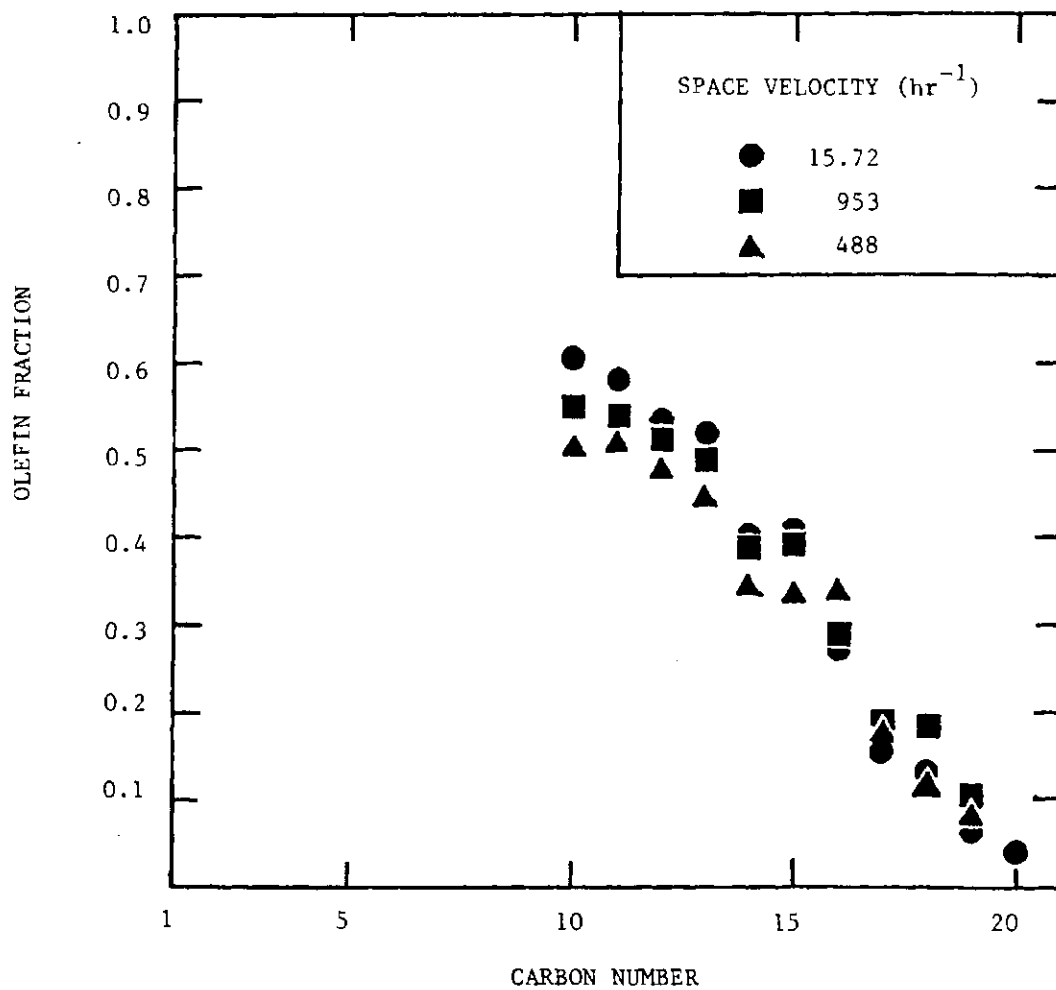


OLEFIN FRACTION VERSUS CARBON NUMBER
FOR DIFFERENT SPACE VELOCITIES



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FIG. 4.5

From a mass balance on all products exiting the reactor, an average F-T product stoichiometry or $\text{CH}_{2.34} \text{O}_{0.01}$ was calculated. This stoichiometry is similar to that obtained in the SASOL Synthol Reactor, $\text{CH}_{2.34} \text{O}_{0.05}$ [Probstein and Hicks (1982)]. From the average product stoichiometry, the following reaction was derived:



Neglecting the small amount of oxygen in the products, the stoichiometry can be approximated as:



The hydrogen to carbon ratio in the average F-T product calculated from the mass balance (2.34) is virtually identical to the ratio obtained from α and the $\text{C}_n\text{H}_{2n+1}$ assumption.

