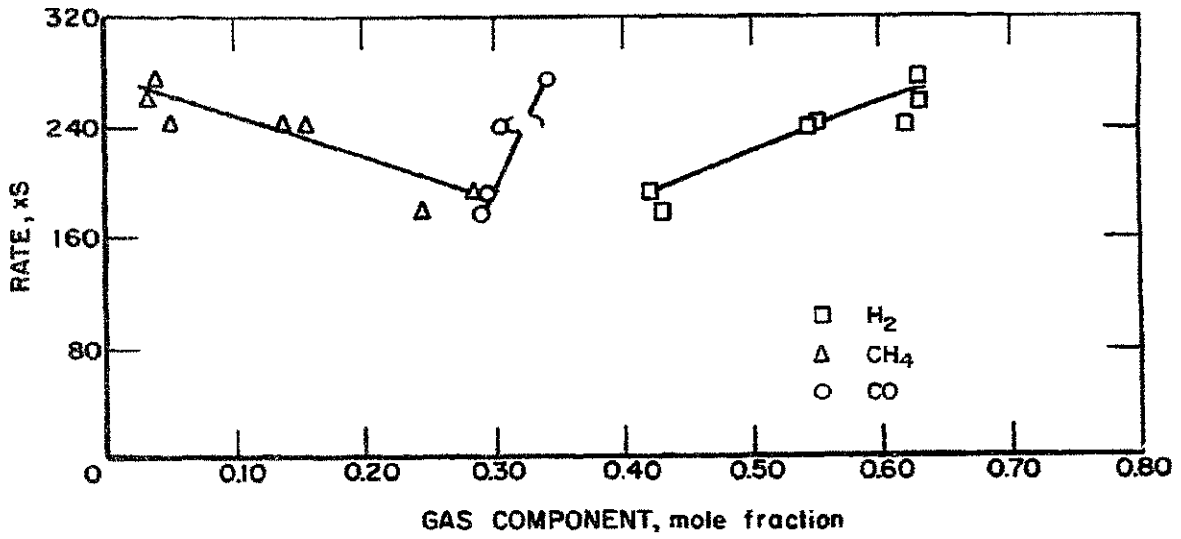

FIGURE 6. - Kinetic Data for Methanation of $2H_2+1CO$ on Raney Nickel at 292° C With Recycle.

Recycle

For recycle experiments the gas conversion per pass wa; 1 percent or less so it was assumed that a constant gas composition persisted throughout the catalyst bed. This procedure approaches differential reactor conditions where rate can be calculated directly as xS (the volume of gas consumed per volume of catalyst space per hour). The composition of recycle gas depends only on fresh feed rate, temperature, and system pressure as long as the catalyst activity remains constant. Rate and gas composition can be plotted as functions of time, or as presented in figures 5 and 6, rate can be plotted directly as a function of each gas component.

The influence of temperature on rate was measured at 261° to 281° C. Rate, xS, was determined at three temperatures using a constant gas composition and plotted according to the Arrhenius equation $\log xS = E/RT$ in figure 7.
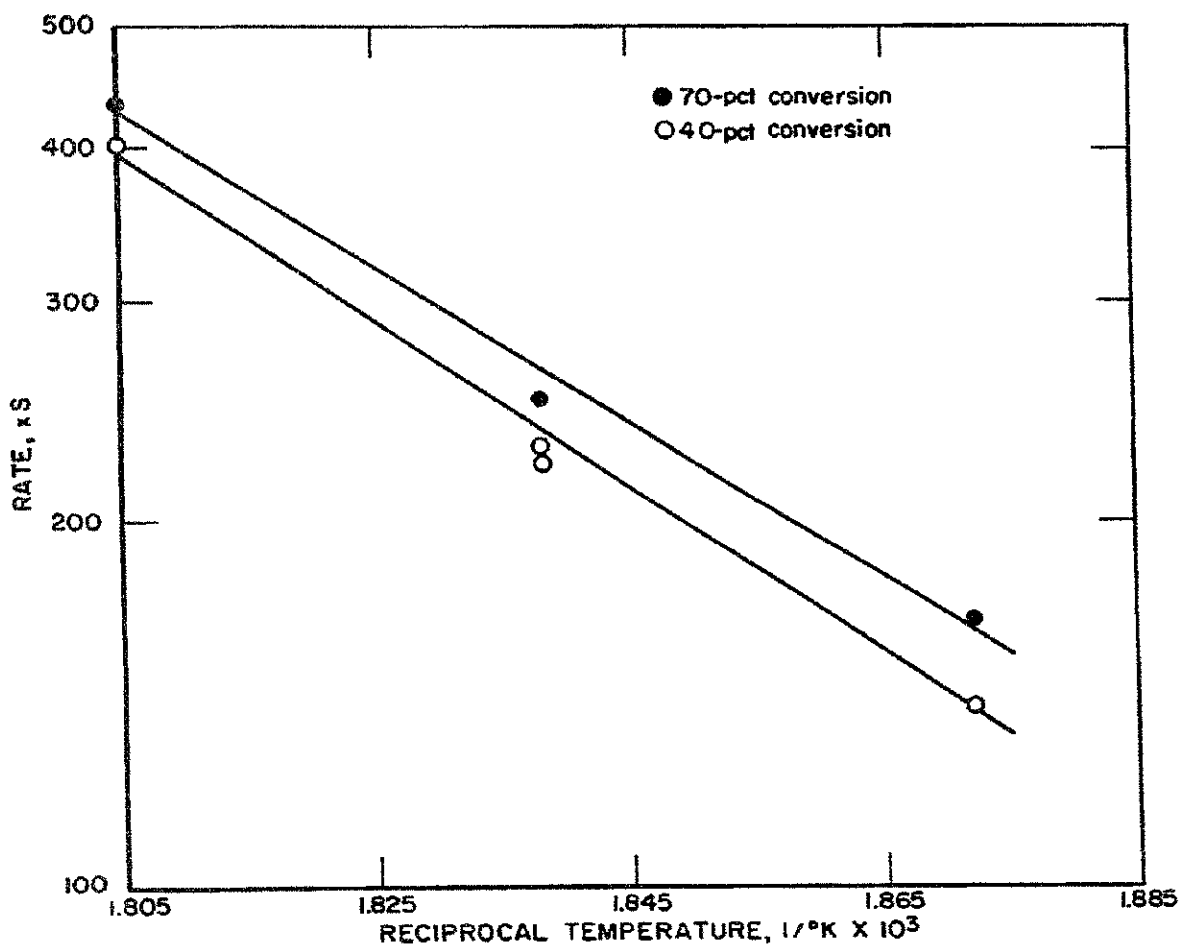

FIGURE 7. - Arrhenius Plot of $3H_2+1CO$ Feed Gas With Recycle.

Pressure dependence was measured for $3H_2+1CO$ fresh feed gas at absolute pressures between 1.0 and 21.4 atmospheres with the fresh feed flow adjusted to give a constant composition of composite gas at 292° C in figure 8.

