

IX. Recommendation for Future Studies

Based on studies carried out in this and our last Contract, areas of major importance have been identified. Many of those areas are recommended for future studies to improve the process economics, the product flexibility, and the scaleup of the slurry F-T reactor. For convenience, these areas of interest are summarized below into four groups.

Slurry F-T Operation

- Development of reaction mechanism, kinetics, catalyst preparation, catalyst activation, and catalyst aging.
- Catalyst settling mechanism and means to improve catalyst suspension.
- Scaleup factors of slurry F-T reactor, including type, maximum size, internals, and hydrodynamics (Axial dispersion and gas-liquid interphase mass-transfer resistance).
- Steam co-feeding to slurry F-T reactor to allow use of a synthesis gas of H₂/CO ratio lower than the usage ratio.
- Effect of varying catalyst loading in slurry reactor on the reactor performance.
- Improved devices for catalyst/reactor-wax separation.

F-T Product Upgrading

- Process development of upgrading technologies, including LPFC, FCC and MOGD.

Process Optimization

- Carbon dioxide removal schemes and their utility integration with other part of the plant.
- Schemes for further conversion of unconverted H₂+CO.

- Schemes for recycle of C₁-C₂ hydrocarbons to the slurry F-T reactor via a steam reformer or a partial oxidation unit.
- Schemes for further conversion of unconverted light olefins.
- Examining benefits or penalties of lower single pass H₂+CO conversion with recycle to the slurry F-T reactor or with the use of multi-staged F-T reactors.

Process Economics

- Detailed economic comparison of this technology against the best alternative.

Further discussions of some of these areas are given below.

Development of F-T reaction mechanism, kinetics, catalyst preparation, catalyst activation, and catalyst aging are essential for the improvement of this technology. These developments would ultimately help us to understand the optimal combination of catalyst and operating conditions. They would also affect the scaleup strategy of the slurry F-T reactor. For instance, if the reaction mechanism and kinetics of catalyst are well-understood, then the effect of the gas-liquid interphase mass-transfer resistance in a large scale reactor can be easily determined. At present, the significance of this interphase resistance in any large scale reactor cannot be assessed.

The phenomenon of F-T catalyst settling observed in Runs CT-256-9, -11, -12 and -13 imposes significant process restrictions. Evidence shows that this phenomenon most probably resulted from catalyst agglomeration. Unfortunately, the mechanism of this catalyst agglomeration is unknown. During this contract, we were able to increase the usage of the F-T catalyst to 350 gHC/gFe (before the settling occurred) by lowering the catalyst loading and imposing a small slurry upflow (0.05 m/s) over the whole bubble-column. Further increase in the catalyst usage may be possible by increasing the slurry velocity. Furthermore, use of stirred-tank reactors should be evaluated from the point of view of improved catalyst suspension.

Another area of major importance is the commercial scaleup of the slurry F-T reactor. The factors that need to be evaluated include the type and size of the reactor, its internals (baffles and/or heat transfer tubes), feed-gas distributor, gas holdup, the liquid- and gas-phase back-mixing, and the gas-liquid

interphase mass-transfer resistance. Among these factors, the gas-liquid interphase mass-transfer resistance is the most important one. The extent of the effect of this resistance on the performance of commercial-scale reactors is a prolonged issue among the F-T experts. If one can successfully quantify this effect in large-scale reactors, then the reactor performance can be confidently predicted once the intrinsic kinetic of the catalyst is known.

Various process optimization schemes need to be examined. In any coal-to-hydrocarbon plant, the amount of carbon dioxide to be removed is directly proportional to the inefficiency of the plant. The amount of carbon dioxide to be removed in the two-stage slurry F-T/ZSM-5 plant is expected to be relatively small because of its high thermal efficiency. However, the investment associated with the carbon dioxide removal is still quite substantial. Examination of other removal schemes and their utility integration with other parts of the plant is warranted. Other possible optimization schemes are further conversion of unconverted H_2+CO and light olefins, and the recycle of methane + ethane to the slurry F-T reactor via a steam reformer or a partial oxidation unit. All these schemes will contribute to higher liquid hydrocarbon yield.

