weight products at high values of P_{H_2}/P_{CO} . Studies of the extent to which 1-alkene incorporation is affected by process variables such as temperature and total pressure may provide fundamental insight into the effects of process variables on the selectivity of the synthesis.

.

Conclusions

The product distributions of the Fischer-Tropsch synthesis on a cobalt catalyst were studied in a continuous-flow, well-stirred slurry reactor at 220 to 240°C and 0.5 to 1.5 MPa. Synthesis gas with H_2/CO ratios between 1.5 and 3.5 was fed to the reactor over a wide range of space velocities yielding H_2 conversions between 6 and 68% and CO conversions between 11 and 73%.

The relative production of $C_{10}+$ on a weight basis increased with increasing space velocity and decreasing reactor H_2/CO , but was independent of reactor pressure or temperature. Conversely, the relative yield C_1 on a weight basis decreased with increasing space velocity and decreasing reactor H_2/CO , and was also relatively insensitive to reactor pressure or temperature.

Above C_3 , the 1-alkene/n-alkane ratio decreased with increasing carbon number. Hydrogenation modelling indicates that a large fraction of the n-alkanes were synthesized by hydrogenation of 1-alkenes, a primary synthesis product. Increasing the reactor H_2/CO ratio decreased the 1-alkene/n-alkane ratio, while increased concentrations of CO in the reactor inhibited the isomerization of 1-alkenes to 2-alkenes.

Acknowledgement. This study was supported by the Office of Fossil Energy, U.S. Department of Energy, under contract No. DE-AC22-87PC79816.

Literature Cited

- (1) Herington, E.F.G. Chemistry and Industry 1946, 65, 346.
- (2) Anderson, R.B. The Fischer-Tropsch Synthesis; Harcourt, Brace & Jovanovich: New York, 1984.
 - (3) Donnelly, T.J.; Yates, I.C.; Satterfield, C.N. Energy & Fuels 1988, 2, 734.
 - (4) König, L.; Gaube, J. Chem.-Ing. Tech. 1983, 55, 14.
 - (5) Huff, G.A., Jr.; Satterfield, C.N. J. Catal. 1984, 85, 370.
 - (6) Dictor, R.A.; Bell, A.T. J. Catal. 1986, 97, 121.
 - (7) Donnelly, T.J.; Satterfield, C.N. Appl. Catal. 1989, 52, 93.
- (8) Schulz, H. Report to the Bundesministerium für Forschung und Technologie, "Katalysatoren und Selektivitätslenkung bei der Fischer-Tropsch-Synthese," BMFT-FB-T 80-124, Nov., 1980.
 - (9) Yates, I.C.; Satterfield, C.N. to be submitted.
- (10) Storch, H.H.; Golumbic, N.; Anderson, R.B. The Fischer-Tropsch and Related Syntheses; John Wiley and Sons: New York, 1951.
- (11) Borghard, W.G.; Bennett, C.O. Ind. Eng. Chem. Process Res. and Dev., 1979, 18, 18.
 - (12) Rautavuoma, A.O.I.; van der Baan, H.S. Appl. Cat., 1981, 1, 247.
- (13) Beuther, H.; Kibby, C.L.; Kobylinski, T.P.; Pannell, R.B. United States Patent 4.399.234, August 16, 1983.
- (14) Schulz, H.; Rosch, S.; Gokcebay, H. Proceedings 64th CIC Coal Symposium-A.M. Al Taweel, ed., <u>C.S.Ch.E.</u>, Ottawa (1982).