4.7 Extent of Water-Gas-Shift Reaction

With a knowledge of the average Fischer-Tropsch reaction product, C_3H_7 (Section 4.6.3), we calculated the H_2 to CO usage ratio, U, defined as the net moles of H_2 consumed per mole CO consumed (H_2 is consumed by the F-T reaction and produced by the water-gas shift reaction), assuming that the water-gas shift reaction was in equilibrium. By comparing this result with experimentally measured usage ratios, we determined whether the water-gas shift reaction was in equilibrium or was kinetically controlled.

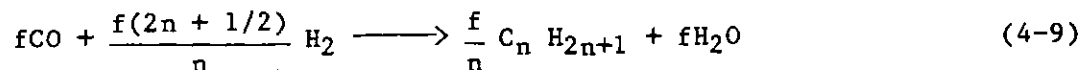
Recalling the Fischer-Tropsch and water-gas shift reactions from Section 2.1, we have:



and



Defining f as the extent of the F-T reaction (moles CO participating in the F-T reaction per mole CO fed), w as the extent of the water-gas shift reaction (moles CO participating in the water-gas shift reaction per mole CO fed), and assuming the hydrocarbons produced by the F-T reaction are of the form $\text{C}_n \text{H}_{2n+1}$, Eqs. (2-1) and (2-2) become:



and



The usage ratio, U, can then be expressed as follows:

$$U = \frac{f(2 + \frac{1}{2n}) - w}{f + w} \quad (4-11)$$

In Eq. (4-11), three terms must be known in order to calculate U; the extent of the Fischer-Tropsch reaction, f, the average carbon number of the F-T products, n, and the extent of the water-gas shift reaction, w. The first term, f, is calculated from the H₂ + CO conversion, X_{H₂+CO}, defined as the moles of H₂ consumed plus the moles of CO consumed divided by the total moles of H₂ and CO fed to the reactor. Using Eqs. (4-9) and (4-10), H₂ + CO conversion can be expressed as:

$$X_{H_2 + CO} = \frac{f(3 + \frac{1}{2n})}{1 + F} \quad (4-12)$$

where F is the moles H₂ per mole CO in the feed. Rearranging Eq. (4-12) yields the following expression for f:

$$f = \frac{(1 + F)(X_{H_2 + CO})}{(3 + \frac{1}{2n})} \quad (4-13)$$

In this equation, F is known, X_{H₂+CO} is measured, and n, as in Eq. (4-11), is determined as shown in Section 4.6.3. For this set of experiments n was equal to 3.

The extent of the water-gas shift reaction, w, is determined by assuming reaction equilibrium. Using a basis of 1 mole of CO and F moles of H₂ entering the reactor, the moles of reactant and product species leaving the reactor are:

$$\text{Moles H}_2 = F + w - f(2 + \frac{1}{2n}) \quad (4-14)$$

$$\text{Moles CO} = 1 - w - f \quad (4-15)$$

$$\text{Moles CO}_2 = w \quad (4-16)$$

$$\text{Moles H}_2\text{O} = f - w \quad (4-17)$$

The equilibrium constant for the water-gas shift reaction, K_p, is defined as follows:

$$K_p = \frac{[H_2][CO_2]}{[CO][H_2O]} \quad (4-18)$$

Substituting Eqs. (4-14) through (4-17) into Eq. (4-8) yields:

$$K_p = \frac{[F + w - f(2 + \frac{1}{2n})]w}{(1 - w - f)(f - w)} \quad (4-19)$$

Solving this equation for w, we obtain

$$w = \frac{-B - (B^2 - 4AC)^{1/2}}{2A} \quad (4-20)$$

where

$$A = K_p - 1 \quad (4-21)$$

$$B = f\left(2 + \frac{1}{2n}\right) - K_p - F \quad (4-22)$$

$$C = K_p (f - f^2) \quad (4-23)$$

The equilibrium constant, K_p , can also be determined from an Arrhenius relationship given by Huff (1982):

$$K_p = 0.0102 \text{ Exp } \left[\frac{4730}{T} \right] \quad (4-24)$$

Where T is expressed in degrees kelvin. For our reaction temperature of 227°C, Eq. (4-24) gives a value for K_p of 131. Knowing this, w can be calculated from Eq. (4-20), and, knowing w, the usage ratio can be calculated using Eq. (4-11).