Hydrogenation of CO_2 Over Raney Nickel Catalyst

The hydrogenation of CO_2 proceeds readily on Raney nickel catalyst, and long life (1 year) with little change in activity was obtained. Hydrogenation of CO_2 is less exothermic, and the tendency to form elemental carbon or carbonyls is decreased. Single-pass studies were made on this system. However, interpretations remain relatively simple because the stoichiometry does not change. About 1 percent CO was found in the exit gas at all conversions, and at least 90 percent of the hydrocarbon product was methane. Figure 9 presents typical data for the reaction $4H_2+1CO_2 \rightarrow CH_4+2H_2O$. The reaction closely followed the stoichiometry of this equation for all conditions of the investigation. The temperature was 230° C, the pressure was 21.4 atmospheres, and the input gas rate ranged from 100 to 700 hourly space velocity. The fraction of
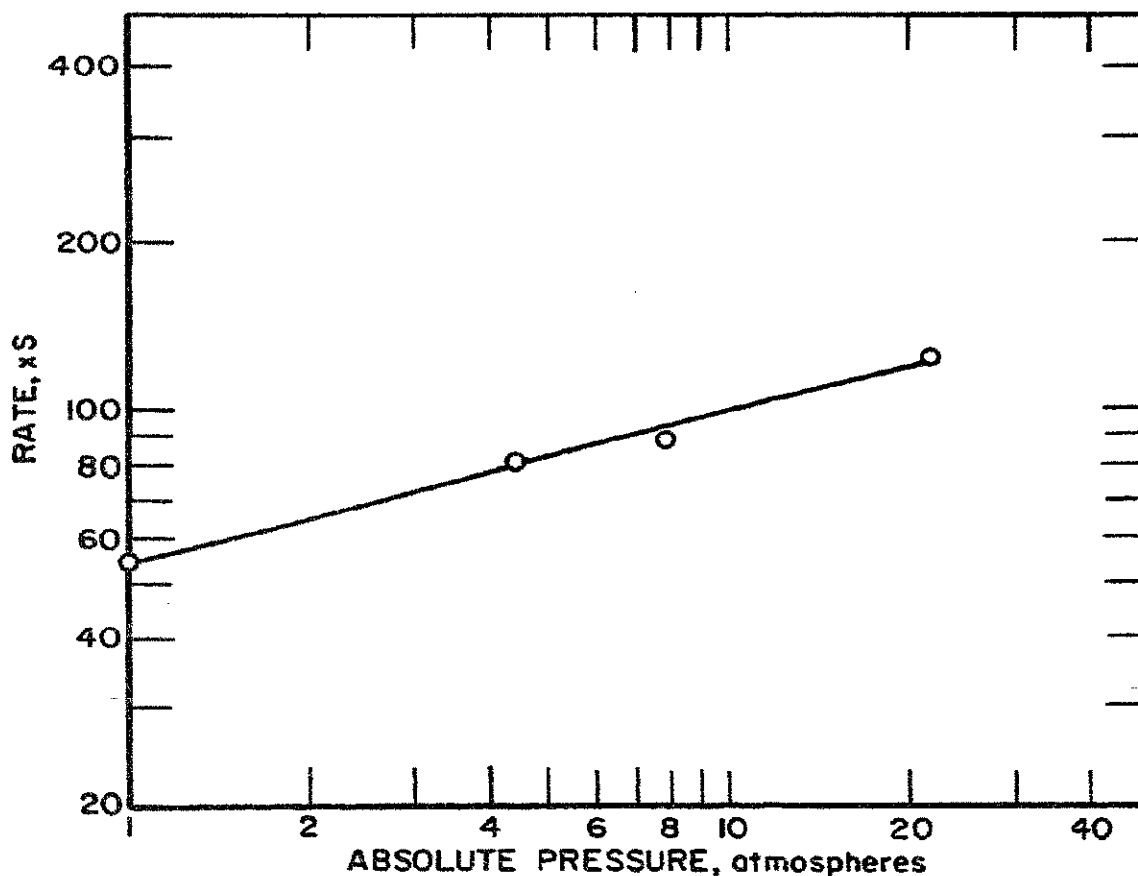

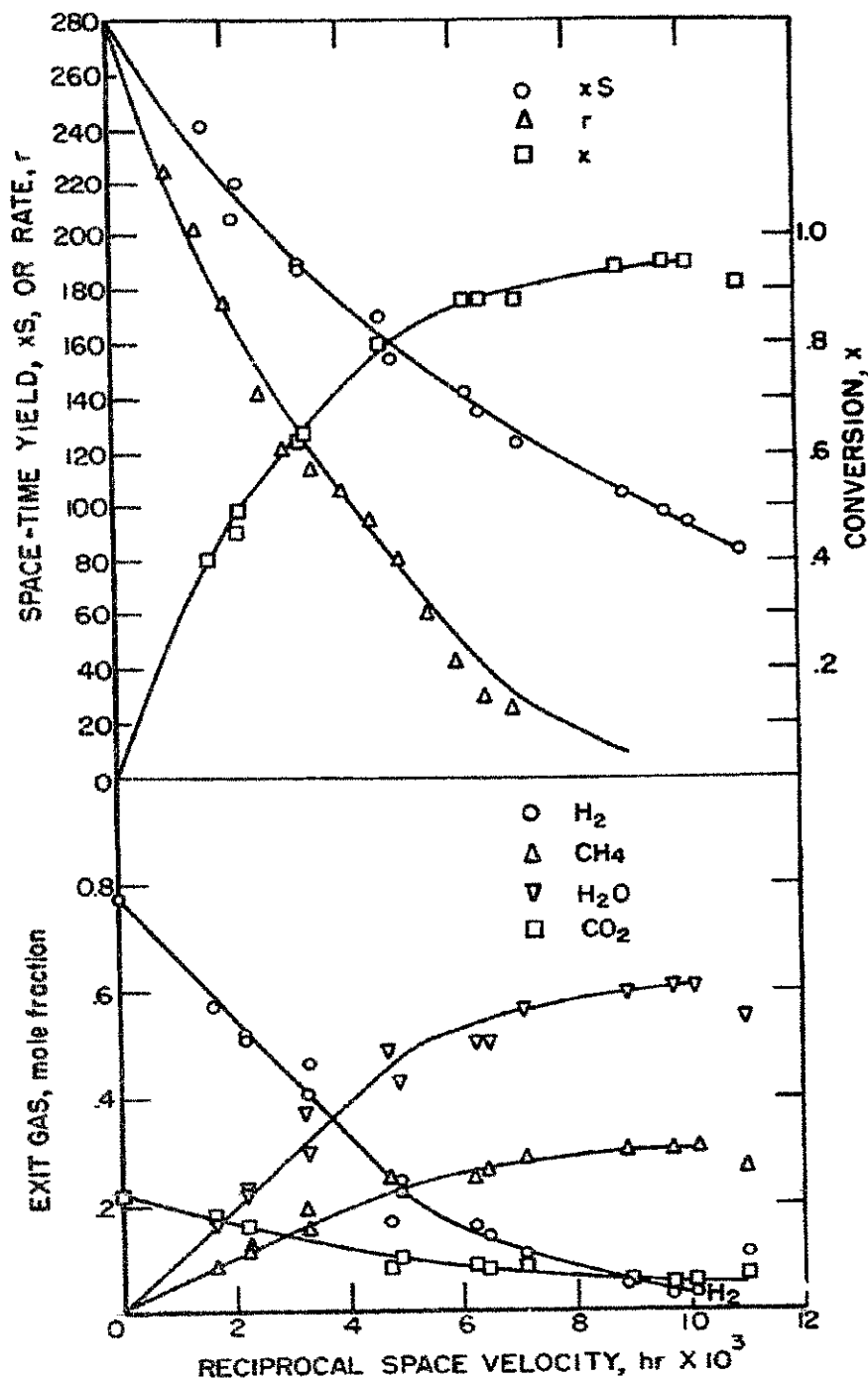FIGURE 8. - Pressure Dependence of Methanation Using $3H_2+1CO$ Gas With Recycle.

gas converted, differential reaction rate, space-time yield, and exit gas mole fractions are all shown as functions of reciprocal space velocity. Rate determined by a graphical method is shown as a solid line (curve r, fig. 9), and rate determined by numerical differentiation (17) is shown by triangular points ($\triangle$). Gas data, with the exception of water which was calculated, were obtained from spot samples using gas chromatography.

