

1973

9. Huebler, J. and Tsaros, C. L. "Coal Gasification Developments," paper presented at the National Meeting of the American Association of Petroleum Geologists, Anaheim, (1973) May 15.
10. Schora, F. C. "Technical and Historical Background," in Symposium Papers: Clean Fuels From Coal, 43-48. Chicago: Institute of Gas Technology (1973).
11. Schora, F. C., Lee, B. S. and Huebler, J. "The HYGAS Process," paper presented at the 12th World Gas Conference, Nice, France (1973).
12. Herwijnen, T., Doesburg, H. and De Jong, W. A. "Kinetics of the Methanation of CO and CO₂ on a nickel Catalyst," Jour. of Catalysis, 28 391-402 (1973).
13. Synthetic Gas-Coal Task Force for the Supply-Technical Advisory Committee, National Gas Survey, Federal Power Commission. Final Report: The Supply-Technical Advisory Task Force - Synthetic Gas-Coal (1973) April.
14. Gregory, D. P. IGT Technical Report No. 11: Thermodynamic Properties of a Lean Natural Gas at Cryogenic Conditions, Institute of Gas Technology, Chicago (1973) March.
15. Linden, H. R. and Parent, J. D. "Analysis of World Energy Supplies," paper presented at the Conference on Energy. Mass. Inst. Tech., Cambridge, Mass., (1973) February 12-14.

1972

16. Feldkirchner, H. L. and Schora, F. C. "Coal Desulfurization Aspects of the HYGAS Process," Proceedings, Second International Conference on Fluidized-Bed Combustion, U. S. Environmental Protection Agency Publication No. AP-109, 111-2-1-9. Research Triangle Park, N. C.: U. S. Environmental Protection Agency (1972).
17. Rostrup-Nielsen, J. R. "Equilibria of Decomposition Reactions of Carbon Monoxide and Methane Over Nickel Catalysts," Jour. Catalysis 27 343-56 (1972).
18. Choudhary, V. R. and Doraiswamy, L. K. "Development of Continuous-Stirred Gas-Solid Reactors for Studies in Kinetics and Catalyst Evaluation," Ind. Eng. Chem. Process Des. Develop. 11:3 420-427, (1972).
19. Vahala, J. "Methanation Catalysis. III. Thermally Stable Catalysts," Int. Chem. Eng. 12:1 60-8 (1972).
20. Schora, F. C. and Matthews, C. W. "Analysis of a HYGAS Coal Gasification Plant Design," paper presented at the 65th Annual Meeting of the American Institute of Chemical Engineers, New York, (1972) November 27-30.

21. Linden, H. R. "The Future Development of Energy Supply Systems," paper presented at the Fuel Conference in Commemoration of the Golden Jubilee of the Fuel Society of Japan, Tokyo, (1972) October 31 to November 2.
22. Lee, B. S. "Status of HYGAS, Electrothermal Gasification, and Steam-Oxygen Gasification Programs," Proceedings of the Fourth Synthetic Pipeline Gas Symposium, Chicago, October 30-31, 1972, 7-16. Arlington, Va: American Gas Association (1973).
23. Johnson, J. L., Schora, F. C. and Tarman, P. B. "Apparatus for Conducting a Continuous Steam-Iron Process." U. S. Patent 3,700,421, (assigned to Consolidation Coal Co.) (1972) October 24.
24. Randhava, S. S. "Method for Selective Methanation of Gaseous Mixture Containing Carbon Monoxide." U. S. Patent 3,663,162, (1972) May 16.
25. Schora, F. C. "Syngas From Coal," paper presented at the Natural Gas Processors Association, New Orleans, La., (1972) April 10-12.
26. Linden, H. "The Outlook for Synthetic Fuels," paper presented at the 2nd Annual Meeting, Division of Production, Amer. Petr. Inst. (Dallas) (1972) March 6-8.
27. Institute of Gas Technology Research Bulletin No. 39: Production of Pipeline Gas by Hydrogasification of Coal, Chicago (1972).

1971

28. Subramaniam, T. K. and Tsaros, C. L. Effect of Accounting Factors on the Economics of Synthetic Pipeline Gas, Office of Coal Research R&D Report No. 22, Interim Report No. 5. Washington, D. C. : U. S. Government Printing Office (1971).
29. Kavlick, V. J., Lee, B. S. and Schora, F. C. "Electrothermal Coal Char Gasification." American Institute of Chemical Engineers Symposium Series 67:116 228-35 (1971).
30. Tsaros, C. L. and Subramaniam, T. K. "Electrothermal HYGAS Process Escalated Costs." Office of Coal Research R&D Report No. 22, Interim Report No. 6. Washington, D. C. : U. S. Government Printing Office (1971).
31. Janka, J. C. and Malhotra, R. "Estimation of Coal and Gas Properties for Gasification Design Calculation," Office of Coal Research R&D Report No. 22, Interim Report No. 7. Washington, D. C. : U. S. Government Printing Office, (1971).
32. Linden, H. R. "Gasification of Coal," in Kirk-Othmer Encyclopedia of Chemical Technology, 2nd Ed., Supplement Vol., 198-217. New York: Wiley Interscience, (1971).