In order to determine the priority on the development of various routes of coal-to-liquid fuel projects, a detailed economic comparison of this technology against the best alternate route of making similar products should be conducted.

X. Nomenclature

A_f	Orifice free area, (cm^2)
A	First-order aging kinetic constant, (1/day)
a_g	Gas bubble interfacial area, $6\epsilon_g/d_B$, (cm^2 gas-liquid area/ cm^3 expanded slurry)
C	Empirical Constant
C	Concentration, (mol/cm^3 liquid or gas)
C_c	Catalyst concentration, (g/cm^3)
C_{Fe}	Iron loading, (gFe/cm^3 liquid)
\bar{C}_g	C_g/C_{gl}^i
\bar{C}_L	C_{LK}/C_{gl}^i
C_o	Orifice discharge coefficient
C_v	Empirical constant, (cm/s)
d_B	Bubble diameter, (cm)
\bar{d}_B	Average bubble diameter, (cm)
d_c	Catalyst particle diameter, (micron)
$d_o; d_o^*$	Orifice diameter; critical orifice diameter, (mm)
d_R	Reactor diameter, (cm)
E	Axial dispersion coefficient, (cm^2/s)
f	Molar H_2/CO ratio at reactor inlet
f_B	Fraction of bubbles of size d_B
g	Gravitational constant = 981, (cm/s^2)
K	Empirical constant

K	Solubility coefficient C_g^*/C_L^* , (cm^3 liquid/ cm^3 gas)
k	First-order kinetic rate constant, (1/s)
k°	Initial k, (1/s)
k_1, k_2	Intrinsic kinetic rate constants for F-T and water-gas shift reactions, respectively, (cm^3 liquid/s-gFe)
k_1', k_1''	Constants used in the rate expressions (VII-27) and (VII-28)
k_2'	Intrinsic kinetic rate constant for water-gas shift reaction used in Equation (VII-28), (mol/s-gFe)
k_3	Constant used in the rate expressions (IV-1) and (IV-2)
k_4	Water-gas shift equilibrium constant
\bar{k}_3	k_3K_2/K_4
\bar{k}_4	$k_4K_1K_3/K_2K_4$
k_L	Liquid side mass-transfer coefficient, (cm^3 liquid/s-(cm^2 gas-liquid area))
L	Reactor or expanded slurry height, (cm)
L_0	Slurry return location, (cm)
L_s	Static slurry height, (cm)
m	Average H/C atomic ratio of F-T products
N	Number of CSTR's in series
n_0	Number of orifices or nozzles
P	Pressure, (Pa)
Q	Gas volumetric flow rate, (cm^3/s)
\bar{Q}	Q/Q^i
R_d	Transport resistance from gas-liquid interface to bulk liquid phase, $K/k_L a_g$, (s-cm^3 expanded slurry/ cm^3 gas)
R_k	Kinetic resistance, $K_1/k_j C_{Fe} (1-\epsilon_g) (1-v_c) C_c$ ($j=1,2$) (s-cm^3 expanded slurry/ cm^3 gas)
r	Pressure ratio, downstream/upstream

r_1	Kinetic rate of F-T reaction, given as Equations (IV-1), (VII-16), and (VII-27), (mol/s-gFe)
r_2	Kinetic rate of water-gas shift reaction, given as Equations (IV-2), (VII-18), and (VII-28), (mol/s-gFe)
\bar{r}_1	$\bar{C}_{L1}\bar{C}_{L2}/(\bar{C}_{L2} + \bar{k}_3\bar{C}_{L4})$
\bar{r}_2	$K_1(\bar{C}_{L2}\bar{C}_{L4}-\bar{C}_{L1}\bar{C}_{L3}/\bar{k}_4)(\bar{C}_{L2} + \bar{k}_3\bar{C}_{L4})$
S_{ij}	Elements of stoichiometric matrix $i = 1, \dots, 4$; and $j = 1, 2$
T	Temperature, ($^{\circ}\text{C}$)
T_c	Synthesis gas-catalyst contact time, (s)
t	Time, (s)
t^*	Time for the large bubbles to disengage, (s)
t_c	Catalyst age, (day)
u	Superficial velocity, (cm/s)
u_B	Bubble-rise velocity, (cm/s)
\bar{u}_B	Average bubble-rise velocity, (cm/s)
u_o	Gas orifice or nozzle velocity, (cm/s)
u_{cs}	Catalyst settling velocity, (cm/s)
u_{sl}	Slurry circulation velocity, (cm/s)
V	Expanded slurry volume in each reactor, (cm^3 slurry and gas)
v_c	Volumetric fraction of catalysts in slurry, $\rho_L w_c / (\rho_s + w_c(\rho_L - \rho_s))$, (cm^3 catalyst/ cm^3 slurry)
w	Weight flow rate, (g/s)
w_c	Weight fraction of catalyst in slurry, (gCat/g slurry)
$X_{\text{H}_2+\text{CO}}$	Molar H_2+CO conversion
x	Axial distance, (cm)
Y	Expansion factor