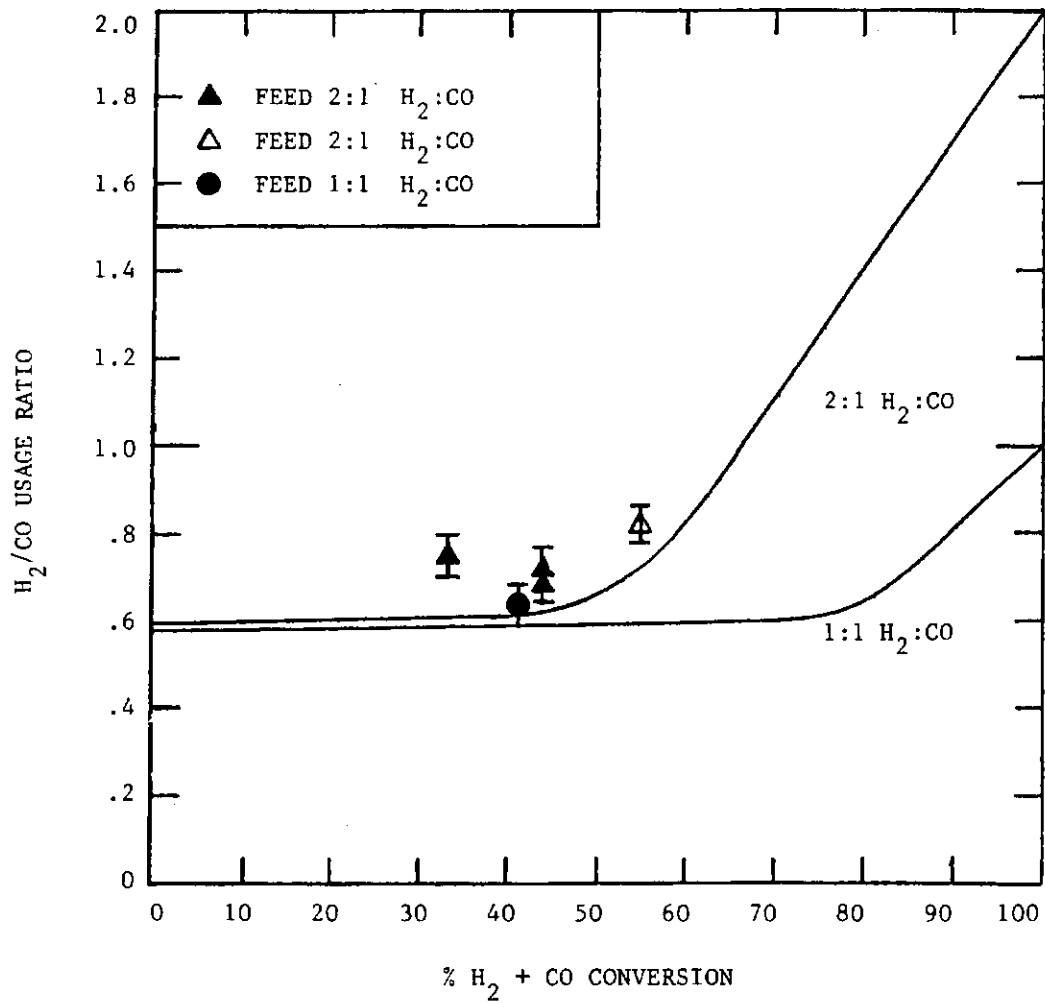
Theoretical curves of U vs. $X_{\text{CO+H}_2}$ assuming an average chain length of 3, a temperature of 227°C, and equilibrium of the water-gas shift reaction are plotted for H₂ to CO feed ratios of 2:1 and 1:1 together with experimental points for runs 1 through 5 in Fig. (4-6). Run 6 was not included due to catalyst deactivation. All of the experimental points are above their respective equilibrium lines, indicating that the water-gas shift reaction is kinetically controlled at our reaction conditions. This was confirmed by significant amounts of water being found in the 0°C trap.

