Task 5. Oxygenates

The objective of this task is to obtain a better understanding of the factors that affects catalyst selectivity toward oxygenates for iron-based Fischer-Tropsch catalysts.

No scheduled activity to report.

Task 6. Literature Review of Prior Fischer-Tropsch Synthesis with Co Catalysts

The objective of this task is to prepare a critical review of prior work on cobalt Fischer-Tropsch catalysts.

Work is continuing on an extensive review of FTS kinetics.

Task 7. Co Catalyst Preparation

The objective of this task is to prepare a limited number of cobalt-based Fischer-Tropsch catalysts that can be used to obtain baseline data on cobalt-based Fischer-Tropsch synthesis.

No scheduled activity to report.

Task 8. Cobalt Catalyst Testing for Activity and Kinetic Rate Correlations

The objective of this task is to conduct initial screening of the cobalt catalysts prepared in Task 7 to select three baseline catalysts that will then be used to generate a data base on the performance of cobalt-based Fischer-Tropsch catalysts in slurry reactors.

A. Co Kinetics

Preparation of Cobalt Catalysts

The Co/Al_2O_3 catalyst was prepared by incipient wetness impregnation of Al_2O_3 (Condea Vista B alumina, BET surface area 200 m^2/g, pore volume 0.4 cm^3/g) with cobalt nitrate solution. The preparation procedure includes three step impregnations of cobalt salt and then followed by impregnation of promoter. Finally, the sample was calcined at 400°C in a flow of air and helium.

Pretreatment of the catalysts

The catalysts were pretreated, first ex-situ and then in-situ, according to the following procedure. The catalysts were reduced ex-situ using 30% H_2 and 70% He (V/V) in a fixed bed reactor at a space velocity of 10,000 GHSV at 350°C. The temperature was ramped to 350°C at 1°C/min and held at 350°C for 10 hours. The reduced catalyst was transferred to the CSTR in an inert atmosphere. This was accomplished by over-pressuring the fixed bed reactor that contain the reduced catalyst and then opening the appropriate valves to force the entire catalyst volume into the CSTR containing startup solvent. The reduction reactor was weighed prior to and after catalyst transfer to ensure that a quantitative transfer of catalyst had been accomplished. The catalyst was then reduced in-situ in the CSTR; the hydrogen was introduced to reactor at atmospheric pressure with the flow rate of 30 SL/hr. The reactor temperature was increased to 230°C at a ramp rate of 1°C during 12 hours.

Reaction conditions

~20 g of catalyst was transfer into a 1 liter stirred autoclave which had been charged with 300 g of C_{30} oil(decene trimer obtained from Ethyl Corp.). The catalyst was reduced with hydrogen at 230°C in-situ at atmospheric pressure for 10 hours. After reduction, the reactor temperature was lowered to 180°C and synthesis gas was introduced into the reactor. Then the reactor was pressurized to 275 psig and temperature was slowly increased to 220°C during 3 hours.

FT-Kinetic Studies of 15%Co/Al$_2$O$_3$ Catalysts

Typically, the activity of the fresh catalyst decreases with time on stream and then levels off in 5-7 days. After this period, the deactivation is slow and linear. The kinetic study was performed under the "steady state" slow deactivation periods. Two sets of kinetic studies were carried out with constant CO partial pressure (table 1) and constant H_2 partial pressure (table 2).

Four H_2/CO ratios and five space velocities (8, 5, 3, 2, 1 SL/g/h) has been used to determine the rates. Argon gas used as the makeup gas to adjust the space velocity. The CO conversion with different space times at different H_2/CO ratios are presented in Fig. 1 and Fig. 2. The liquid products were collected and analyzed. Since, they were not representative, the rate of C_{5+} was calculated using carbon balance and single α assumption. The rate of H_2O production is also calculated from CO conversion, assuming no oxygenates generation.

Under some reaction conditions, hydrocarbon products are separated into two phases, liquid and vapor, in the reactor. It was assumed that H_2, CO, H_2O, CO_2 are insoluble in the reactor liquid. The fraction of hydrocarbons in vapor phase was obtained by flash calculation under reaction conditions, assuming they are in thermodynamical equilibrium. Thus, the gas composition and, therefore, partial pressures of CO, H_2, and H_2O at the reactor outlet can be determined.