- (15) Sarup, B.; Wojciechowski, B.W. Can, J. Chem. Eng., 1984, 62, 249.
- (16) Fu, L.; Rankin, J.L.; Bartholomew, C.H. C1 Mol. Chem., 1986, 1, 369.
- (17) Huff, G.A., Jr.; Satterfield, C.N. Ind. Eng. Chem. Fund., 1982, 21, 479.
- (18) Donnelly, T.J.; Satterfield, C.N. Appl. Catal. 1989, <u>56</u>, 231.
- (19) Huff, G.A., Jr.; Satterfield, C.N. Ind. Eng. Chem. Process Des. Dev., 1984, 23, 696.
- (20) Huff, G.A., Jr. Fischer-Tropsch Synthesis in a Slurry Reactor, Sc.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1982.
- (20a) Huff, G.A., Jr.; Satterfield, C.N.; M.H. Wolf, Ind. Eng. Chem. Fund., 1983, 22, 258
- 22, 258.
 (21) Matsumoto, D.K., The Effects of Selected Process Variables on the
 Performance of an Iron Fischer-Tropsch Catalyst, Sc.D. Thesis, Massachusetts Institute of
 Technology, Cambridge, Massachusetts, 1987.
 - (22) Donnelly, T.J., <u>Product Distributions of the Fischer-Tropsch Synthesis</u>, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1989.
 - (23) Yates, I.C., <u>The Slurry-Phase Fischer-Tropsch Synthesis</u>, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1990.
 - (24) Yates, I.C.; Satterfield, C.N. Energy & Fuels, 1991, 5, 168.
 - (25) Hanlon, R.T.; and Satterfield, C.N. Energy & Fuels, 1988, 2, 196.

Figure Captions

- Figure 1 Representative Schulz-Flory Diagram showing a double- α -type distribution (220°C, 1.48 MPa, feed rate = 0.032 Nl/min/gcat). (H₂/CO)_{in} = 1.64. (H₂/CO) in reactor = 1.65. α_1 = 0.54, α_2 = 0.91, and Ω = 5.4.
- Figure 2 Representative Schulz-Flory Diagram showing a double- α -type distribution (230°C, 0.79 MPa, feed rate = 0.020 Nl/min/gcat). (H₂/CO) in reactor = 1.39. (H₂/CO)_{in}=1.55. α_1 =0.54, α_2 =0.88, and Ω =5.
- Figure 3 Schulz-Flory diagram for reactor liquid at completion of run. $\alpha_2 = 0.87$.
- Figure 4 The C_{10} + yield is greater at higher space velocities. Data at 240°C, 0.79 MPa, and $(H_2/CO)_{in} = 2$.
- Figure 5 Pressure has no noticeable effect on the product distribution.

 Data at 220°C and feed rate of 0.017-0.018 Nl/min/gcat. $(H_2/CO)_{in} = 2$.
- Figure 6 Temperature has no effect on product distributions. Total synthesis gas conversions are between 31 and 33%, allowing comparison of similar product to reactant ratios.
- Figure 7 Weight fraction of C₁ increases with increasing H₂/CO ratio, 220°C.
- Figure 8 Weight fraction of C₁₀+ decreases with increasing H₂/CO ratio, 220°C.
- Figure 9 Component product distribution showing primary products, n-alkanes, 1-alkenes, and n-alcohols (220°C, 1.48 MPa, and feed rate of 0.015 Nl/min/gcat). $(H_2/CO)_{in} = 1.66$.

- Figure 10 Component product distribution showing primary products, n-alkanes, 1-alkenes, and n-alcohol (240°C, 0.79 MPa, and feed rate of 0.035 Nl/min/gcat). (H₂/CO)_{in}=2.15.
- Figure 11 The rate of methane plus methanol formation is well fitted by equation 1.
- Figure 12 Rate of formation of C_2 + compounds is well fitted by equation 1.
- Figure 13 Most ethane is produced from ethene, according to a simple hydrogenation model, data at 220°C.
- Figure 14 Most n-butane is produced from 1-butene, according to a simple hydrogenation model, data at 220°C.
- Figure 15a Most 2-butene is produced from 1-butene, according to a simple isomerization model (see equation 2), 220°C.
- Figure 15b Most 2-butene is produced from 1-butene, according to a simple isomerization model (see equation 2), 240°C.