Greek Letters

α	Contraction factor, molar contraction per mol of H_2+CO converted
β	Ratio of orifice to reactor diameter
γ	Ratio of specific heats
ϵ_g	Gas holdup, (cm^3 gas/ cm^3 expanded slurry)
ϵ_g^*	Gas holdup at t^* , (cm^3 gas/ cm^3 expanded slurry)
μ_L	Liquid viscosity, ($g/cm-s$)
ρ	Density, (g/cm^3)
ρ_s	Catalyst solid density, (gCa^{+}/cm^3 catalyst solid)
ρ^u	Upstream density, (g/cm^3)
σ	Surface tension, (dyne/cm)
ν	Kinematic viscosity, μ/ρ , (cm^2/s)

Dimensionless Numbers

Fr_o	Froude number (orifice), $u_o/(gd_o)^{0.5}$
Pe_L	Axial Peclet number (liquid), $u_g^i L/E_L(1-\epsilon_g)(1-v_c)$
St_d	Stanton number (diffusion resistance), $V/NQ^i R_d$
St_k	Stanton number (kinetic resistance), $V/NQ^i R_k$
We_o	Weber number (orifice or nozzle), $u_o^2 d_o \rho_g / \sigma$

Acronyms

ASME	American Society of Mechanical Engineers
BC	Bubble-Column
BFW	Boiler Feed-Water
BGC	British Gas Corporation
BSU	Bench-Scale Unit
CSTR	Continuous Stirred-Tank Reactor
CW	Cooling Water
D	Distillate
DOE	Department Of Energy
DOS	Days On Stream
DP	Differential Pressure
ERDA	Energy Research And Development Administration
ERT	Equivalent Residence Time, (s)
FCC	Fluid Catalytic Cracking
FIMS	Field-Ionization Mass Spectrometry
F-T	Fischer-Tropsch
G	Gasoline
GC	Gas Chromatography
GHSV	Gas Hourly Space Velocity, (NL per hr/L-Cat.)
GPC	Gel Permeation Chromatography
HC	Hydro-Carbons
HF	Hydro-Fluoric Acid
HOS	Hours On Stream
ID	Inside Diameter
LC	Liquid Chromatography

LPHC	Low Pressure Hydrocracking
MOGD	Mobil Olefin to Gasoline and Distillate Process
MRDC	Mobil Research And Development Corporation
MTG	Methanol-To-Gasoline process
MW	Molecular Weight, (g/mol)
NDIR	Non-Dispersed Infra-Red
SASOL	South African Coal, Oil and Gas Corporation, Ltd.
SFT	Slurry Fischer-Tropsch
SMP	Sintered-Metal-Plate
SV	Space Velocity, (NL/gFe-hr)
TBP	True Boiling Point

Superscripts

i At reactor inlet
e At reactor exit
* At gas-liquid interface

Subscripts

c Catalyst
g Gas
i Components, $i = 1, 2, 3, 4$ for H_2 , CO, CO_2 ,
 H_2O , respectively
L Liquid
L Large bubble
S Small bubble
o At $t=0$