For H₂ + CO conversions of less than 45%, the measured usage ratios were relatively constant (within experimental error) at approximately 0.7 moles H₂/mole CO. At 55% H₂ + CO conversion, a usage ratio of 0.8 moles H₂/mole CO was observed. These results are consistent with Huff (1982), who found that the water-gas shift reaction attained equilibrium at temperatures greater than approximately 250°C.

4.8 Mass Balance Closures on Carbon and Oxygen

Mass balances were performed on the carbon and oxygen passing through the system for all runs. Closures ranging from 88% to 94% for carbon and 91% to 99% for oxygen were achieved (see Table (4-5)). Discrepancies between the amount of material entering and leaving the reactor are the result of accumulation in the reactor, as well as errors in detection and measurement of products (see Section 3.7).

THEORETICAL USAGE RATIO VS $H_2 + CO$ CONVERSION



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FIG

4.6

Table (4-5)
Mass Balance Closures on Carbon and Oxygen

Run	Space Velocity (hr ⁻¹)	% Closure on Carbon	% Closure on Oxygen
1	1572	90.1	98.7
2	953	92.5	96.1
3	388	90.4	91.2
4	923	88.9	98.7
5	828	89.2	97.3
6	935	93.7	93.2

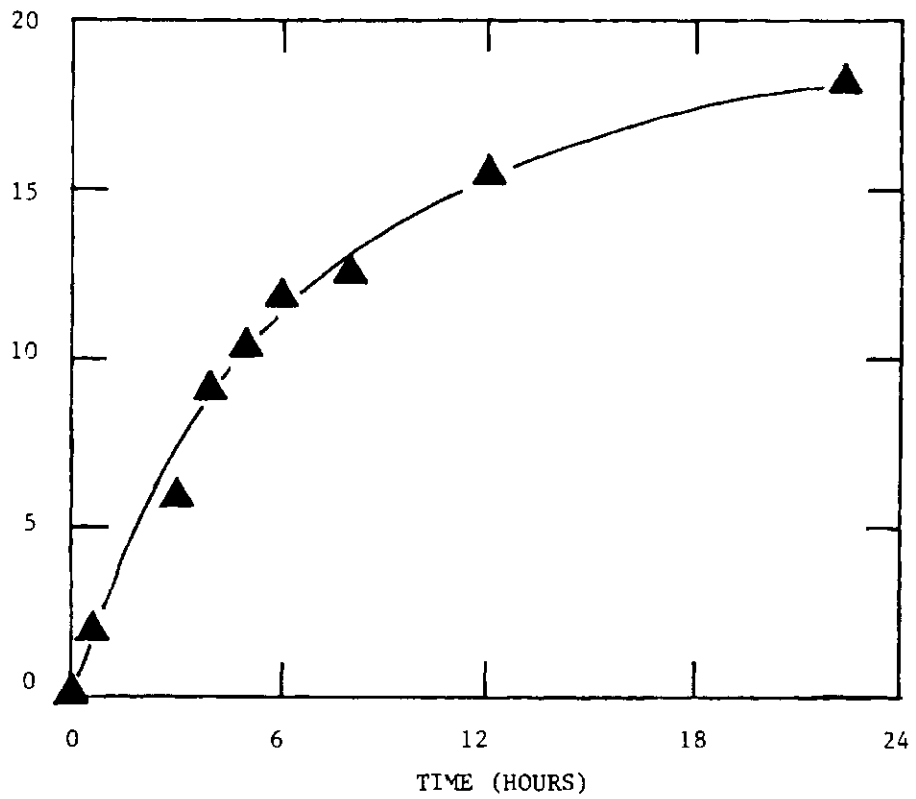
4.9 Methanol Incorporation

To determine if methanol could be adsorbed on to the catalyst surface and participate in the Fischer-Tropsch synthesis, liquid methanol was added continuously to the reactor at a rate of 0.072 ml/min. The amount of methanol added comprised approximately 0.4% of the total carbon in the feed, and was four orders of magnitude greater than the amount normally produced in the F-T reaction. Two results were found. First, methanol was not incorporated into the F-T synthesis. By a material balance, we accounted for 98% of the methanol, well within the 10% error expected from the GC. Two-thirds of the methanol leaving the reactor was collected in the liquid traps and the remaining third exited in the gaseous phase.