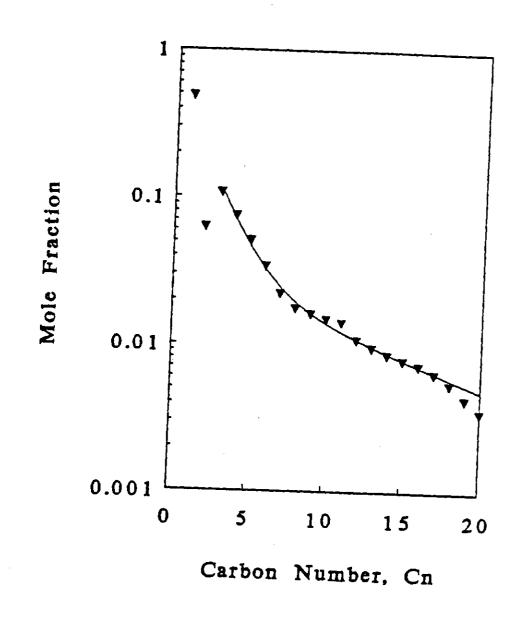


Figure 1 Representative Schulz-Flory Diagram showing a double- α -type distribution (220°C, 1.48 MPa, feed rate = 0.032 Nl/min/gcat). (H₂/CO)_{in} = 1.64. (H₂/CO) in reactor = 1.65. α_1 = 0.54, α_2 = 0.91, and Ω = 5.4.

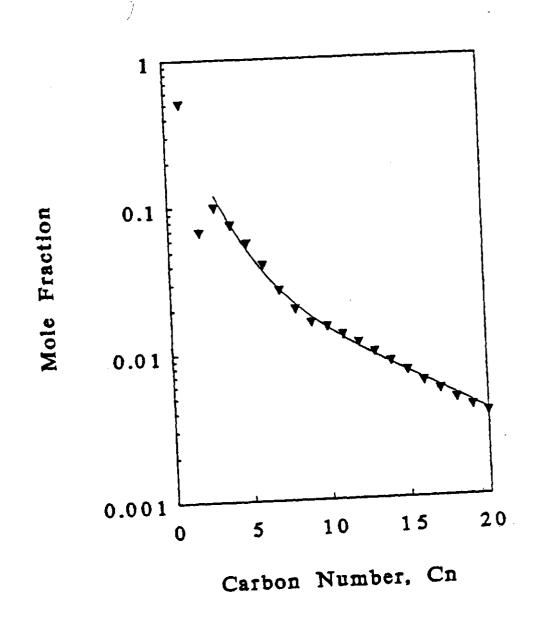


Figure 2 Representative Schulz-Flory Diagram showing a double- α -type distribution (230°C, 0.79 MPa, feed rate = 0.020 Nl/min/gcat). (H₂/CO) in reactor = 1.39. (H₂/CO)_{in}=1.55. α_1 =0.54, α_2 =0.88, and Ω =5.

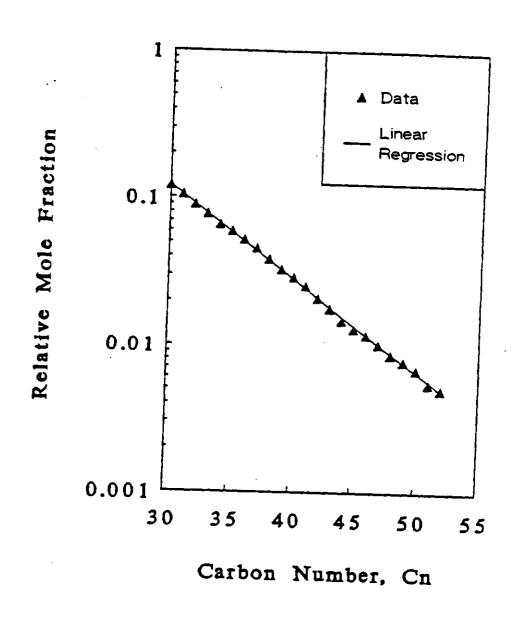


Figure 3 Schulz-Flory diagram for reactor liquid at completion of run. $d_2 = 0.87$