33. Vahala, J. "Methanation Catalysis: Part 1 – Precipitation on the Properties of Nickel-Chrome Catalysts," Int. Chem. Eng. 11:3 488-95 (1971).
34. Vahala, J. and Jadernik, P. "Methanation Catalysis. Part 2 – Effect of the Conditions of Reduction, Passivation, and Tableting on the Properties of Nickel-Chrome Catalysts," Int. Chem. Eng. 11:3 496-502 (1971).
35. Richardson, J. T. "Sulfiding of Nickel Catalyst Beds," J. Catalysis 21 122-29 (1971).
36. Richardson, J. T. "Dual-Functional Activities in Nickel Acid Catalysts," J. Catalysis 21 122-29 (1971).
37. Codell, R. B. and Engel, A. J. "A Theoretical Study of a Controlled-Cycle Stirred-Tank Reactor," AICHE Jour. 17:1 220-225 (1971).
38. Gioia, F. "Poisoning of Porous Catalyst Particles," IEC Fundam. 10:2 204-11 (1971).
39. JANAF Thermochemical Tables, Distributed by: Clearinghouse for Federal Scientific and Technical Information, Springfield, Va. (1971).
40. Csuha, R. S. and Happel, J. "Structure of Rate Equations for Heterogeneous Catalysis," AICHE Jour. 17:4 927-32 (1971).
41. Koestenblatt, S. and Ziegler, E. N. "Kinetics and Deactivation on Large Catalytic Particles," AICHE Jour. 17:4 891-98 (1971).
42. Matthews, C. W. "Coal Gasification by the IGT HYGAS Process," Proceedings, Gas Appliance Engineers Society Annual Conference 58-77 (1971).
43. Linden, H. R. "Gasification of Coal and Hydrocarbons," A. G. A. Monthly 53, 35-36 (1971) December.
44. Lee, B. S. "Status of the HYGAS Process, Proceedings of the 3rd Synthetic Pipeline Gas Symposium, Rosemont, Ill., (1970) November 17-18, 99-197. Arlington, Va.: American Gas Association (1971).
45. Lee, B. S. "Development of the HYGAS Process for Converting Coal to Synthetic Pipeline Gas," Preprint SPE-3587, presented at the 46th Annual Fall Meeting of the Society of Petroleum Engineers of AIME, New Orleans, October 3-6, 1971; and Journal of Petroleum Technology 24, 1407-10 (1972) December.
46. Adams, H. W., van Heek, K. H. and Sulimma, A. "Untersuchungen an Amerikanischen Kohlen und Deren Vergasungstückstanden, "entwicklung von Verfahren zur Umwandlung fester Fossiler Rohstoffe mit Wärme Aus Hocheemperatur-Kernreaktoren, (1971) June 23.

47. Schora, F. C. "Studies of Coal Gasification," paper presented at the Synthetic Fuels From Coal Conference, Univ. Oklahoma (Stillwater) (1971) May 3.
48. Chase, V. D. Editor "Dole Calls for Coal Gasification to Become Model Industry," Institute of Gas Technology Gas Scope 17, 6, 8-11 (1971) January-February.
49. Chase V. D. Editor "Coal Gasification Pilot Plant Soon to Be in Full Operation," (Institute of Gas Technology) Gas Scope 17 1-5 (1971) January-February.

1970

50. Subramaniam, T. K. and Tsaros, C. L. "The Effect of Accounting Factors on the Economics of Synthetic Pipeline Gas," OCR R&D Report No. 22, Interim Report No. 5, Washington, D. C. : Office of Coal Research, (1970).
51. Lee, A. L., Feldkirchner, H. L. and Tajbl, D. G. "Methanation for Coal Hydrogasification," paper presented at the Joint Meeting of Fuel Chemistry and Petroleum Chemistry of the ACS, Chicago, (1970) September.
52. Curran, G. P. and Gorin, E. "Phase II, Bench-Scale Research on CSG Process - Laboratory Physico-Chemical Studies," OCR R&D Report No. 16, Interim Report No. 3, Book 2, Washington, D. C. : U. S. Government Printing Office, 1970.
53. Lee, B. S., Pyrcioch, E. J. and Schora, F. C. "Hydrogasification of Coal in High-Pressure Fluidized Bed," Chem. Eng. Sym. Series 66:105 152-6 (1970).
54. Lee, B. S. "Synthetic Pipeline Gas From Coal by the HYGAS Process." Proceedings of the American Power Conference 32, 421-27 1970.
55. Aldridge, C. L. "Preventing Catalyst Poisoning by Sulfur," U. S. Patent 3,539,297. (1970) November 10.
56. Tsaros, C. L. "Hydrogen: A Key to the Economics of Pipeline Gas From Coal," paper presented at the 158th National Meeting of the Division of Fuel Chemistry of the American Chemical Society (Chicago) (1970) September 13-18.
57. Haynes, W. P., et al. "Operation of a Sprayed Raney Nickel Tube-Wall Reactor for Production of a High-Btu Gas," ACS Division of Fuel Chem. 14:4 26-48, Chicago (1970) September.
58. Linden, H. R. "Current Trends in U. S. Gas Demand and Supply," Public Util. Fortn. 86 27-38 (1970) July 30.
59. Mason, D. M. "Reflectance of Low-Rank Coals," American Chemical Society Division of Fuel Chemistry Preprints 14:1 75-80 (1970) May.