The second result was that methanol deactivated the iron-copper catalyst. In Fig. (4-7), the ratio of methanol to methane (the most common product) in the gaseous effluent is plotted as a function of time. At the beginning of the experiment, this ratio was near zero, but it increased to a value of 18 moles of methanol per mole of methane after 23 hours of operation, indicating that methanol was the major component of the reactor effluent. At the same time, the total amount of the other gaseous products decreased, suggesting a decrease in catalyst activity. Examination of the liquids in both of the liquid traps revealed that less than 0.25 ml of organic product was produced compared to an average of 6.5 ml collected over the same time period without methanol addition.

The deactivation of the catalyst was not irreversible. When pure H₂ was bubbled through the reactor for 16 hours at 250°C, catalyst activity was restored. Water was present in the cold traps, indicating that a surface oxide was reduced by the hydrogen. Then, when 2:1 syngas was fed at a space velocity of 676 hr⁻¹, a CO conversion of 89% was observed, in agreement with the results of previous runs before methanol incorporation (see Section 4.4.1). Thus, we believe that the methanol reversibly oxidized the catalyst and was not incorporated to a significant extent in the reaction.

RATIO OF METHANOL TO METHANE
IN REACTOR EFFLUENT
WITH METHANOL ADDITION



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FIG
4.7

5 CONCLUSIONS

- (1) The conversions and product distributions obtained using an iron-copper catalyst were consistent with those obtained with iron catalysts in previous Fischer-Tropsch studies.
- (2) The Fischer-Tropsch products fit a Flory distribution with a chain growth probability (α) of 0.67 ± 0.02 .
- (3) The chain growth probability was independent of synthesis gas ratio and space velocity.
- (4) The water-gas shift reaction was kinetically limited at 227°C.
- (5) Methanol was not incorporated in the Fischer-Tropsch reaction to a significant extent at 227°C and 100 psig.
- (6) Methanol oxidized and deactivated the catalyst.

6 RECOMMENDATIONS

6.1 Recommendations for Future Work

- (1) Run reactor for longer periods of time so that:
 - (a) catalyst lifetime can be determined, and
 - (b) the concentration of higher molecular weight products in the reactor effluent can reach steady-state.
- (2) Repeat runs with 1:1 syngas to confirm its effect on the catalyst.
- (3) Repeat CSTR experiments with the Fe-Cu catalyst at higher temperatures and pressures to characterize their effects on conversion and product distribution.
- (4) Add methanol to the reactor at different temperatures and pressures to determine if it can be incorporated under other reaction conditions.

6.2 Recommended Changes in Equipment

- (1) Use new wax for each catalyst loading to decrease the possibility of impurities being present and to decrease the down time between runs.
- (2) Use smaller, conical liquid traps with sampling points on the bottom so that all of the liquid products may be removed after each run.
- (3) Add a sampling port to the reactor, so that the liquid phase in the reactor can be analyzed for products with low volatilities.
- (4) Use a more reliable on-line GC for hydrogen analysis.
- (5) Use a GC system for gas analysis that can detect water and distinguish paraffins, olefins, alcohols, and isomers (e.g., a Carle III refinery gas analyzer).
- (6) For organic liquid analysis, use a capillary column in a GC that can cool the column below room temperature at the beginning of the program, so that all the products can be resolved, including C₅ to C₈ paraffins and olefins and heavy alcohols.
- (7) Add a small known amount of an inert gas to the feed as an internal standard for the gas GC's.

7 . ACKNOWLEDGMENTS

We would like to thank Rich Sapienza and Bill Siegeir for their guidance and support. The help of Mike Foran, Ruth Trinidad, and Bob Smoll was also greatly appreciated. Finally, we would like to thank George Huff for helpful conversations and advice concerning the project.