Temperature-dependence data are presented in figure 10. Rate was expressed as the space velocity of feed gas required to produce a given conversion at a given temperature. Two sets of data were obtained using catalysts of different activities. These sets of data gave activation energies of 30 and 32 kcal at several conversions.

Pressure-dependence data are summarized

Upper graph

SPACE-TIME YIELD, xS, OR RATE, r

CONVERSION, x

Legend:
- O xS
- $\triangle$ r
- $\square$ x

Lower graph

EXIT GAS, mole fraction

Legend:
- O H_2
- $\triangle$ CH_4
- $\triangledown$ H_2O
- $\square$ CO_2

RECIPROCAL SPACE VELOCITY, hr X 10^3

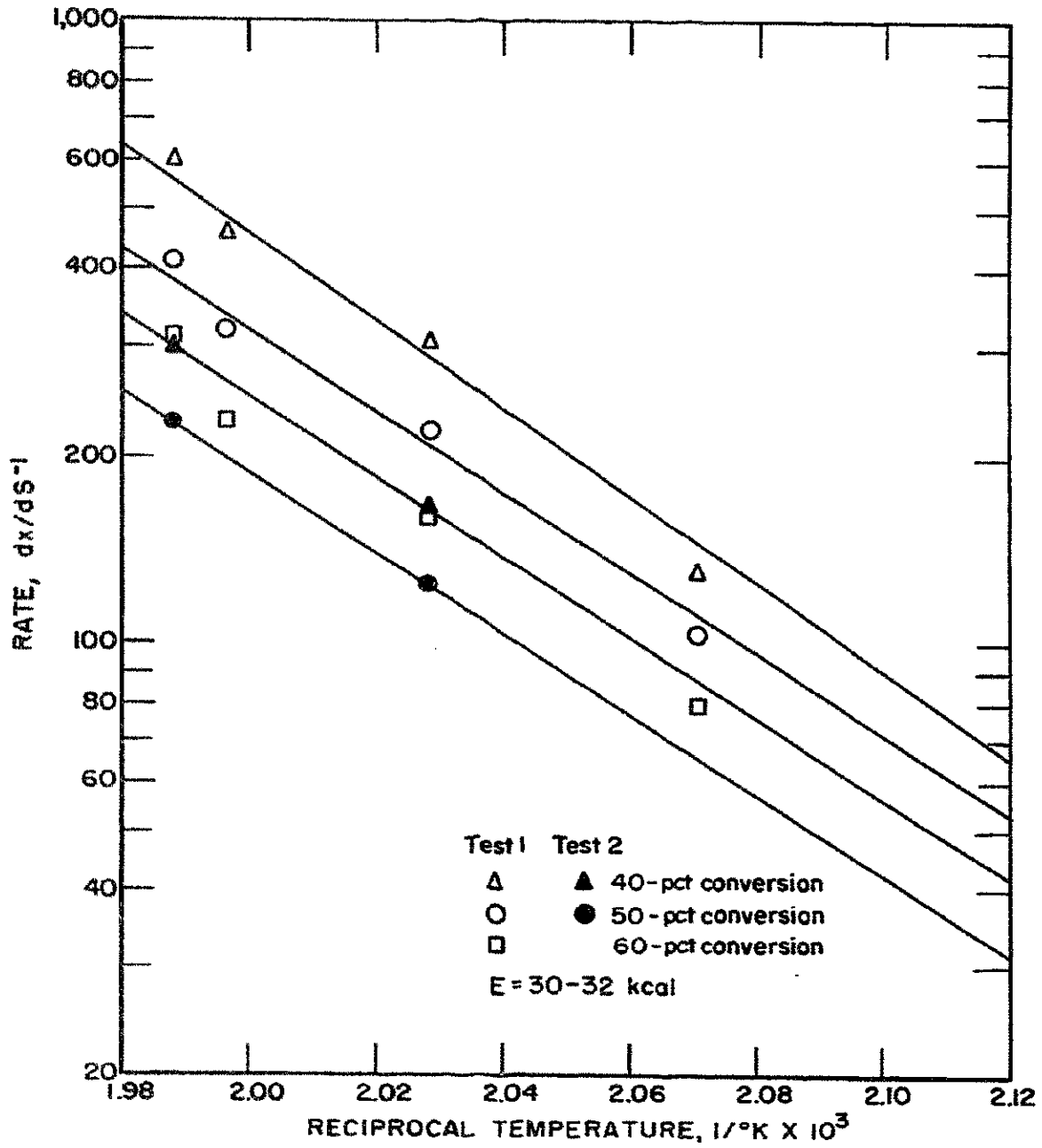FIGURE 9. - Rate Data for the Reaction $4H_2 + 1CO \rightarrow CH_4 + 2H_2O$ Over Raney Nickel at 230° C.

FIGURE 10. - Activation Energy for $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ Over Raney Nickel Catalyst.

in figure 11. A series of pressures were established at constant temperature, and the gas input rate was varied at each pressure. Rates were compared at constant conversions. They varied as the half power of the pressure, although there is a small decrease in this exponent at high conversions.

Hydrogenation of CO Over Nitrided Fused-Iron Catalyst

Two nitrided fused-iron catalysts were studied at a series of temperatures and hourly space velocities at high recycle rates. Test Z372 was run for 172 days at either 274° or 284° C. X-ray analysis of the catalyst showed Fe_3O_4 and Hägg Fe_2C, although it had started as ς-Fe_2N. Test Z388 was run for 31 days at 218° or 228° C. The X-ray analysis showed ς-carbonitride and Fe_3O_4.