1969

60. Schoubye, P. "Methanation of CO on Some Ni Catalysts," J. Catalysis 14 238-46 (1969).
61. Caldwell, A. D. and Calderbank, P. H. "Catalyst Dilution - A Means of Temperature Control in Packed Tubular Reactors," Brit. Chem. Eng. 14:9 4, 70-2 (1969).
62. Andrew, S. P. S. "Catalysts and Catalytic Processes in the Steam Reforming of Naphtha," I. EC Proc. Res. Develop. 8, 321-24 (1969).
63. Linden, H. R. "Coal Gasification and the Coal Mining Industry," SME Preprint 69-F-22, presented at the 98th Annual Meeting of the American Institute of Mining, Metallurgical and Petroleum Engineers. Washington, D. C., February 16-20, 1969; Published as: "Coal Gasification and the Coal Mining Industry," Transactions of the Society of Mining Engineers of AIME 244, 417-26 (1969) December.
64. Sastry, N. V. S., Mallikarjunan, M. M. and Vaidyeswaran, R. "Kinetic Investigations of Hydrogasification of Semicoke in an Integral Reactor," Brennst.-Chem. 50, 363-67 (1969) December (German test).
65. Schora, F. C. "Present Status of the IGT Hydrogasification Process," Proceedings of Second Synthetic Pipeline Gas Symposium (Pittsburgh), November 22, 1968, 5-19. New York: American Gas Association (1969).
66. Tsaros, C. L., Arora, J. L. and Bodle, W. W. "Sulfur Recovery in the Manufacture of Pipeline Gas From Coal," American Chemical Society Division of Fuel Chemistry Preprints 13:4 252-69 (1969) September; I&EC Product Research and Development 9, 362-68 (1970) September.
67. Zahradnick, R. L. and Glenn, R. A. "Direct Methanation of Coal," paper presented at 158th National Meeting of the American Chemical Society, Division of Fuel Chemistry, New York, (1969) September 7-12.
68. Lee, B. S., Pyrcioch, E. J. and Schora, F. C. "Hydrogasification of Coal in High-Pressure Fluidized Bed," Preprint 45b, 64th National Meeting of the American Institute of Chemical Engineers (New Orleans) (1969) March 16-20; Chemical Engineering Progress Symposium Series 66:105 152-56 (1970).
69. Kavlick, V. J. and Lee, B. S. "High-Pressure Electrothermal Fluid-Bed Gasification of Coal Char," Preprint 45d 64th National Meeting of the American Institute of Chemical Engineers (New Orleans) (1969) March 16-20; Chemical Engineering Progress Symposium Series 66:105 145-51 (1970).
70. Feldkirchner, H. L., Linden, H. R., Kahn, A. R. and Todesca, F. "Steam-Reforming of Hydrocarbons for Production of High Methane Content Gas," U. S. Patent 3,433,610, (1969) March 19.

71. Schora, F. C. and Lee, B. S. "IGT Hydrogasification Process." Preprint 29b 65th National Meeting of the American Institute of Chemical Engineers, Cleveland (1969) May 4-7.
72. Schora, F. C. "IGT Hydrogasification Process," American Gas Association Monthly 51, 90-0 (1969) February.
73. Schora, F. C. "Hydrogasification Process," SME Preprint 69 - AIME-92 98th Annual Meeting of the American Institute of Mining, Metallurgical and Petroleum Engineers, Washington, D. C., (1969) February 16-20.
74. Ballain, M. D. and Pulsifer, A. H. "Electrode Temperature and Resistance of an Electrothermal Fluidized Bed," paper presented at the 62nd Annual Meeting of A.I. Ch. E., Washington, D. C., (1969) November 16-20.
- 1968
75. Tsaros, G. L. et al. "Cost Estimate of a 500 Billion Btu/day Pipeline Gas Plant Via Hydrogasification and Electrothermal Gasification of Lignite," Office of Coal Research, 1968, PB 193,928. National Technical Information Service, Springfield, Va. (1970).
76. Nicklin, T. and Whittaker, R. J. "The Influence of Uranium on Nickel/alpha-Alumina Catalysts," I. G. E. Jour. 8, Communication 755, 15-32 (1968).
77. Shendalman, L. H. "A Kinetic Theory of Catalysis and Mass Transfer in a Cylinder," AICHE Jour. 14:4 599-605 (1968).
78. Hammer, V. H. and Schmal, M. "Optimierung von Gas-Flussigphase-Reaktoren mit Suspendiertem Katalysator," Brennstoff-Chemie 49:8 225-256 (1968).
79. Lee, B. S., Pyrcioch, E. J. and Schora, F. C. "Electrical Resistivity of a High-Pressure Fluidized Bed," Preprint 29b 61st Annual Meeting of the American Institute of Chemical Engineers, Los Angeles (1968) December 1-5.
80. Mason, D. M. "Coal and Char Transformation in Hydrogasification-Lignite to Low-Volatile Bituminous Coal," American Chemical Society, Division of Fuel Chemistry Preprints 12:3 83-94 (1968) September; I&EC Process Design and Development 9, 298-303 (1970) April.
81. Lee, A. L. "Heat Capacity of Coal," American Chemical Society Division of Fuel Chemistry 12:3 19-31 (1968) September.
82. Wen, C. Y., et al. "Optimization of Fixed-Bed Methanation Processes," ACS Fuel Chemistry Preprints 12:3 104-163 (1968) September.
83. Feldkirchner, H. L. and Johnson, J. L. "High Pressure Thermo-balance," Rev. Sci. Instrum. 39, 1227-29 (1968) August.