The following power law kinetic equation was used in this study.

$$r_{co} = k\left(1 - m\frac{P_{H_2O}}{P_H}\right)P_{co}^a P_H^b \qquad (1)$$

In Equation (1), the partial pressures of H_2 (P_H), CO (P_{co}), and water vapor (P_{H_2O}) are local values in the reactor. Water effect is characterized using parameter m. In order to determine the orders of CO and H_2 at a certain reaction temperature and pressure, constant CO inlet partial pressure was used for each H_2/CO ratio. Argon was used as the makeup gas to adjust the space velocity. The CO reaction rate is calculated using Equation (2)

$$r_{CO} = 0.0115 \frac{dX_{CO}}{d(1/GHSV)} \quad (mole/h/g\ cat) \qquad (2)$$

Where X_{CO} is CO conversion and GHSV is inlet syngas hourly space velocity (SL/h/g). The

constant 0.0115 comes from (0.25/22.415) since the CO fraction in the inlet syngas is always

25%.

The CO conversions at 19.72 atm (275 psig) and 220 °C are shown in Figure 1 and their

regressed equations in Table 3. At the same conversion, the CO outlet partial pressure is

approximately the same, independent of the inlet H_2/CO ratio. To start with, it is assumed that the

presence of water does not affect CO reaction rate (m=0). Equation (1) is thus reduced to

Equation (3):

$$r_{co} = k'P_H^b \qquad\qquad (3)$$

A plot of ln (r_{co}) vs. ln(P_H) allows a determination of values of b. The b value found from the

slope was 0.9 (Fig. 3).

Similarly, at constant H_2 partial pressure, the equation reduced to

$$r_{co} = k'P^a_{co}$$

The CO conversions at 19.72 atm and 220°C are shown in Figure 2 and their regressed

equations in Table 4. A plot of ln (r_{co}) vs. ln(P_{co}) allows the determination of values of a. The a

value found from the lope was -0.4 (Fig. 4).

Thus the kinetic expression becomes

$$r_{CO} = k\left(1 - m \frac{P_{H_2O}}{P_H}\right) P_{CO}^{0.4}P_H^{0.9}$$

A plot of $r_{co}/P_{co}^{-0.4}/P_H^{0.9}$ vs P_{H2O}/P_H over the range of experimental data allows a determination of k

and m as shown in Fig. 5. The final kinetic expression at 19.72 atm and 220°C is:

$$r_{CO} = 0.278 \left(1 - 0.097 \frac{P_{H_2O}}{P_H} \right) P_{CO}^{0.4} P_H^{0.9}$$

In this rate equation, the units of partial pressure and reaction rate are atm and mole/h/gcat, respectively.

Table 1 : Inlet gas composition for the kinetic studies (constant CO partial pressure)

H$_2$/CO ratio	1.0	1.5	2.0	2.4
CO%	25	25	25	25
H$_2$%	25	37.5	50	60
Ar%	50	37.5	25	15

Table 2 : Inlet gas composition for the Kinetic studies (constant H2 partial pressure)

H$_2$/CO ratio	1.0	1.5	2.0	2.4
CO%	25	16.7	12.5	10.4
H$_2$%	25	25	25	25
Ar%	50	58.3	62.5	64.6

Table 3   Regression of CO conversion vs. space time t (1/GHSV, h·g/SL) at 19.72 atm and

220 ºC (Constant CO partial pressure)

H2/CO	Regressed Equation
1.0	$X_{co} = -15.529\ t^2 + 52.645\ t$
1.5	$X_{co} = -14.606\ t^2 + 68.772\ t$
2.0	$X_{co} = -21.227\ t^2 + 92.496\ t$
2.4	$X_{co} = -22.288\ t^2 + 115.8\ t$

Table 4   Regression of CO conversion vs. space time t (1/GHSV, h·g/SL) at 19.72 atm and