Figures 12 and 13 show the percentage of gas reacted, x, volume of gas converted per hour, xS, and recycle gas composition--all as a function of reciprocal space velocity of fresh feed gas. The relative usage of hydrogen, moles of H_2 consumed per mole of H_2+CO consumed, is shown as a function of conversion and feed gas ratio in figure 14. Constants obtained for the rate constant a of the rate equation

$$r = a\ p_{H_2}^{0.6} p_{co}^{0.4}$$

are shown in table 1 and figure 15.
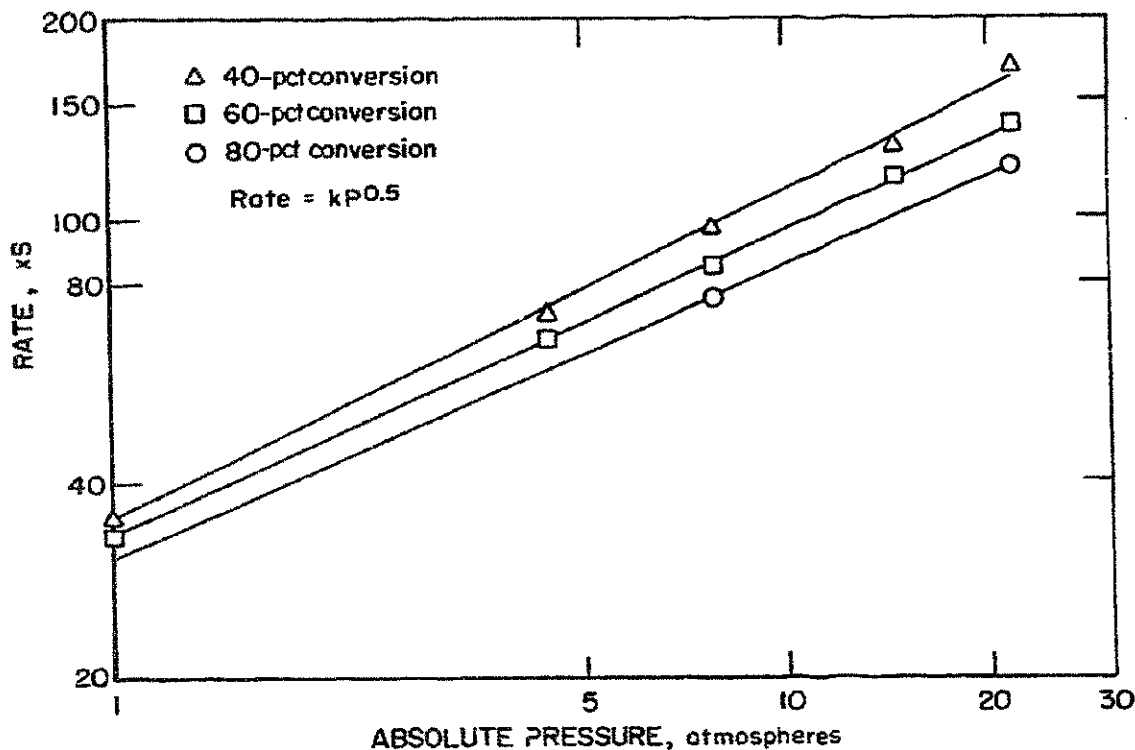
FIGURE 11. - Pressure Dependence of the Hydrogenation of CO_2.

14

FIGURE 13. - Recycle Data for $2H_2 + 1CO$ Feed Gas at 284° C, Nitrided Catalyst.
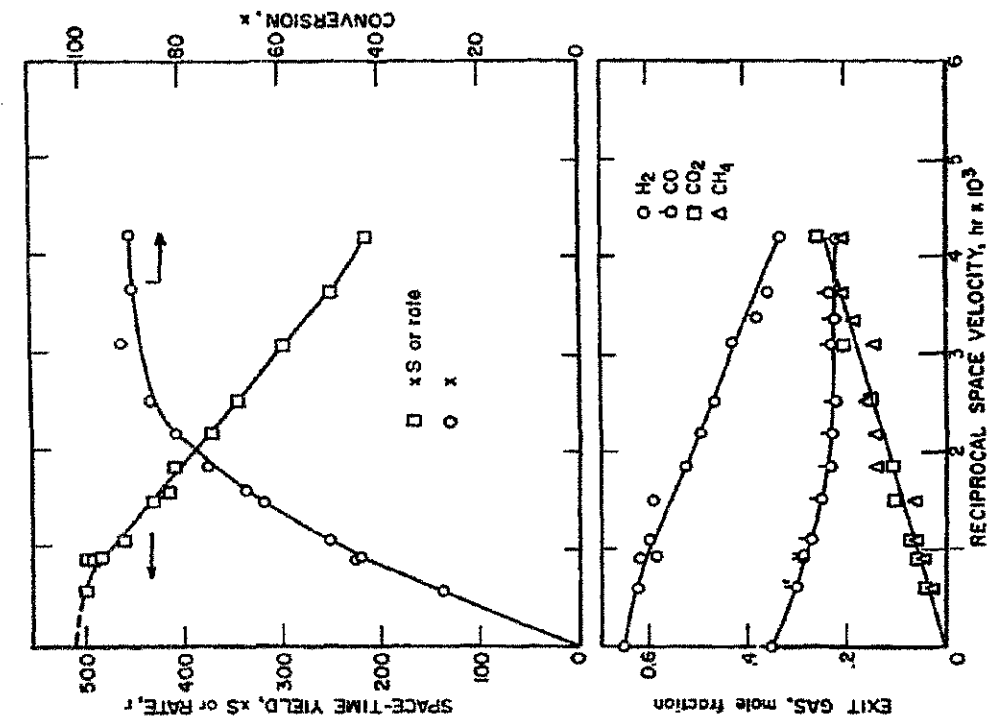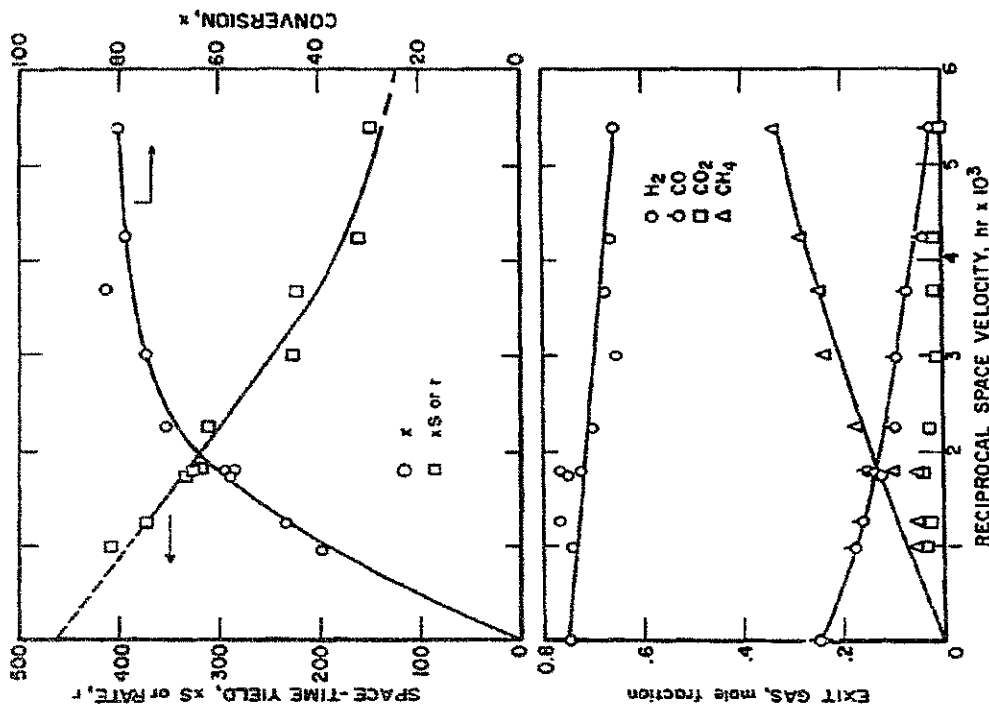