84. Iowa State University, 2nd Quarterly Progress Report on Contract No. 14-01-0001-479, Dept. of the Interior, Office of Coal Research, Washington, D. C. (1968).

1967

85. Lee, A. L. et al. "Heat of Reaction of Hydrogen and Coal," ACS Preprints 11:2 393-401 (1967) April; I&EC Process Design and Development 7, 244-49 (1968) April.
86. Moseley, F. and Paterson, D. "The Rapid High-Temperature High-Pressure Hydrogenation of Bituminous Coal," J. Inst. of Fuel, 523-30 (1967).
87. Binford, Jr. J. S., Strohmenger, J. M. and Hebert, T. H. "A Modified Drop Calorimeter, The Heat Content of Aluminum Carbide and Cobalt (II) Fluoride Above 25°," J. Phy. Chem. 71, 2404-8 (1967).
88. Kanbel, S. J. and Tsaros, C. L. "Process Design and Cost Estimate for a 258 Billion Btu/Day Pipeline Gas Plant - Hydrogasification Using Synthesis Gas Generated by Electrothermal Gasification of Spent Char," R&D Rep. No. 22, Interim Report No. 3, Washington, D. C. : Office of Coal Research, 1967.
89. McKee, D. W. "Interaction of H₂ and CO on Platinum Group Metals," J. Catal. 8., 240-49 (1967).
90. Yamada, T., et al. "Co-Cu Catalyzer for Low Temperature Co-Conversion," Nagoya Institute of Tech. Bull. 19 (1967).
91. Feldkirchner, H. L., Linden, H. R. and Pyrcioch, E. J. "Conversion of Solid Fossil Fuels to High-Btu Pipeline Gas," U. S. Patent 3,347,647, (1967) October 17.
92. Blackwood, J. D., Cullis, B. D. and McCarthy, D. J. "Reactivity in the System Carbon-Hydrogen-Methane," Aust. J. Chem. 20, 1561-70 (1967) August.
93. Morlock, R. J., Naso, A. C. and Cameron, J. R. "Heat Requirements for Coking," presented at the Canadian Coal Conferences, Ottawa, Canada, (1967) March 30.
94. Iowa State University, Coal Processing by Electrofluidics Phase I Report (1967) May 11, 1965-April 1.

1966

95. Wen, A. C. Y., Abraham, O. C. and Talwalkar, A. T. "Kinetic Study of the Reaction of Coal Char with Hydrogen-Steam Mixtures," ACS Society Division of Fuel Chemistry Preprints 10:4 168-85 (1966) September; Advances in Chemistry Series 69, 251-71, American Chemical Society (1967).

96. Tsaros, C. L. and Joyce, T. J. "The Economics of Coal Hydrogasification," Proceedings of the Synthetic Pipeline Gas Symposium 43-56. New York: American Gas Association (1966).
97. Tsaros, C. L., Knable, S. J. and Sheridan, L. A. "Process Design and Cost Estimate for Production of 266 Million SCF/day of Pipeline Gas by the Hydrogasification of Bituminous Coal - Hydrogen by the Steam-Iron Process," Office of Coal Research, 1966. PB 174-064. Clearinghouse for Federal Scientific and Technical Information, 1966.
98. Takemura, Y., Morita, Y., and Yamamoto, K. "Reduction and Oxidation of Nickel-Aluminum Oxide Catalysts," Int. Chem. Eng. 6:4 725-36 (1966).
99. Skaperdas, G. T. "The Kellogg Coal Gasification Process," Proc. of Syn. Pipeline Gas Symp. AGA. 95-103 (1966) November.
100. Huebler, J. and Schora, F. C. "Coal Hydrogasification," Chem. Eng. Progr. 62 87 (1966).
101. Shultz, J. F. et al. "Kinetics of Gas Synthesis Using Recycle Systems," U.S. Dept. of the Interior, Bureau of Mines Report No. 694 (1967).
102. Lacey, J. A. "The Gasification of Coal in a Slagging Pressure Gasifier," ACS Preprints 10:4 151-167 (1966) September.
103. Schora, F. C. "Hydrogasification Process," Proceedings of the Synthetic Pipeline Gas Symposium, American Gas Association 3-11 (1966).
104. Kavlick, V. J. and Lee, B. S. "Coal Pretreatment in Fluidized Bed," ACS Preprints 10:4 131-39 (1966) September; Advances in Chemistry Series 69, 8-17, American Chemical Society (1967).
105. Phinney, J. A. "The CO₂ Acceptor Process - A Status Report," Proceedings of the Synthetic Pipeline Gas Symposium, American Gas Association 35-42 (1966) November.
106. Gasior, S. J., Forney, A. J. and Field, J. H. "Decaking of Coal in Free Fall," ACS Preprint 10:4 123-30 (1966).
107. Rich, J. and Newling, W. B. "Process for Reducing the Carbon Monoxide Content of Industrial Combustible Gases," British Patent 1,051,626 (1966) December 14.
108. Pyrcioch, E. J., Lee, B. S. and Schora, F. C. "Hydrogasification of Pretreated Coal for Pipeline Gas Production," Amer. Chem. Soc. ACS Preprints 10:4 206 (1966) September.
109. Glenn, R. A. et al. "Gasification of Coal Under Conditions Simulating Stage 2 of the BCR Two-Stage Super-Pressure Process," ACS Preprints 12:10 97-122 (1966) September.