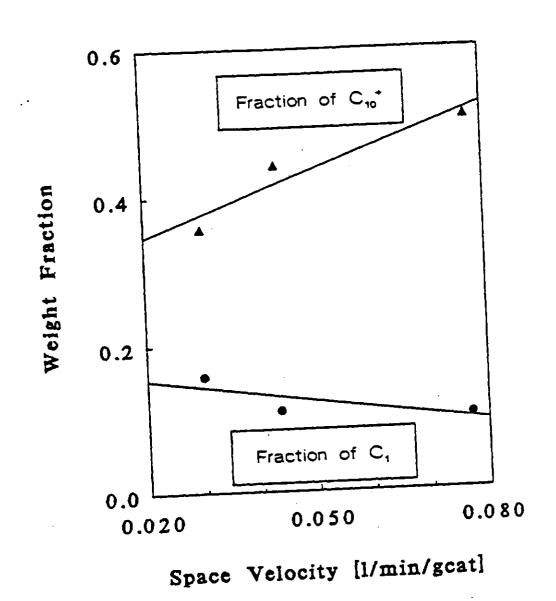


Figure 4 The C_{10} + yield is greater at higher space velocities. Data at 240°C, 0.79 MPa, and $(H_2/CO)_{in}=2$.

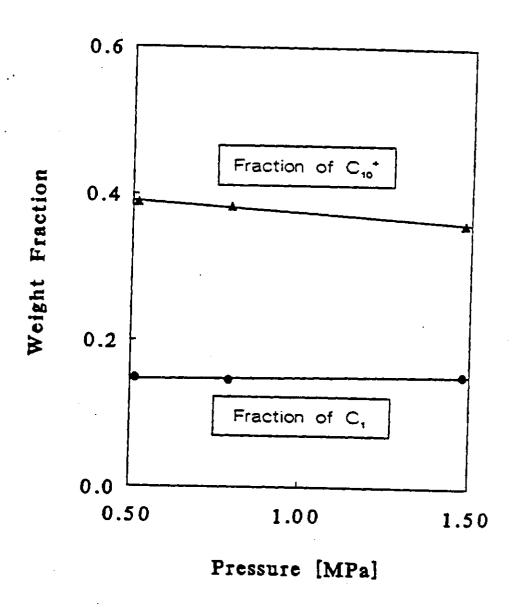


Figure 5 Pressure has no noticeable effect on the product distribution. Data at 220°C and feed rate of 0.017-0.018 Nl/min/gcat. $(H_2/CO)_{in}=2$.

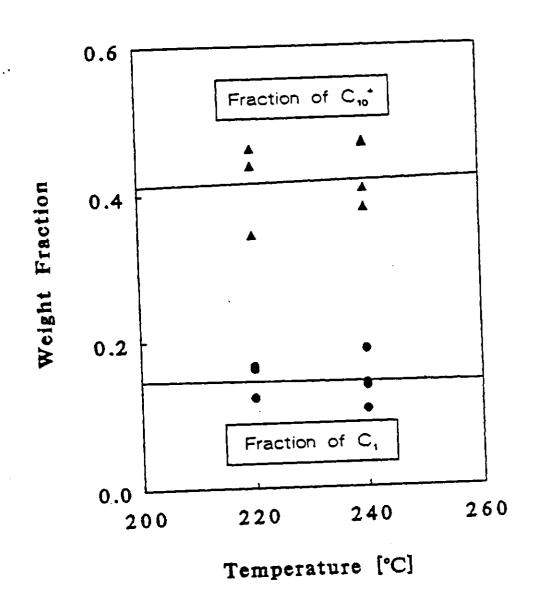


Figure 6 Temperature has no effect on product distributions. Total synthesis gas conversions are between 31 and 33%, allowing comparison of similar product to reactant ratios.