220 ºC (Constant H_2 partial pressure)

H2/CO	Regressed Equation
1.0	X_{co} = -15.529 t^2 + 52.645 t
1.5	X_{co} = -16.076 t^2 + 73.313 t
2.0	X_{co} = -54.034 t^2 + 145.33 t
2.4	X_{co} = -86.727 t^2 + 183.4 t
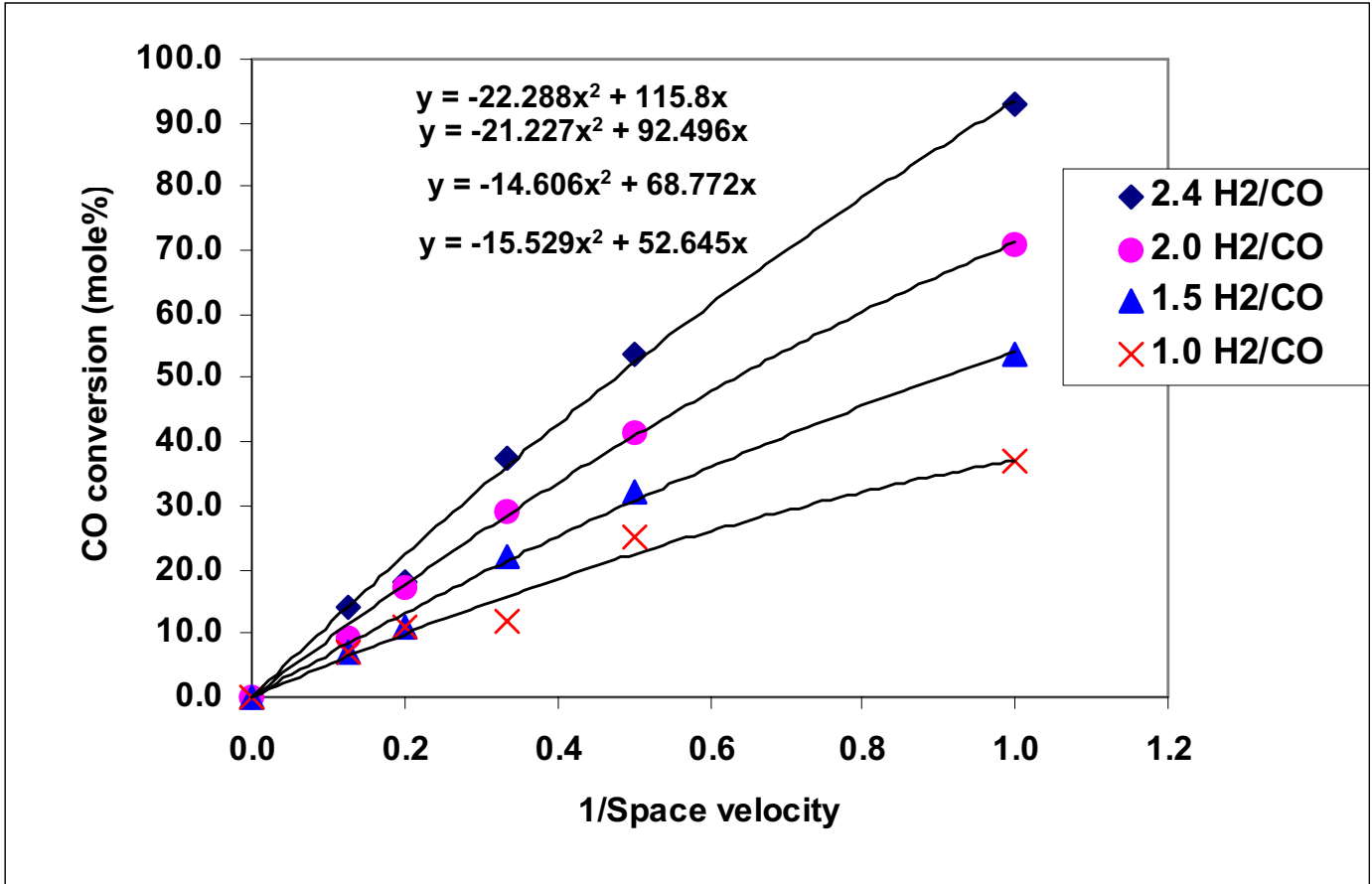
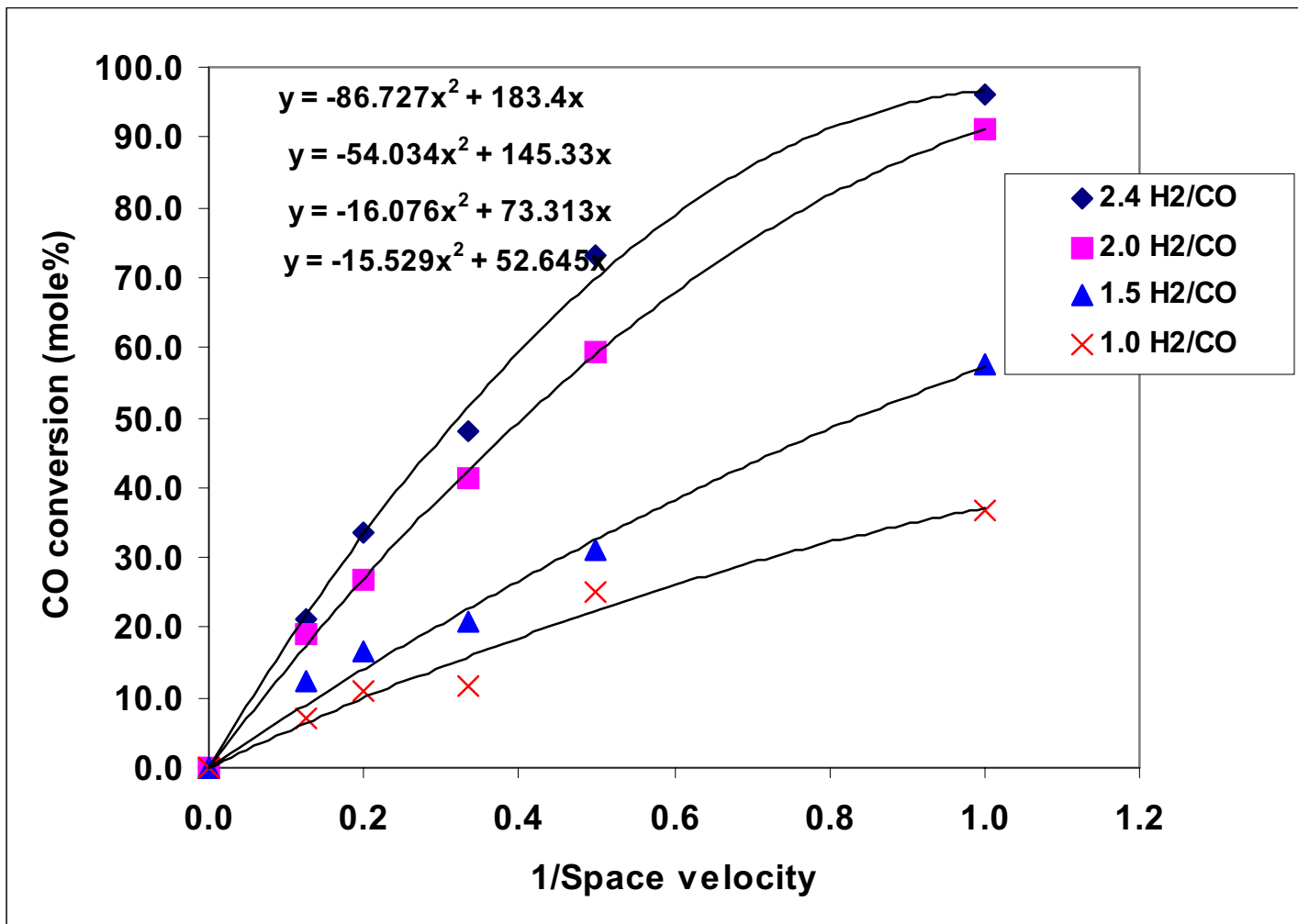Figure 1.   CO conversion versus space time (constant CO partial pressure).