FIGURE 12. - Recycle Data for $3H_2 + 1CO$ Feed Gas at 284° C, Nitrided Catalyst.
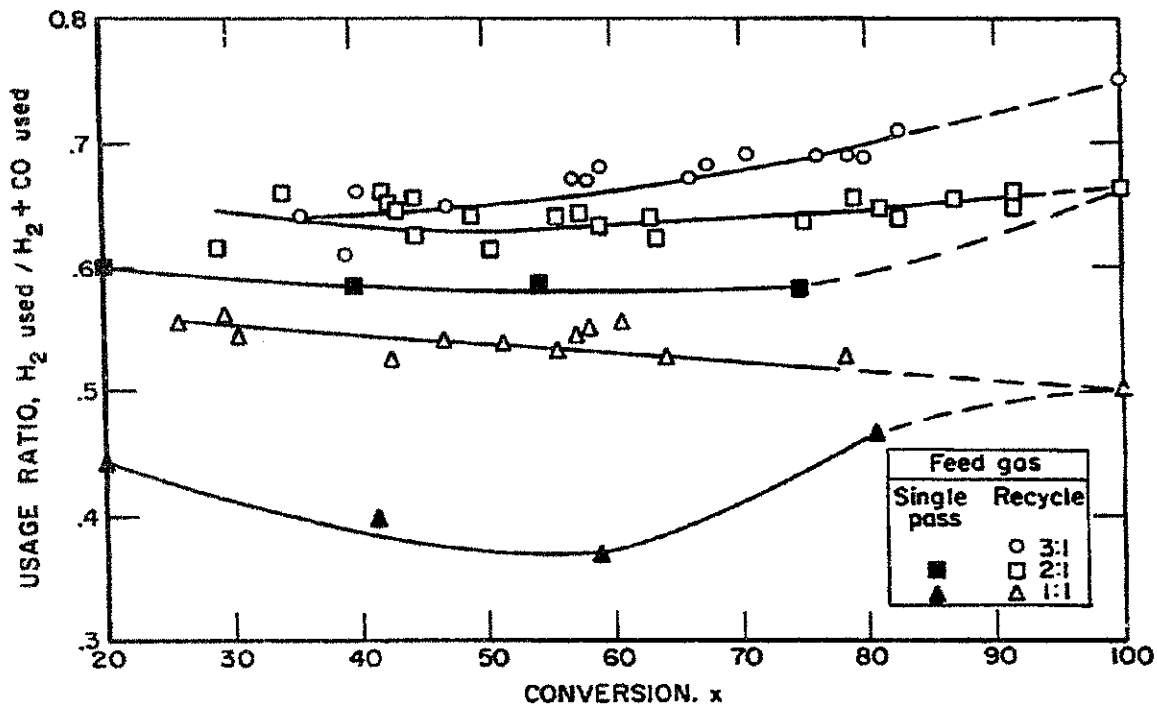
FIGURE 14. - Relative Usage of Hydrogen as a Function of Conversion for a Nitrided-Iron
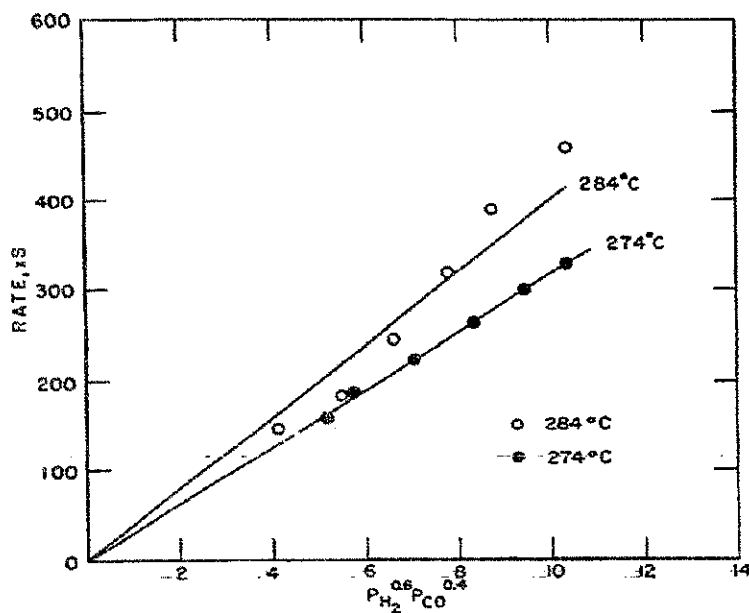Catalyst With Recycle and Single Pass (ref. 1).

FIGURE 15. - Rate Equation $r = a$
$P_{H_2}^{0.6} P_{CO}^{0.4}$ Us-
ing $3H_2 + 1CO$ Fresh-
Feed Gas.

TABLE 1. - <u>Values of constant of rate equation</u>[1]

Test	t., ° C	Values of a		
		$3H_2+1CO$	$2H_2+1CO$	$1H_2+1CO$
Z372.........	284	42	42	-
Z372.........	274	32	37	-
Z388.........	228	-	-	42
Z388.........	218	-	-	24

[1]From equation $r = xS = a \, p_{H_2}^{0.6} p_{CO}^{0.4}$. Units of constant
a are volumes (STP) of H_2+CO consumed per volume of
catalyst X atmosphere X hour.

Hydrogenation of CO or CO_2 Over Raney Nickel Catalyst

amination of the upper portion of figure 2 shows that the slope of the
.on curve x at several values of 1/S plus corresponding exit gas analy-
rate data in terms of gas composition. This shows that the relation-
..p between x and 1/S is linear over a wide range of flows. Thus rate is not
greatly influenced by flow, conversion, or gas composition. Nevertheless, an
attempt was made to base a rate equation on total system pressure and on par-
tial pressures of H_2 and CH_4. Figure 16 is a log-log plot of these data sub-
stituted in the equation

$$r = k \, p_{CH_4}^{0.29} p_{H_2}^{n} / p_{CH_4}^{n}.$$

The curve is linear and thus could be expressed as

$$r = k \, p_{H_2}^{0.29}.$$

The slope of the curve in figure 4 shows that the rate of reaction using
$3H_2+1CO$ is proportional to the 0.29 power of the pressure at pressures up to
at least 14.6 atmospheres and conversions of 40 percent.

For the recycle system the activation energies for 70- and 40-percent
conversions can be obtained by an Arrhenius plot of rate (xS) versus recipro-
cal of temperature (1/K°)(fig.7). The slopes of these curves give a value of
29 kcal/mole for 70-percent conversion and 31 kcal/mole for 40-percent
conversion.

A log-log plot of the rate (xS) as a function of the pressure showed a
linear curve in figure 8. The slope of this line gave a rate proportional to
the 0.27 power of the absolute pressure. This is a confirmation of the single-
pass observation. Since nickel is not a good water-gas shift catalyst
($H_2O+CO \rightarrow H_2+CO_2$) and because the water concentration was kept low by cooling
the recycle stream, the composite gas was simplified to H_2, CO, and CH_4. An
attempt was made to evaluate rate in terms of total pressure and partial

pressures. Figure 17 is an evaluation of the equation

$$r = k \ p_{H_2}{}^{n} p_{CH_4}{}^{0.27-n}.$$

The data were taken from three separate runs.