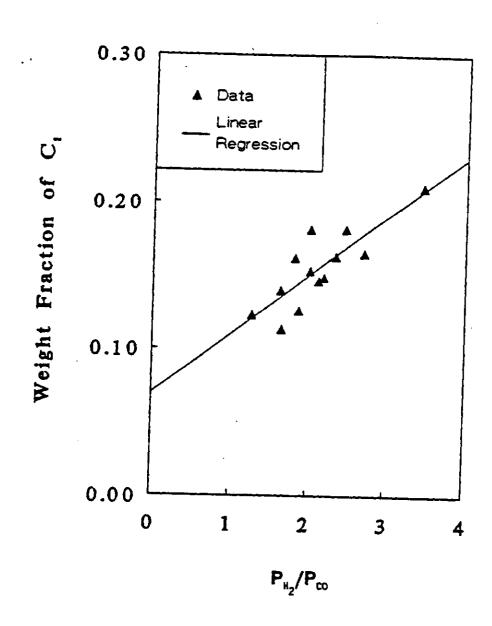


Figure 7 Weight fraction of C₁ increases with increasing H₂/CO ratio, 220°C.

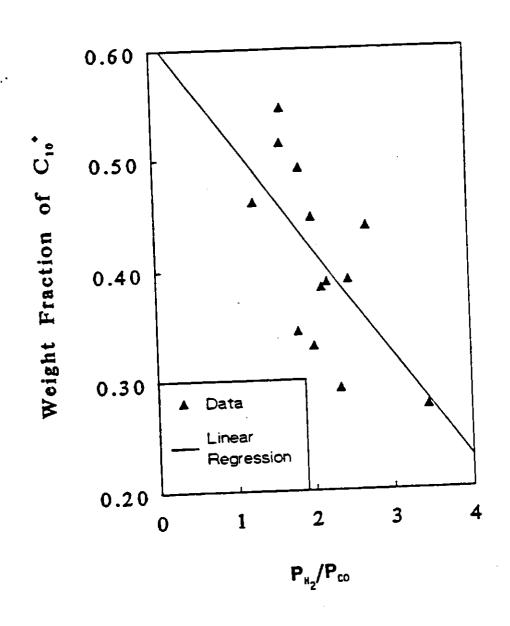


Figure 8 Weight fraction of C₁₀+ decreases with increasing H₂/CO ratio, 220°C.

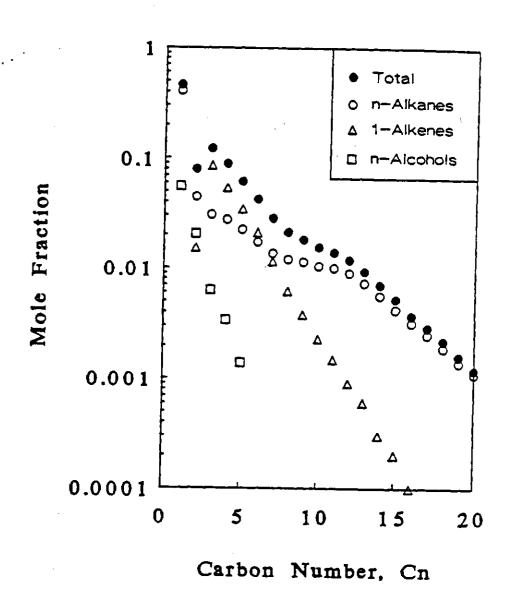


Figure 9 Component product distribution showing primary products, n-alkanes, 1-alkenes, and n-alcohols (220°C, 1.48 MPa, and feed rate of 0.015 Nl/min/gcat). (H₂/CO)_{in} = 1.66.