XI. References

- Abou-El-Hassan, M. E., Chem. Eng. Commun., 22, 243 (1983).
- Akita, K., and Yoshida, F., Ind. Eng. Chem., Proc. Des. Dev., 12, 76 (1973).
- Anderson, R. B., in: Catalysis IV, Emmett, P. H., Ed., Reinhold Publishing, New York, NY (1956).
- Bach, H. F., and Pilhofer, T., Germ. Chem. Eng., 1, 270 (1978).
- Bhavaraju, S. M., Russel, T. W. F., and Blanch, H. W., AIChE J., 24, 454 (1978).
- Brink, A., Preprint N.85-1, 50th API Refining Department Mid-Year Meeting, Kansas City, MO, May 13-16, 1985.
- Calderbank, P. H., Evans, F., Farley, R., Jepson, G., and Poll, A., Catalysis in Practice, Sym. Proc. (Instr. Chem Engrs., London), p. 60, (1963).
- Cova, D. R., Ind. Eng. Chem., Proc. Des. Dev., 5, 20 (1966).
- Cunningham, R. G., Trans. ASME, 73, 625 (1951).
- Deckwer, W.-D., Kokuun, R., Ledakowicz, S., and Sanders, E., Session 14, Paper 14d, AIChE National Meeting, Philadelphia, PA, August 19-22, 1984.
- Deckwer, W.-D., Louisi, Y., Zaidi, A., and Ralek, M., AIChE Annual Meeting, Session 76 (Group 1b), Paper A1, San Francisco, CA, November 25-29, 1979.
- Ibid, Ind. Eng. Chem., Proc. Des. Dev., 19, 699 (1980).
- Deckwer, W.-D., Serpemen, Y., Ralek, M., and Schmidt, B., Chem. Eng. Sci., 38, 791 (1981).
- Ibid, Ind. Eng. Chem., Proc. Des. Dev., 21, 222 (1982).
- Fair, J. R., Chemical Engineer, July 3, 67 (1967).
- Farley, R., and Ray, D. J., J. Inst. Pet., 50, 27 (1964).
- Fischer, F., and Tropsch, H., Brennstoff Chem., 4, 276 (1923).

- Flory, P. J., Principles of Polymer Chemistry, Cornell University Press, Ithaca, NY (1967).
- Gestrich, W., and Raehse, W., Chem. Ing. Tech., 47, 8 (1975).
- Godbole, S. P., Monath, M. F., and Shah, Y. T., Chem. Eng. Commun., 16, 119 (1982).
- Gray, D., Lytton, M., Neuworth, M., and Tomlinson, G., "The Impact of Developing Technology on Indirect Liquefaction," the MITRE Corp., Final Report (MTR-80W326), DOE Contract No. EF-77-C-01-2783, November 1980.
- Hughmark, G. A., Ind. Eng. Chem., Process Des. Dev., 6, 211 (1967).
- Joshi, J. B., Pandit, A. B., and Sharma, M. M., Chem. Eng. Sci., 37, 813 (1982).
- Kam, A. Y., and Lee, W., "Fluid Bed Process Studies on Conversion of Methanol to High Octane Gasoline," Mobil Research and Development Corp., Final Report (FE-2490-15), DOE Contract No. EX-76-C-01-2490, April 1978.
- Kastanek, F., Zahradnik, J., Rylek, M., and Cermak, J., Int. Chem. Eng., 20, 56 (1980).
- Koelbel, H., Ackerman, P., and Engelhardt, F., Proceeding of Fourth World Petroleum Congress, Section IV/C, p. 227, Carlo Colombo Publishers, Rome (1955).
- Koelbel, H., Hammer, H., and Langemann, H., Chemiker ZTG/Chem. Appar., 92, 581 (1968).
- Koelbel, H., and Ralek, M., Cat. Rev. - Sci. Eng., 21, 225 (1980).
- Kuo, J. C. W., "Slurry Fischer-Tropsch/Mobil Two-Stage Process of Converting Syngas to High Octane Gasoline," Mobil Research and Development Corp., Final Report (DOE/PC/30022-10), DOE Contract No. DE-AC22-80PC30022, June 1983.
- Kuo, J. C. W., Chap. 5, "Gasification and Indirect Liquefaction," in: The Science and Technology of Coal and Coal Utilization, Ed. by B. R. Cooper and W. A. Ellingson, Plenum Pub. Corp., New York, NY (1984).