Figure 2.　　CO conversion versus space time (constant H_2 partial pressure).
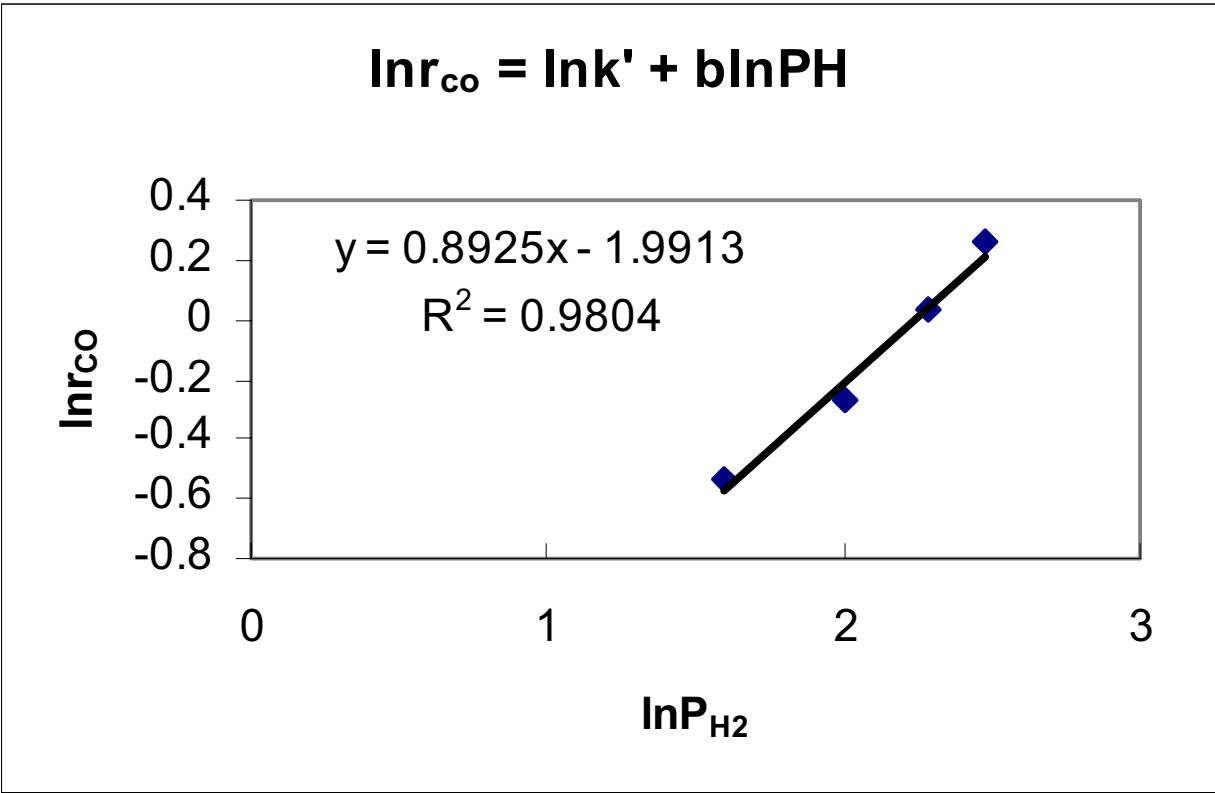
The chart contains the following equations:

$y = -86.727x^2 + 183.4x$

$y = -54.034x^2 + 145.33x$

$y = -16.076x^2 + 73.313x$

$y = -15.529x^2 + 52.645x$

Axis labels: CO conversion (mole%) versus 1/Space velocity

Legend: 2.4 H2/CO, 2.0 H2/CO, 1.5 H2/CO, 1.0 H2/CO

Figure 3.   Plot of ℓnP_H versus ℓnr_{CO}.
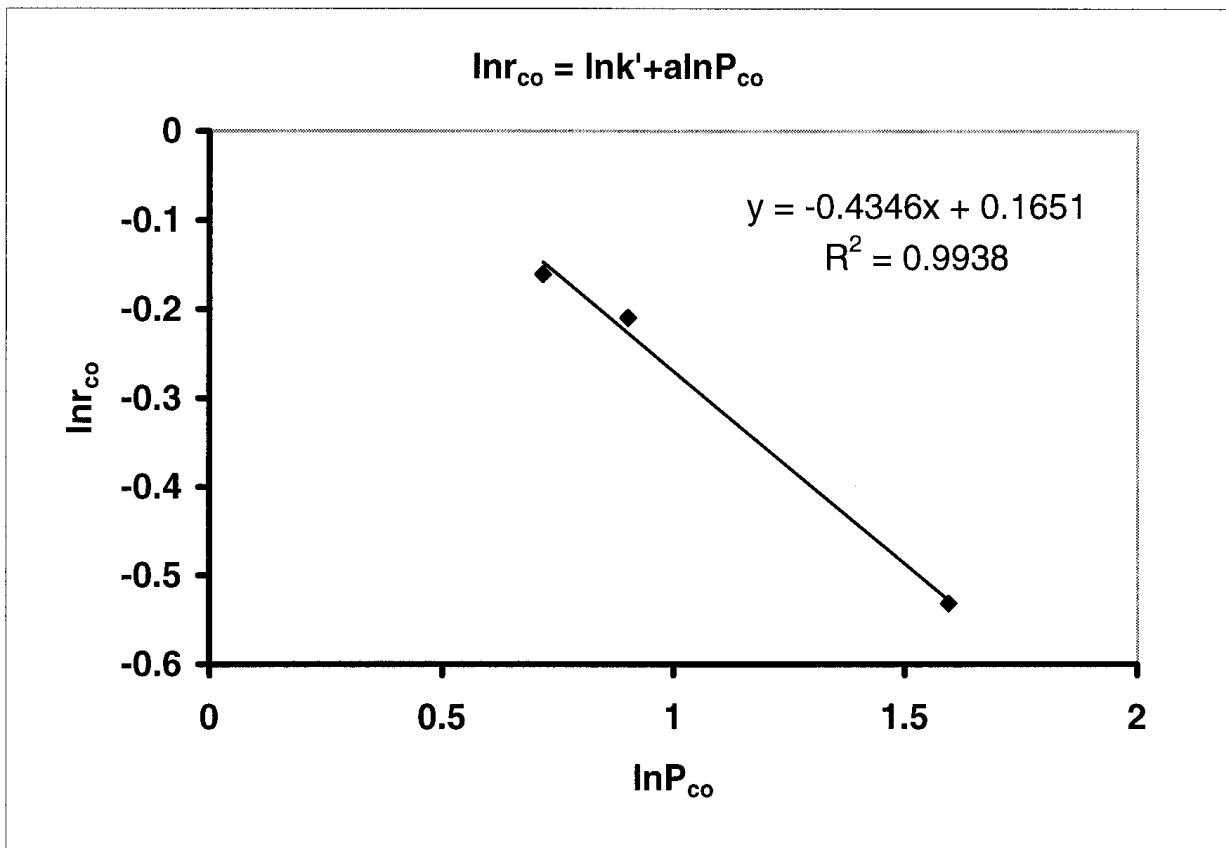
Figure 4.   Plot of $\ell n P_{CO}$ versus $\ell n r_{CO}$.
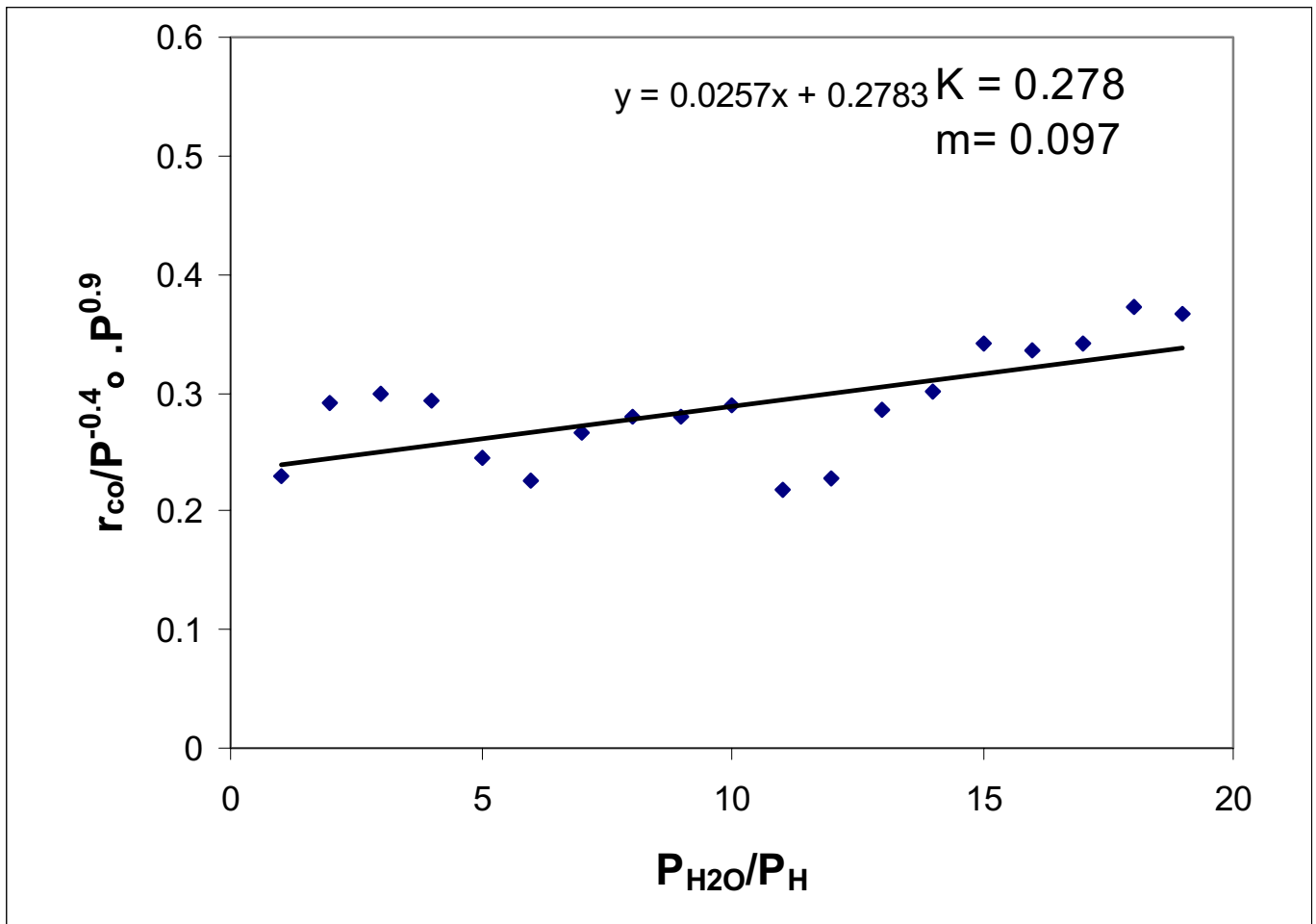
Figure 5.   Determination of rate constant K and water effect parameter m a 275 psig and

220ºC.

Task 9. Cobalt Catalyst Life Testing

The objective of this task is to obtain life data on baseline cobalt Fischer-Tropsch catalysts.

Runs are underway to obtain data for this task.

Task 10. Cobalt Catalyst Mechanism Study

The objective of this task is to determine the impact of secondary reactions on the relationship of cobalt Fischer-Tropsch catalysts under conditions appropriate to slurry bubble column reactors.

No scheduled activity to report.

Task 11. University of California, Berkeley (Subcontract)

The objective of this task is the characterization of the structure and function of active sites involved in the synthesis of high molecular weight hydrocarbons from CO and H_2 on multi-component catalysts based on Fe as the active component.