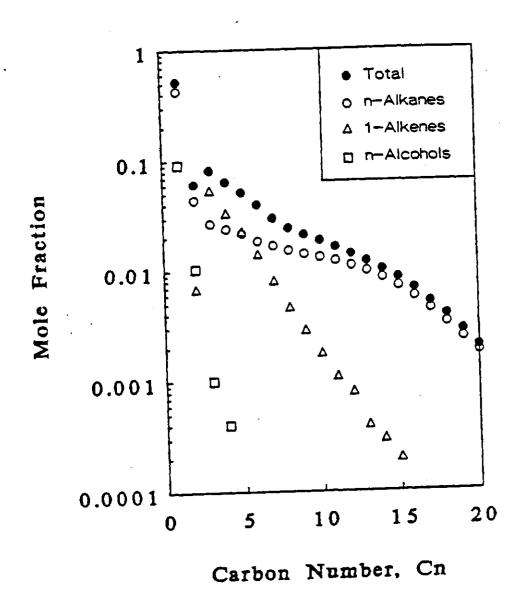


Figure 10 Component product distribution showing primary products, n-alkanes, 1-alkenes, and n-alcohol (240°C, 0.79 MPa, and feed rate of 0.035 Nl/min/gcat). (H₂/CO)_{in}=2.15.

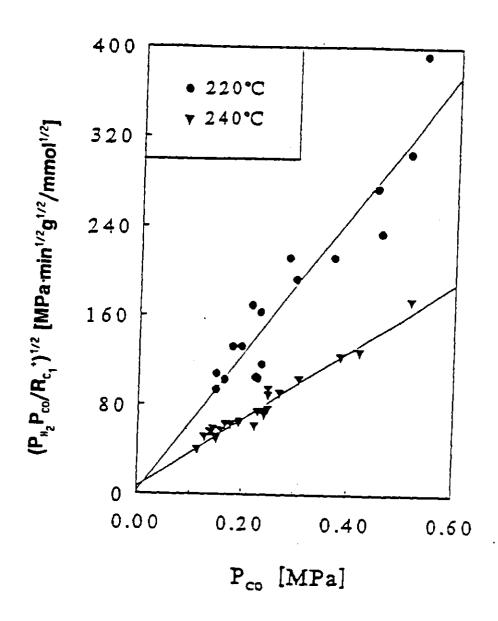


Figure 11 The rate of methane plus methanol formation is well fitted by equation 1.

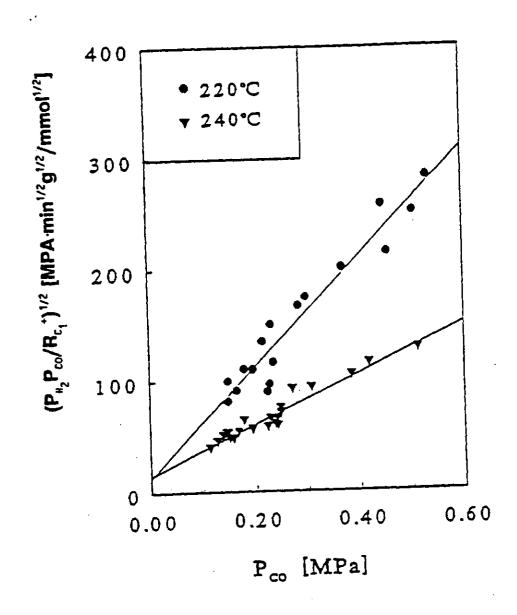


Figure 12 Rate of formation of C_2 + compounds is well fitted by equation 1.

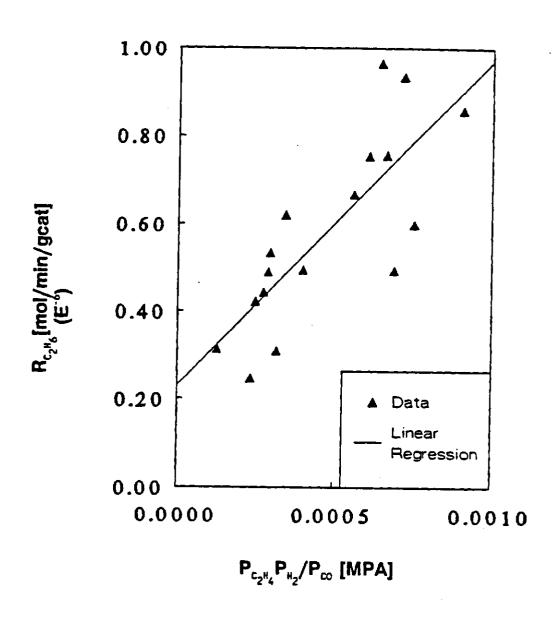


Figure 13 Most ethane is produced from ethene, according to a simple hydrogenation model, data at 220°C.