Although there are differences in catalytic activities between the runs, the activities within each run have the same dependence on gas composition and fit the equation

$$r = k \ p_{H_2}{}^{0.34} p_{CH_4}{}^{-0.07}.$$
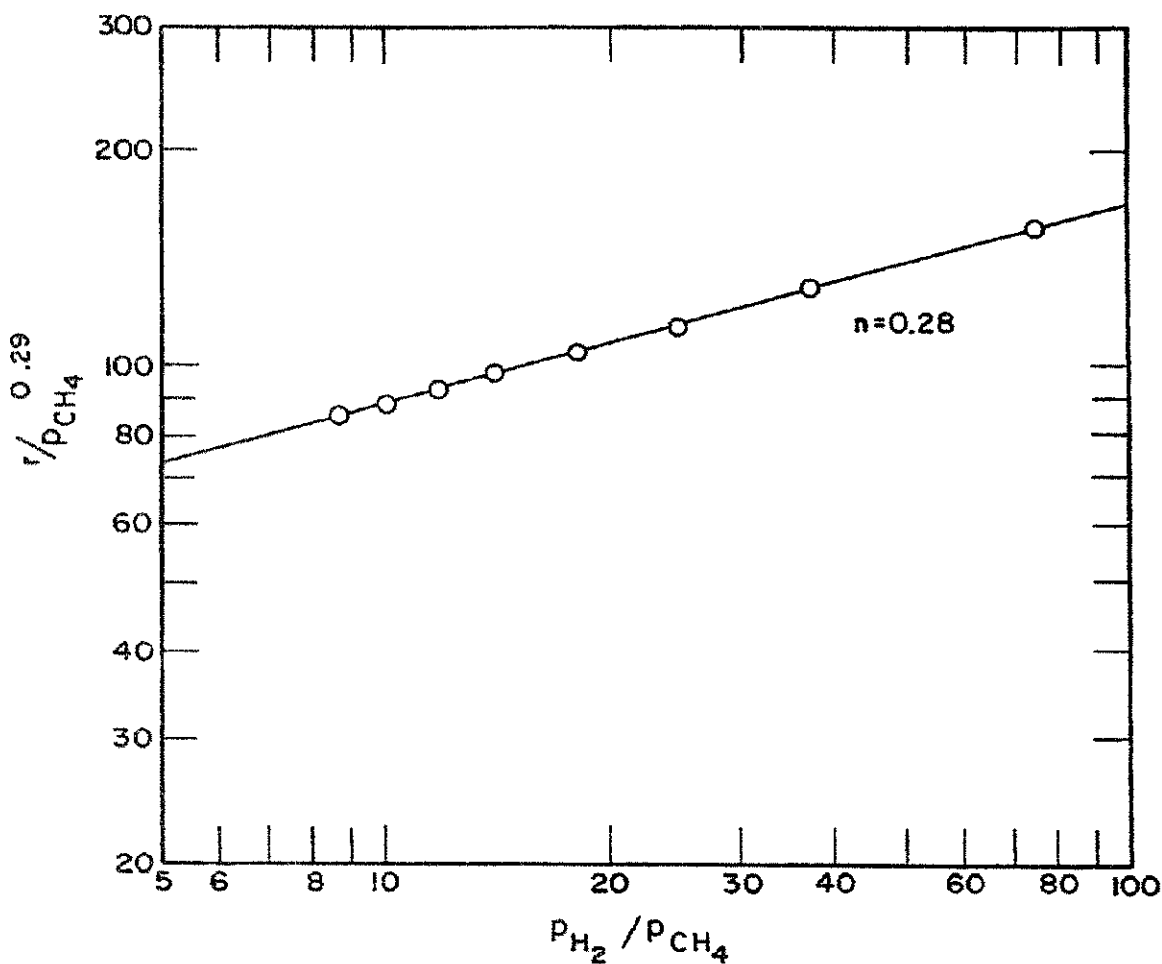

FIGURE 16. - Test of Equation $r = k \ p_{CO}{}^{0.29} p_{H_2}{}^{n}/p_{CH_4}{}^{n}$ for the Reaction $3H_2+CO \rightarrow CH_4+H_2O$ Over Raney Nickel at 240° C.
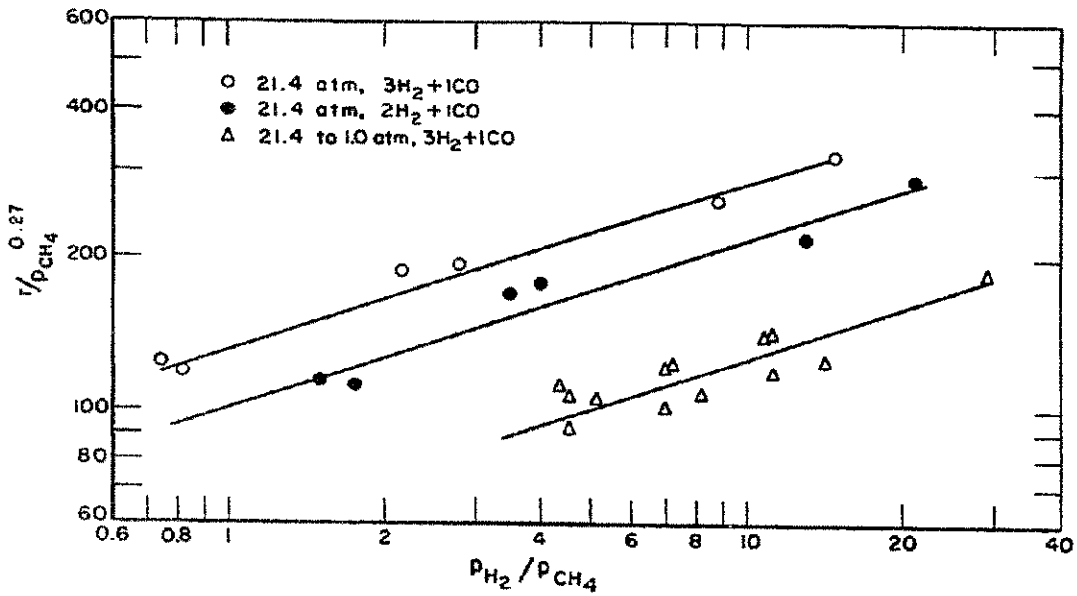
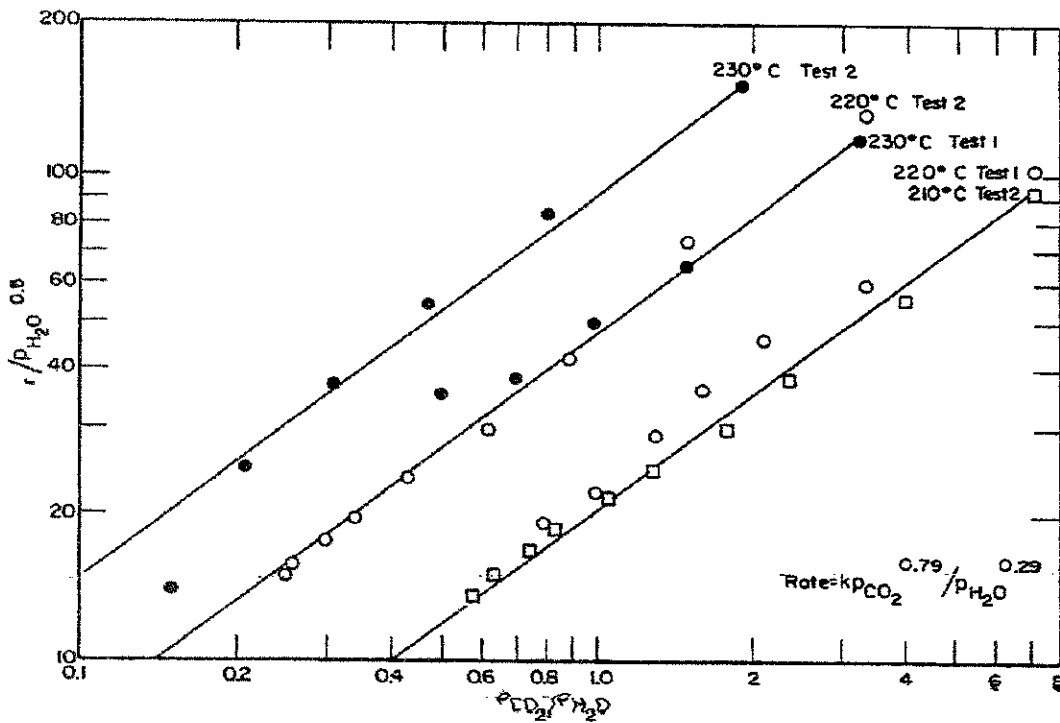FIGURE 17. - Logarithmic Plot of Kinetic Data for Methanation With Recycle at 292° C.