8 APPENDIX

8.1 Location of Original Data

The original data for this report are located in file MIT/BNL-83-4 at the M.I.T. School of Chemical Engineering Practice, Cambridge, MA.

8.2 Summary of Raw Data

8.2.1 Feed Ratio, Space Velocity, and Conversions.

Run	H ₂ :CO Feed Ratio	Space Velocity (hr ⁻¹)	Conversions (%)		
			CO	H ₂	CO + H ₂
1	2:1	1572	58.2	20.3	32.9
2	2:1	953	76.9	28.1	44.4
3	2:1	488	91.9	37.6	55.7
4	2:1	923	78.1	27.7	44.5
5	1:1	828	50.2	31.7	41.0
6	2:1	935	48.9	21.5	30.6

8.2.2 Partial Pressures of Components in the Reactor.

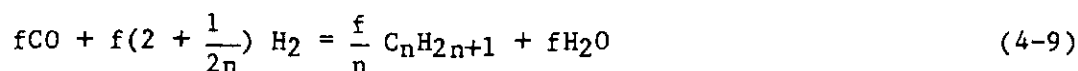
Partial Pressures in kPa (psig)					
Run	H ₂	CO	CO ₂	Hydrocarbons	H ₂ O ^a
1	520 (66)	134 (17)	87 (11)	20 (2.6)	20 (2.5)
2	529 (67)	79 (10)	126 (16)	37 (4.5)	17 (2.2)
3	496 (63)	32 (4)	158 (20)	56 (7)	47 (6)
4	524 (67)	80 (10)	133 (17)	36 (4.6)	15 (2)
5	363 (46)	260 (33)	118 (15)	22 (2.8)	21 (2.7)
6	513 (65)	167 (21)	62 (8)	18 (2.3)	28 (3.6)

^aH₂O values are estimated from the stoichiometry of the F-T and water-gas shift reactions along with hydrogen conversions. The partial pressure of water is a small fraction (2%-6%) of the total pressure in the reactor.

8.3 Estimating Hydrogen Conversions from Mass Balances

Because the hydrogen-measuring GC broke down during two of our runs, we developed three methods of estimating the hydrogen conversion from other measurements. These estimates were compared with hydrogen conversions from the four runs in which GC measurements were available, and the accuracy of the estimates was determined.

In the first method, we assumed the the F-T and water-gas shift were the only reactions consuming CO, and used measured CO₂ production and CO conversion to calculate H₂ conversion. For a basis of F moles of H₂ and 1 mole of CO fed, the F-T and water-gas shift reactions are (Section 4.7)



and



where f and w are the number of moles of CO consumed by the F-T and water-gas shift reactions, respectively for each mole of CO fed. The extent water-gas shift reaction, w, is also the number of moles of CO₂ produced per mole of CO fed. Carbon dioxide production was experimentally determined. The total CO conversion, X_{CO}, is also an experimentally determined quantity, and can be expressed as:

$$X_{\text{CO}} = f + w \quad (8-1)$$

Knowing X_{CO} and w, we can determine f by rearranging Eq. (8-1):

$$f = X_{\text{CO}} - w \quad (8-2)$$

The conversion of H₂, from Eq. (4-9) and (4-10) is

$$X_{\text{H}_2} = \frac{f\left(2 + \frac{1}{2n}\right) - w}{F} \quad (8-3)$$

and can now be determined from a knowledge of CO₂ production and CO conversion.

In the second method of estimating hydrogen conversion, we used contraction in flow rate, CO conversion, and the fractions of water and hydrocarbons produced in the reactor that exit the 0°C trap as vapor. From Eq. (4-9) and (4-10), the number of moles in the reactor are effluent per 1 mole of CO and F moles of H₂ fed are:

$$\text{moles H}_2 = F + w - f\left(2 + \frac{1}{2n}\right) \quad (4-14)$$

$$\text{moles CO} = 1 - w - f \quad (4-15)$$

$$\text{moles CO}_2 = w \quad (4-16)$$

$$\text{moles H}_2\text{O} = f - w \quad (4-17)$$

$$\text{moles C}_n\text{H}_{2n+1} = \frac{f}{n} \quad (4-18)$$

The change in moles in the reactor is then:

$$\Delta M_{\text{RXN}} = f \left(\frac{1}{2n} - 2 \right) \quad (8-5)$$

When the effluent gas goes through the traps, there is an accumulation of condensed water and hydrocarbons. The amounts condensed per mole of CO fed are given by:

$$\text{Accumulation of C}_N \text{H}_{2N+1} = (1 - K) f/n \quad (8-6)$$

$$\text{Accumulation of H}_2\text{O} = (1 - K') (f - w) \quad (8-7)$$

where K and K' are the fractions of hydrocarbons and water, respectively, which do not condense in the traps. K was determined for each run by a mass balance on liquid and gaseous hydrocarbons and was approximately 0.2. K' was estimated, assuming vapor liquid equilibrium in the traps, to be 0.65. Thus, the change in number of moles of gas across the traps is:

$$\Delta M_{\text{traps}} = - (1 - K) f/n + (1 - K') (f - w) \quad (8-8)$$

and the total change in the number of moles between the feed and the effluent from the traps is

$$\Delta M = f \left(\frac{2K - 1}{2n} - 3 + K' \right) - w(K' - 1) \quad (8-9)$$

The contraction in gas flow rate, C, is given by

$$C = \frac{\text{moles in} - \text{moles out}}{\text{moles in}} = \frac{\Delta M}{1 + F} \quad (8-10)$$

By substituting this into Eq. (8-9), the extent of the F-T reaction, f, can be determined:

$$f = \frac{X_{\text{CO}} (1 - K') + C(1 + F)}{\left(\frac{1 - 2K}{2n} \right) + 4 - 2K'} \quad (8-11)$$

X_{H_2} can then be calculated from Eq. (8-11) and Eq. (8-3).

The third method of estimating X_{H_2} was by a mass balance on the gaseous effluent from the 0°C trap. With the exception of hydrogen, the concentrations of the major gaseous species were experimentally measured

using a gas chromatograph (H₂O and hydrocarbons above C₇ were not detected, but they consisted of only about 3% of the effluent). Assuming the remainder of the gas was hydrogen, the H₂ concentration and H₂ conversion could be calculated.

In Table 8.1 we present hydrogen conversions estimated with the three methods described above along with measured values, when available. The average of the three estimated values for hydrogen conversion deviated from the measured values by 0.4% to 9% in runs 1, 2, 4, and 6. Since these averages agreed well with measured values, we used the average estimated values in our calculations for runs 3 and 5, when the H₂ conversion could not be obtained experimentally.

Table (8-1)
H₂ Conversion

Space Velocity	Percent H ₂ Conversion Based On:				
	Stoichiometry and CO ₂	Contraction	Mass Balance	Measured	Average
1570	19.6	21.9	19.3	21.9	20.3
950	27.5	30.3	26.5	26.3	28.1
490	36.4	50.7*	38.8	----	37.6
920	26.2	30.3	26.5	27.8	27.7
830	35.9	31.2	27.9	----	31.7
940	21.8	23.0	19.7	19.8	21.5

*This value was artificially high due to equipment failure and was not used in the average.

8.4 Nomenclature

C = flow contraction, $\frac{\text{moles in} - \text{moles out}}{\text{moles in}}$

F = feed ratio, moles H₂ fed/mole CO fed

K = equilibrium constant

M_n = mole fraction of carbon number n,

$\frac{\text{moles of product with n carbons}}{\text{total moles of hydrocarbon product}}$

P_s = standard pressure

R = ideal gas constant

T = temperature

T_s = standard temperature

- U = usage ratio, $\frac{\text{moles H}_2 \text{ consumed}}{\text{moles CO consumed}}$
 X_i = conversion of i , $\frac{\text{moles } i \text{ consumed}}{\text{moles } i \text{ fed}}$
 f = extent of Fischer-Tropsch reaction,
 $\frac{\text{moles CO participating in Fischer-Tropsch}}{\text{moles CO fed}}$
 k = Langmuir - Hinshelwood rate constant
 k' = first-order rate constant,
 $\frac{\text{moles CO participating in Fischer-Tropsch}}{\text{atm hour}}$
 m = molar flowrate, moles/hour
 n = number of carbon atoms in average product
 p_i = partial pressure of component i , atm
 r = reaction rate, moles/hour
 w = extent of water-gas-shift reaction,
 $\frac{\text{moles CO participating in water-gas shift}}{\text{mole CO fed}}$
 y = mole fraction in gas phase, dimensionless
 α = Flory chain-growth probability, dimensionless