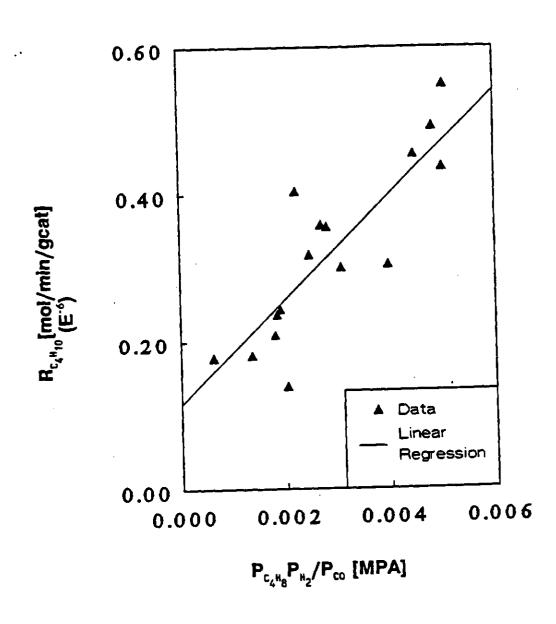


Figure 14 Most n-butane is produced from 1-butene, according to a simple hydrogenation model, data at 220°C.

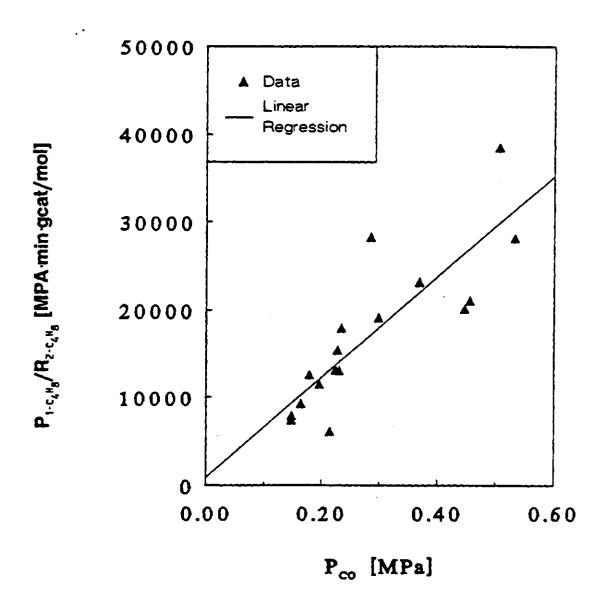
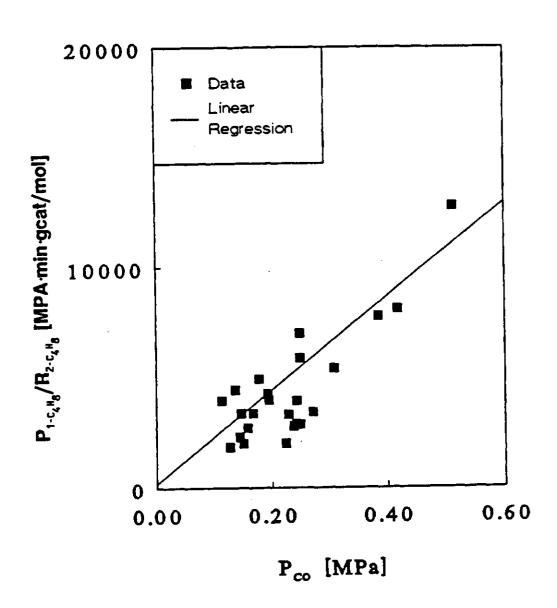


Figure 15a Most 2-butene is produced from 1-butene, according to a simple isomerization model (see equation 2), 220°C.



M

Figure 15b Most 2-butene is produced from 1-butene, according to a simple isomerization model (see equation 2), 240°C.