FIGURE 18. - Rate as a Function of CO_2 and H_2O Concentrations for the Reaction $4H_2+CO_2 \rightarrow CH_4+2H_2O$ Over Raney Nickel.

In the hydrogenation of carbon dioxide the stoichiometry of the process is constant. Thus several acceptable equations can be used to relate rates and gas components. Figure 18 shows that rate is proportional to the CO_2 concentration and inversely proportional to the water concentration. Five separate sets of data were represented by

$$r = k \ P_{CO_2}{}^{0.79} P_{H_2O}{}^{-0.29}.$$

Another equation was based on the following reaction mechanism:

1. The water-gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) is fast and maintains a concentration of CO dependent on $P_{CO} = P_{H_2}P_{CO}/k_w P_{H_2O}$, where k_w is the equilibrium of the water-gas shift reaction.

2. The rate-determining step is dependent on both the hydrogen and carbon monoxide concentrations.

3. The overall rate of methane synthesis increased with total pressure to the half power.

These assumptions, incorporated in a rate equation, give

$$r = k \ P_{H_2}{}^{0.5} P_{CO_2}{}^{n} P_{H_2O}{}^{-n}.$$

Figure 19 is a test of these postulates and an evaluation of n. Several sets of data fall on parallel lines with a slope of 1/4, and the equation becomes

$$r = k \ P_{H_2}{}^{0.5} P_{CO_2}{}^{0.25} P_{H_2O}{}^{-0.25}.$$

The study of the kinetics of the Fischer-Tropsch synthesis on a nitrided fused-iron catalyst under recycle conditions was carried out over several months. The first catalyst (test Z372) was operated for nearly 6 months, during which time modifications had t~ be made in the apparatus to permit operations without recycle pump failure. The catalyst activity had decreased considerably by the time valid experiments were obtained, and operation at our standard conditions required 274° C compared with 240° C for a fresh nitrided catalyst. At the end of this test the catalyst was a mixture of Fe_3O_4 and Hägg carbide, the only case where a nitrided catalyst had been converted to Hägg carbide during nonpoisoning synthesis. Low catalyst activity and loss of the nitrogen may be due to the use of $2H_2 + 1CO$ synthesis gas without recycle and to the prolonged period of operation.

In the second test, Z388, the first inlet gas was $2H_2 + 1CO$ and recycle was started almost immediately. Satisfactory conversions were obtained at 218° to 228° C, and epsilon iron carbonitride was found in the used catalyst. Rate data for the two tests were similar, despite the differences in activity. The rate, xS, decreased rapidly as space velocity was decreased; that is, as the partial pressures of H_2 and CO were decreased. The rate data were expressed very well by the rate equation presented previously; that is,
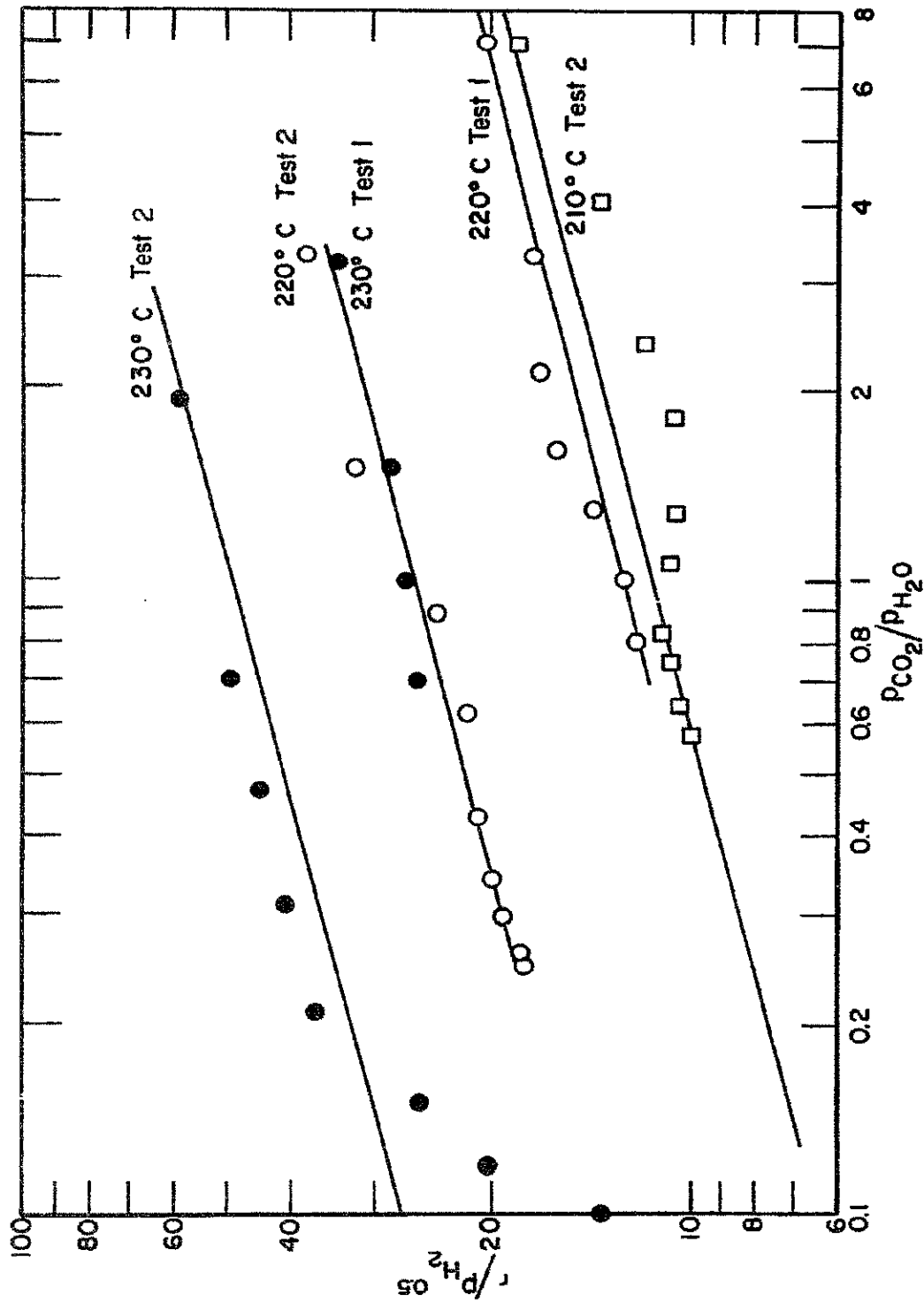
FIGURE 19. - Test of the Equation $r = k_2 p_{H_2}^{0.5} p_{CO_2}^{n} p_{H_2O}^{-n}$ for the Reaction $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$ Over Raney Nickel.