110. Tajbl, D. G., Feldkirchner, H. L. and Lee, A. L. "Cleanup Methana-
tion for the Hydrogasification Process," ACS Preprints 10:4 235-45
(1966) September; also in Advances in Chemistry Series 69, 166-79.
American Chemical Society (1967).
111. Reed, A. K. and Goldberger, W. M. Chem. Eng. Progr. Symp.
Ser. 62, 71 (1966).
112. Graham, W. and Harvey, E. A. "Electrical Conductivity of Fluidized
Beds of Coke and Graphite up to 1200°F," Can. J. Chem. Eng. 44 17
(1966).
113. Mason, D. M. and Schora, F. C. "Coal and Char Transformation in
Hydrogasification," ACS Preprints 10:4 140-50 (1966) September:
Advances in Chemistry Series No. 69 18-30. American Chemical
Society (1967).
114. Tsaros, C. L. and Feldkirchner, H. L. "Production of High Btu Gas,"
Chemical Engineering Progress 62, 49-54 (1966) August.
115. Chambers, R. P. and Boudart, M. "Lack of Dependence of Conversion
of Flow Rate in Catalytic Studies," J. Catal. 6 141-45 (1966) August.
116. Dirksen, H. A. and Lee, B. S. "Balanced-Pressure Pilot Reactor,"
Chemical Engineering Progress 62 98-102 (1966) June.
117. Kipling, J. J. and Shooter, P. V. "Factors Affecting the Graphitization
of Carbon: Evidence From Polarized Light Microscopy," Carbon 4
1-4 (1966) May.
118. Blackwood, J. D. and McCarthy, D. J. "The Mechanism of Hydrogena-
tion of Coal to Methane," Aust. J. Chem. 19, 797-813 (1966) May.
119. Wen, C. Y. and Huebler, J. "Kinetic Study of Coal Char Hydrogasifi-
cation, Rapid Initial Research," Industrial and Engineering Chemistry
Process Design and Development 4, 142-47 (1966) April.
120. Linden, H. R. "Pipeline Gas From Coal: Status and Future Prospects,"
Coal Age 71 64-71 (1966) January.

1965

121. Tsaros, C. L., Knabel, S. J. and Sheridan, L. A. "Process Design
and Cost Estimate for Production of 265 Million SCF/Day of Pipeline
Gas by the Hydrogasification of Bituminous Coal," R&D Report No. 22,
Interim Report No. 1, Office of Coal Research (1965).
122. Agroskin, A. A. and Goncharov, E. I. "The Specific Heat of Coal,"
Coke and Chemistry USSR 7, 9-14 (1965).
123. Agroskin, A. A. and Goncharov, E. I. "Determination of the Specific
Heat of Coals During Carbonization," Coke and Chemistry USSR 11,
16-20 (1965).

124. Carlton, H. E. and Goldberger, W. M. "Fundamental Considerations of Carbonyl Metallurgy," J. of Metals. 611-615 (1965).
125. Vlasenko, V. M., Yuzefovich, G. E. and Rusov, M. T. "Kinetics of the Hydrogenation of Carbon Monoxide on a Nickel Catalyst," Kinetika i Kataliz 6:4 688-694 (1965).
126. Vlasenko, V. M., Yuzefovich, G. E. and Rusov, M. T. "Hydrogenation of CO and CO₂ on Nickel Catalyst," Kinetika Kataliz 6 938-41 (1965).
127. Forney, A. J. et al. "Recent Catalyst Developments in the Hot-Gas-Recycle Process," U. S. Dept. of Interior, Bureau of Mines Report No. 66-9 (1965).
128. Feldkirchner, H. L. and Huebler, J. "Reaction of Coal With Steam-Hydrogen Mixtures at High Temperatures and Pressures," Ind. Eng. Chem. Process Design Develop. 4, 134 (1965).
129. Kazmina, V. V. "Determination of the Specific Heat of Cokes," Coke & Chem USSR 11 26-29 (1965).
130. Linden, H. R. "Conversion of Solid Fossil Fuels to High-Heating-Value Pipeline Gas," Chemical Engineering Progress Symposium Series 61:54 76-103 (1965).
131. Gasior, S. J., Forney, A. J. and Field, J. H. "Destroying the Caking Quality of Bituminous Coal by Thermal and Oxidation Treatment in a Fixed Bed on a Pilot-Plant Scale," U. S. Bur. Mines Rep. Invest. No. 6805 (1965).
132. Schora, F. C. and Huebler, J. "Current Status of Coal Hydrogasification Process Development Work." Interim Reports on Projects for the Production of Pipeline-Quality Gas from Coal, Washington, D. C. : Office of Coal Research, 1965. American Gas Association Operating Section Proceedings - 1965, 65-P-156-61.
133. Linden, H. R. "Current Status of Pipeline Gas From Coal Process Development," Proceedings of the Illinois Mining Institute 73, 37-58 (1965).
134. Linden, H. R. "Pipeline Gas From Coal and Oil Shale," Pacific Coast Gas Association Proceedings 56 34-41 (1965).
135. von Fredersdorff, C. G. and Vandaveer, F. E. "Substitute Natural Gas From Coal." In Gas Engineers Handbook, Section 3, Production and Conditioning of Manufactured Gas, Chapter 9, 3/100 - 3/123. The Industrial Press, New York (1965).
136. Huebler, J. and Schora, F. C. "Development of the IGT Coal Hydrogasification Process." Preprint 47B presented at the 58th Annual Meeting of the American Institute of Chemical Engineers, Philadelphia, December 5-9, 1965. Published as "Coal Hydrogasification," Chemical Engineering Progress 62 87-91 (1966) February.