- Kurten, H., and Zehner, P., *Germ. Chem. Eng.*, 2, 220 (1979).
- Langemann, H., and Koelbel, H., *Verfahrenstechnik*, 1, 5 (1967).
- Ledakowicz, S., Nettelhoff, H., Kokuun, R., and Deckwer, W.-D., *Ind. Eng. Chem., Proc. Des. Dev.*, 24, 1,043 (1985).
- Lehrer, L. H., *Ind. Eng. Chem., Proc. Des. Dev.*, 10, 37 (1971).
- Levenspiel, O., *The Chemical Reactor Omnibook*, OSU Book Stores, Inc., Corvallis, OR, p. 64.7 (1979).
- Mashelkar, R. A., *British Chem. Engng.*, 15, 1,297 (1970).
- Meisel, S. L., McCullough, J. P., Lechthaler, C. H., and Weisz, P. B., *Chem. Tech.*, 6, 86 (1978).
- Mendelson, H. D., *AIChE J.*, 13, 250 (1967).
- Mersmann, A., *Chem. Ing. Tech.*, 49, 679 (1977).
- Miller, D. N., *AIChE J.*, 20, 445 (1974).
- Nagel, E. J., Kirillov, V. A., and Ray, W. H., *Ind. Eng. Chem., Prod. Res. Dev.*, 19, 372 (1980).
- Newsome, D. S., *Cat. Rev. - Sci. Eng.*, 21, 275 (1980).
- Ostergaard, K., in: *Advances in Chemical Engineering*, Vol. 7, Academic Press, New York, NY (1980).
- Perry, J. H., Ed., *Chemical Engineers Handbook*, McGraw-Hill, New York, NY, Fifth Edition, pp. 5-11 to -13 (1973).
- Pilhofer, T., Bach, H. F., and Mangartz, K. H., *ACS Symposium Series 68*, Washington, DC, Paper #31, p. 372, (1978).
- Podolski, W. F., and Kim, Y. G., *Ind. Eng. Chem., Proc. Des. Dev.*, 13, 415 (1974).
- Quicker, G., and Deckwer, W.-D., *Chem. Eng. Sci.*, 36, 1,579 (1981a).
- Ibid*, *Chem. Ing. Tech.*, 53, 474 (1981b).

Schreiner, M., "Research Guidance Studies to Assess Gasoline from Coal by Methanol to Gasoline and SASOL-Type Fischer-Tropsch Technologies," Mobil Research and Development Corp., Final Report (FE-2447-13), DOE Contract No. EF-76-C-01-2447, August 1978.

Shah, Y. T., and Deckwer, W.-D., in: Scaleup of Chemical Processes, Ed. by A. Risio, John Wiley and Sons, New York, NY (1985).

Shah, Y. T., Kelkar, B. G., Godbole, S. P., and Deckwer, W.-D., AICHE J., 28, 353 (1982).

Shinnar, R., and Kuo, J. C. W., "Gasifier Study for Mobil Coal to Gasoline Processes," Mobil Research and Development Corp., Final Report (FE-2766-13), DOE Contract No. EF-77-C-01-2766, October 1978.

Sriram, K., and Mann, R., Chem. Eng. Sci., 32, 571 (1977).

Storch, H. H., Golumbic, N., and Anderson, R. B., The Fischer-Tropsch and Related Syntheses, John Wiley and Sons, New York, NY (1951).

Van Landeghem, H., Chem. Eng. Sci., 35, 1,912 (1980).

Voltz, S. E., and Wise, J. J., "Development Studies on Conversion of Methanol and Related Oxygenates to Gasoline," Mobil Research and Development Corp., Final Report (FE-1773-25), ERDA Contract No. E(49-18)-1773, November 1976.

Wise, J. J., and Silvestri, A. J., Oil and Gas J., 140 (November 22, 1976).

Zaidi, A., Louisi, Y., Ralek, M., and Deckwer, W.-D., Ger. Chem. Eng., 2, 94 (1979).