$$r = a\, p_{H_2}^{0.6} p_{CO} - f\, r^{0.5} p_{H_2O}^{0.5},$$

where r is the differential reaction rate; p_{H_2}, p_{CO}, and p_{H_2O} are the partial pressures of H_2, CO, and H_2O, and a and f are rate constants. Here it was assumed that hydrocarbon synthesis is the result of competition with the water-gas shift reaction. Rates are proportional to concentrations of H_2, CO, and H_2O on the surface and these are proportional to their concentrations in the gas stream. Since the concentration of water vapor is low in the recycle system, the rate equation can be simplified to

$$r = xS = a\, p_{H_2}^{0.6} p_{CO}^{0.4}.$$

Values of the rate constant are between 24 and 42 (table 1), increasing with temperature. The activation energy, calculated according to the Arrhenius equation, is 12 or 13 kcal for fresh feed gases of $3H_2+1CO$ or $2H_2+1CO$. Using the same type of catalyst in a single-pass system, activation energies of 19 to 21 kcal were obtained.

The relative usage of hydrogen in recycle operations as a function of conversion is shown in figure 14. Data are available only for conversions greater than 20 percent. Relative usages of hydrogen are larger in recycle than in single-pass operations, as might be expected from the lower concentration of water vapor in the recycle tests. The relative usage of hydrogen appears to change monotonically toward the feed ratio as the conversion is increased.

CONCLUSIONS

This study of gas synthesis kinetics using a gas recycle system has generally verified the studies made with a single-pass system. Using a Raney nickel catalyst and a synthesis gas of either H_2+CO or H_2+CO_2 the activation energy was between 29 and 32 kcal/mole. Methane synthesis from H_2+CO gas varied as the 0.3 power of the absolute pressure, and methane synthesis from H_2+CO_2 gas varied as the 0.5 power. The fundamental equation for the hydrogenation of CO may be written

$$r = k\, p_{H_2}^{0.29},$$

and the fundamental equation for the hydrogenation of CO_2 may be written

$$r = k\, p_{CO_2}^{0.79} p_{H_2}^{-0.29}.$$

Using a nitrided fused-iron catalyst in a recycle system the H_2 to CO usage was higher than in corresponding single-pass tests and it approached the feed gas ratio as conversion increased. Rate in terms of total H_2+CO reacted was proportional to

$$p_{H_2}^{0.6} p_{CO}^{0.4}$$

which is consistent with the rate equation developed previously for single-pass operation. Activation energy was 12 to 13 kcal/mole for single-pass operation.

REFERENCES

1. Anderson, R. B., and F. S. Karn. A Rate Equation for the Fischer-Tropsch Synthesis on Iron Catalysts. J. Phys. Chem., v. 64, June 1960, pp. 805-808.

2. Anderson, R. B., F. S. Karn, and J. F. Shultz. Kinetics of the Fischer-Tropsch Synthesis on Iron Catalysts. BuMines Bull. 614, 1964, 45 pp.

3. Anderson, R. B., A. Krieg, B. Seligman, and W. E. O'Neill. Fischer-Tropsch Synthesis. I. Test of Cobalt Catalysts at Atmospheric Pressure. Ind. and Eng. Chem., v. 39, December 1947, pp. 1548-1554.

4. Anderson, R. B., J. F. Shultz, B. Seligman, W. K. Hall, and H. H. Storch. Studies of the Fischer-Tropsch Synthesis. VII. Nitrides of Iron as Catalysts. J. Am. Chem. Soc., v. 72, August 1950, pp. 3502-3508.

5. Bienstock, D., J. H. Field, A. J. Forney, J. G. Myers, and H. E. Benson. The Fischer-Tropsch Synthesis in the Oil-Circulation Process: Experiments With a Nitrided Fused-Iron Catalyst. BuMines Rept. of Inv. 5603, 1960, 32 pp.

6. Dirksen, H. A., and H. R. Linden. Pipeline Gas by Methanation of Synthesis Gas Over Raney Nickel Catalyst. Ind. and Eng. Chem., v. 52, July 1960, pp. 584-589.

7. Field, J. H., J. J. Demeter, A. J. Forney, and D. Bienstock. Development of Catalyst and Reactor Systems for Methanation. Ind. and Eng. Chem., Product Research and Development, v. 3, June 1964, pp. 150-153.

8. Greyson, M. Methanation. Ch. in Catalysis, ed. by P. H. Emmett. Reinhold Publishing Corp., New York, v. 6, 1956, pp. 473-511.

9. Greyson, M., J. J. Demeter, M. D. Schlesinger, G. E. Johnson, J. Jonakin, and J. W. Meyers. Synthesis of Methane. BuMines Rept. of Inv. 5137, 1955, 50 pp.

10. Karn, F. S., J. F. Shultz, R. B. Anderson. Kinetics of the Fischer-Tropsch Synthesis on Iron Catalysts. I. Rate Data on Reduced and Nitrided Catalysts. J. Phys. Chem., v. 62, September 1958, pp. 1039-1043.

11. Karn, F. S., J. F. Shultz, and R. B. Anderson. Kinetics of the Fischer-Tropsch Synthesis on Iron Catalysts. Pressure Dependence and Selectivity of Nitrided Catalysts. J. Phys. Chem., v. 64, April 1960, pp. 446-451.

12. _____. Kinetics of the Fischer-Tropsch Synthesis on Iron Catalysts. III. Influence of Water Vapor. Proc. 2d International Congress on Catalysis. Edition Technik, Paris, France, v. 2, 1961, pp. 2439-2452.

13. Krieg, A., A. P. Dudash, and R. B. Anderson. Improved Caustic Scrubber. Ind. and Eng. Chem., v. 41, July 1949, p. 1508.

14. Scarborough, J. B. Numerical Mathematical Analysis. Johns Hopkins Press, Baltimore, Md., 1930, 416 pp.

15. Schlesinger, M. D., J. J. Demeter, and M. Greyson. Catalyst for Producing Methane From Hydrogen and Carbon Monoxide. Ind. and Eng. Chem., v. 48, January 1956, pp. 68-70.

16. Shultz, J. F. A Small-Scale Recycle Pump. Ind. and Eng. Chem., v. 54, April 1962, pp. 34-35.

17. Storch, H. H., R. B. Anderson, L. J. E. Hofer, C. O. Hawk, H. C. Anderson, and N. Golumbic. Synthetic Liquid Fuels From Hydrogenation of Carbon Monoxide. Pt. 1--Review of Literature; Bureau of Mines Research on Effect of Catalyst Preparation, Reduction, and Induction Procedures on Activity; Correlation of Physical Properties of the Catalysts With Their Activity. BuMines Tech. Paper 709, 1948, pp. 71-130.