137. Moscley, F. and Paterson, D. "The Rapid High-Temperature Hydrogenation of Coal Chars. Part 1: Hydrogen Pressures Up to 100 Atmospheres," J. Inst. Fuel 38, 13-23 (1965) January; Part 2: "Hydrogen Pressures Up to 1,000 Atmospheres," ibid., 378-91 (1965) September.
138. Benson, H. E. and Tsaros, C. L. "Gas From Coal and Shale: How Close?" Hydrocarbon Processing and Petroleum Refiner 44 191-98 (1965) September.
139. Benson, H. E. and Tsaros, C. L. "Conversion of Fossil Fuels to Utility Gas." ACS Preprints 9:2 104-09 (1965) April.
140. Wen, C. Y. and Huebler, J. "Kinetic Study of Coal Char Hydrogasification, Second-Phase Reaction." Industrial and Engineering Chemistry Process Design and Development 4 147-54 (1965) April.
141. Feldman, H. and Huebler, J. "Hydrogasification of Oil Shale in a Continuous Flow Reactor." Ind. Eng. Chem. 4, 155 (1965) April.
142. Graham, W. and Harvey, E. A. "Electrical Resistance of Fluidized Beds of Coke and Graphite," Can. J. Chem. Eng. 43 146 (1965).
143. Goldberger, W. M., Hanway, J. E. and Langston, B. G., "Electrothermal Fluidized Bed." Chem. Eng. Progr. 61, 63 (1965) February.
144. Paquet, J. L. and Foulkes, P. B. "Calcination of Fluid Coke in an Electrically Heated Fluidized Bed." Can. J. Chem. Eng. 43 94 (1965) April.
145. Bloomer, O. T., et al. IGT Research Bulletin No. 21: Thermodynamic Properties of Methane-Nitrogen Mixtures, and Supplement, Institute of Gas Technology, Chicago (1965) February.
- 1964
146. Field, J. H. et al. "Development of Catalysts and Reactor Systems for Methanation," I&EC Prod. Res. Develop. 3, 150-53 (1964).
147. Carberry, J. J. "Designing Laboratory Catalytic Reactors," I&EC 56 39-46 (1964).
148. Hiteschue, R. W., Friedman, S. and Madden, R. "Hydrogasification of a High-Volatile A Bituminous Coal," U. S. Bur. Mines Rep. Invest. No. 6376 (1964).
149. Gomez, M., Gayle, J. B. and Taylor, A. P., Jr. "Heat Content and Specific Heat of Coals and Related Products," U. S. Bureau of Mines, Report 6607, (1964).
150. Cole, D. L. and Berry, W. F. Preparation and Polishing of Coal and Coke for Petrographic Analysis. Monroeville, Pa., Bituminous Coal Research, Inc., 1965.

151. Demeter, J. J., Haynes, W. P. and Youngblood, A. J. "Experiments with a Self-Generated Carbon-Expanded Iron Catalyst for Synthesis of Methane," Report No. 6425 Washington, D. C.: U. S. Dept. Interior, Bureau of Mines (1964).
152. Ivanovskii, F. P., Braude, G. E. and Semenova, T. A. "A Study of the Kinetics of the Reaction of Carbon Monoxide and Water Vapor at High Pressure," Kinetika i Kataliz 5:3 496-7 (1964).
153. Elliott, M. A. "Forecasts of Total Energy Requirements and Supply," American Gas Association Operating Section Proceedings (1964) 64-P-211-17. Also as "What's Ahead in Energy?" American Gas Journal 191, 30-38 (1964) October; and in Petroleum Management 36 70-78 (1964) October.
154. Bayer, J. L. "Report on Comparative Coal Petrographic Analyses by U. S. Laboratories," paper presented at meeting of Coal Petrographers at the Illinois State Geological Survey (Urbana) (1964) October 8.
155. Macriss, R. A. et al. IGT Research Bulletin No. 34: Physical and Thermodynamic Properties of Ammonia-Water Mixtures, and Supplement, Institute of Gas Technology, Chicago (1964) September.
156. Feldkirchner, H. L. and Linden, H. R. "Pipeline Gas From Oil Shale by Direct Hydrogasification," I&EC Process Des. Dev. 3, 218-26 (1964) July.
157. Huebler, J. and Feldkirchner, H. L. "Pipeline Gas From Coal - Hydrogenation: Reactions of Coal with Hydrogen and Steam at High Temperatures and Pressures," PB-23a, Report No. 6, (1964) May.
158. March, J. D. and Rich, J. "Methods of Regenerating Catalysts Comprising Nickel and Sulphur," British Patent 1,051,625. (1964) May 25.
159. Wen, C. Y. "Pipeline Gas From Coal - Hydrogenation: A Kinetic Study of Coal Hydrogasification - The Rapid Initial Reaction," A. G. A. Project PB-23a, Report No. 5 (1964) May.
160. Wen, C. Y. "A Kinetic Study of Coal Hydrogasification - The Rapid Initial Reaction," ACS Preprints 8:1 147-59 (1964) April; also as "Kinetic Study of Coal Char Hydrogasification Rapid Initial Reaction," Wen, C. Y. and Huebler, J. Ind. Eng. Chem. Process Des. Develop. 4 142-47 (1965) April.
161. Feldkirchner, H. L. and Huebler, J. "Reaction of Coal With Steam-Hydrogen Mixtures at High Temperatures and Pressures," ACS Preprints 8:1 160-83 (1964) April; Ind. Eng. Chem. Process Des. Develop. 4 134-42 (1965) April.