9 REFERENCES

- Anderson, R. B. in Catalysis, Vol. 4, P. H. Emmett, Ed., Rheinhold, NY (1956).
- Deckwer, et al., Ind. Eng. Chem. Process Des. Dev., 19, 699 (1980).
- Dry, M. E., Ind. Eng. Chem, Chem. Prod. Res. Dev., 15, 282, 1976.
- Dry, M. E., in Catalysis-Science and Technology, Vol. 1, J. R. Anderson and M. Bondart, Eds., pp. 231-233, Springer-Verlag, Berlin (1981).
- Dwyer, D. J. and G. A. Somorjai, J. Catal., 56, 249 (1979).
- Farley, R. and D. J. Ray, J. Inst. Pet., 50, 27 (1964).
- Feiner, J. L., P. L. Silveston, and R. R. Hudgins, Ind. Eng. Chem. Prod. Res. Dev., 20, 609 (1981).
- Flory, P. J., J. Amer. Chem. Soc., 58, 1877 (1936).
- Hall, C. C., D. Gall, and S. L. Smith, J. Inst. Pet., 38, 845 (1952).
- Hall, W. K., R. J. Kokes, and P. H. Emmett, J. Amer. Chem. Soc., 82, 1027 (1960).
- Huff, G. A., Jr., Personal Communication (1983).
- Huff, G. A., Jr., Doctoral Thesis, Mass. Inst. of Tech. (1982).
- Karn, F. S., J. F. Shultz, and R. B. Anderson, Actes du Deuxiem Congres Intern. de Catalyse, Paris, Tome 2, 2439 (1960).
- Kölbel, H., P. Ackerman, and F. Engelhardt, "Proceedings, Fourth World Petroleum Congress," Rome Section IV 227 (1955).
- Kölbel, H. and M. Ralek, "Chemical Feedstocks from Coal," J Falbe Ed., Wiley, New York, NY, pp. 370-392 (1982).
- McNair, H. M. and E. J. Bonelli, Basic Gas Chromatography, Varian Aerograph, Walnut Creek, CA (1968).
- Morrison, R. T. and Boyd, R. N., Organic Chemistry, second edition, Allyn and Bacon, Boston, MA (1968).
- Probststein, R. and E. Hicks, Synthetic Fuels, McGraw Hill, New York, NY (1982).
- Raymond, J. P., P. Meriandeau, B. Pommier, and C. O. Bennett, J. Catal., 64, 163, (1980).

- Roofer-DePorter, C. K., Chem. Rev., 81, 447-474 (1981).
- Sapienza, R. and W. B. Slegeir, personal communication (1983).
- Satterfield, C. N., G. A. Huff, Jr., and R. Summerhayes, J. Catal., 80, 486-490 (1983).
- Satterfield, C. N., G. A. Huff, Jr., J. P. Longwell, Ind. Eng. Chem. Process Des. Dev., 21, (3) (1982).
- Satterfield, C. N., and G. A. Huff, Jr., J. Catal., 73, 187 (1982).
- Satterfield, C. N., Mass Transfer in Heterogeneous Catalysis (1981).
- Satterfield, C. N., Heterogeneous Catalysis in Practice, McGraw-Hill, New York, NY (1980).
- Schlesinger, M. D., J. H. Crowell, M. Leva, and H. H. Storch, Ind. Eng. Chem., 43, 1474 (1951).
- Schultz, H., B. R. Rao, and M. Elstner, Erdöl Kohle Endgas Petrochem. Brennst. Chem., 23, 651 (1970).
- Shinnar, R., Chemtech 8, 686 (1978).
- Summerhayes, R., Masters' Thesis, Mass. Inst. of Tech., Cambridge, MA (1982).
- Weingaertner, E., Erdöl und Kohle, 9, 368 (1956).