162. Forney, A. J., et al. "Destruction of Caking Properties of Coal by Pretreatment in a Fluidized Bed," I&EC Prod. Res. Dev. 3, 48-53 (1964) March.
163. Gasior, S. J., Forney, A. J. and Field, J. H. "Destruction of the Caking Quality of Bituminous Coal in a Fixed Bed," I&EC Prod. Res. Dev. 3 43-47 (1964) March.
164. Feldkirchner, H. L., et al. "Novel Laboratory Equipment for Physical Property and Reaction Kinetic Studies," paper presented at 52nd National Meeting, American Institute of Chemical Engineers, Memphis, February 3-5, 1964.
165. Khan, A. R., Feldkirchner, H. L. and Joyce, T. J. "Techno-Economic Evaluation of Hydrogasification of Coal and Char," Report to PB-23a Supervising Committee (1964) January.
- 1963
166. von Fredersdorff, C. G. and Elliott, M. A. "Coal Gasification" In Chemistry of Coal Utilization, H. H. Lowry, ed., Supplemental Volume, 892-1022. New York: John Wiley, 1963.
167. Terchick, A. A., et al. "Mechanical and Related Properties of Some Eastern Coals," ACS Div. Fuel Chem. Prepr. 7, 95-109 (1963).
168. Ihnatowicz, M. "Chemical and Caking Properties of Hard Coals Treated With Alkaline Solutions and Heated Under Pressure," Pr. Gl. Inst. Gorn. Komun. No. 320 (1963) (Polish text).
169. Lowry, H. H., Chemistry of Coal Utilization, Supplementary Volume, John Wiley & Sons, N. Y., 1963.
170. Wen, C. Y. and Huebler, J. "A Kinetic Study of Coal Char Hydrogasification," Preprints 14d presented at the 56th Annual Meeting of the American Institute of Chemical Engineers, Houston, December 1-5, 1963.
171. Kini, K. A. and Stacy, W. O. "The Adsorption of Helium by Carbonaceous Solids," Carbon 1, 17-24 (1963) October.
172. Dirksen, H. A. and Linden, H. R. "Pipeline Gas From Coal by Methanation of Synthesis Gas," IGT Res. Bull. No. 31, Chicago, July 1963.
173. Carberry, J. J. "Transport Phenomena and Heterogeneous Catalysis," Chem. Process Eng. 306-15 (1963) June.
174. Feldkirchner, H. L. and Linden, H. R. "Reactivity of Coals in High-Pressure Gasification With Hydrogen and Steam," I&EC Process Des. Dev. 2, 153-62 (1963) April.

175. Cartan, F. O. and Curtis, G. J. "Apparatus for the Determination of Particle Density of Porous Solids," Anal. Chem. 35, 423-24 (1963) March.

1962

176. Hiteschue, R. W., Friedman, S. and Madden, R. "Hydrogenation of Coal to Gaseous Hydrocarbons," U. S. Dept. of the Interior, Bureau of Mines RI 6027 (1962).
177. Elliott, M. A. "Role of Fossil Fuels in Meeting Future Energy Demands," American Power Conference Proceedings 24, 541-62 (1962).
178. Hiteschue, R. W., Friedman, S. and Madden, R. "Hydrogasification of Bituminous Coals; Lignite, Anthracite, and Char," U. S. Bur. Mines Rep. Invest. No. 6125 (1962).
179. Voloshin, A. L., et al. "Determination of the Heat of Coking Under Laboratory Conditions," Coke & Chemistry USSR 3 17-20 (1962).
180. Forney, A. J., et al. "Use of a Large-Diameter Reactor in Synthesizing Pipeline Gas and Gasoline by the Hot-Gas-Recycle Process," U. S. Department of the Interior, Bureau of Mines Report No. 6126 (1962).
181. Hiteschue, R. W., Friedman, S. and Madden, R. "Hydrogenation of Coal to Gaseous Hydrocarbon," U. S. Bur. Mines Rep. Invest. No. 6027 (1962).
182. Shrikhande, K. Y., Das Gupta, A. K. and Lahiri, A. "Low-Temperature Oxidation of Coal Under Fluidized Condition," J. Mines. Met. Fuels 10 1-13 (1962).
183. Sylvander, N. E. (assigned to Consolidation Coal Co.), "Fluidized Low Temperature Carbonization of Caking Bituminous Coal," U. S. Patent 3,070,515 (1962) December 15.
184. Blackwood, J. D. "The Kinetics of the System Carbon-Hydrogen-Methane," Aust. J. Chem. 15, 397-408 (1962) August.
185. Feldkirchner, H. L. and Linden, H. R. "Reactivity of Coals in High-Pressure Gasification with Hydrogen and Steam," ACS Preprints September 1962 pp. 191-208, also, Industrial and Engineering Chemistry Process Design and Development 2 163-62 (1963) April.
186. Feldkirchner, H. L. and Kniebes, D. V. "Effect of Nuclear Irradiation on the Activity of Iron Methanation Catalysts," paper presented at ACS Meeting, Washington, D. C., March 20-24, 1962.
187. Elliott, M. A. "Production of Supplemental High-Btu Gas From Coal and Oil Shale." Midwest Engineer 14, 12-13 (1962) March.

188. Perry, H., Elliott, M. A. and Linden, H. R. "Current Developments in the Conversion of Coal to Fluid Fuels in the United States," Transactions of the 6th World Power Conference, Melbourne, Australia, 1962, 7, Paper 33 111, 3/3, 2497-2514; Power (Japanese) 71, 51-58 (1963) January.
189. Hodge, E. S., Boyer, C. B. and Orcutt, F. D. "Gas Pressure Bonding," Ind. Eng. Chem. 54 30-35 (1962) January.
190. Kniebes, D. V. IGT Technical Report No. 4: Utility Gas Analysis by Gas Chromatography, Institute of Gas Technology, Chicago (1962) January.
- 1961
191. Vlasenko, V. M., Yuzefovich, G. E. and Rusov, M. T. "Kinetics of CO₂ Hydrogenation on a Nickel Catalyst," Kinet Kataliz 2, 525-28 (1961).
192. Elliott, M. A. "Coal Gasification for Production of Synthesis and Pipeline Gas," Transactions of the American Institute of Mining, Metallurgical and Petroleum Engineers 220 134-53 (1961).
193. Elliott, M. A., Linden, H. R. and Schultz, E. B. Jr. "Production of Low Molecular Weight Hydrocarbons from Solid Fossil Fuels." U. S. Patent 2,991,164, July 4, 1961; Australian Patent 233,135, December 18, 1962; Canadian Patent 654,289, December 18, 1962; Brazilian Patent 68,087, December 20, 1963.
194. Heffner, W. H. et al. "Pipeline Gas From Bituminous Coal Via Hydrogasification," Study CE-61-215, M. W. Kellogg Co., New York, 1961.
195. Squires, A. M. "Steam-Oxygen Gasification of Fine Sizes of Coal in Fluidized Bed at Elevated Pressure. I. Reaction of Carbon With Hydrogen," Trans. Inst. Chem. Eng. 39, 3-9 (1961); II. "Reaction of Carbon With Steam," ibid., 10-15 (1961); III. "Relation of Integral to Differential Rates: Effect of Carbon Level on Gasification Rate, and Role of the Shift Reaction," ibid., 16-21 (1961).
196. Van Krevelen, D. W. "Coal," Typology - Chemistry - Physics - Constitution, 2nd Ed. 345. Amsterdam: Elsevier, 1961.
197. Pyrcioch, E. J. "Pipeline Gas by Hydrogasification of Char and Lignite in a Solids Upflow Fluid-Bed Reactor," A. G. A. PB-23a Report No. 4 (1961).
198. Shultz, E. B. Jr., Feldkirchner, H. L. and Pyrcioch, E. J. "Hydrogenation Techniques at Combined High Temperatures and Pressures," Chem. Eng. Progr. Symp. Series 57:34 73-80 (1961).
199. Johnson, J. S. "Reactions in a Fluidized Coke Bed with Self-Resistive Heating," Can. J. Chem. Eng. 39, 145 (1961).

200. Mason, D. McA. and Eakin, B. E. IGT Research Bulletin No. 32: Calculation of Heating Value and Specific Gravity of Fuel Gases, Institute of Gas Technology, Chicago (1961) December.
201. Lewis, D. S., Ginsberg, H. H. and Hiteschue, R. W. "Hydrogenation of Coal at Short Retention Times," U. S. Bur. Mines Rep. Invest. 5908 (1961).
202. Foch, P. (assigned to Carboneages de France), "Method and Apparatus for the Carbonization of Fluidized Materials," U. S. Patent 3,011,953 (1961) December 5.
203. Elliott, M. A. "High-Btu Gas From Coal," Proceedings of the Conference on Coal's New Horizons, Southern Research Institute, 35-41 (1961) October; Coal Utilization 15, 26-28 (1961) December; Public Utilities Fortnightly 70, 533-40 (1962) October 11.
204. Tarman, P. B. and Linden, H. R. IGT Research Bulletin No. 33: Soil Adsorption of Odorant Compounds, Institute of Gas Technology, Chicago (1961) July.
205. Morse, W. F. "Cost Accounting Procedure," Research Supervising Committee for Projects PB-19 and PB-23a. New York: American Gas Association, June 13, 1961.
206. Kavanagh, J. F. General Accounting Procedures to Be Used for Processes for the Large-Scale Production of Gas From Coal and Oil Shale. New York: American Gas Association (1961) May 9.
207. Benson, H. E. "Hot Carbonate Plants: How Pressure Affects Costs," Pet. Refiner 40, 107-08 (1961) April.
208. Weil, S. A. IGT Research Bulletin No. 30: Burning Velocities of Hydrocarbon Flames, Institute of Gas Technology, Chicago (1961) March.
209. Leland, T. W. "Enthalpy Deviation From Ideal Gas Behavior for H_2 - CH_4 Mixtures," letter to G. T. Skaperdas, The M. W. Kellogg Co. Houston: Rice Institute, February 4, 1961.

1960

210. Pyrcioch, E. J. and Linden, H. R. "Pipeline Gas by High-Pressure Fluid-Bed Hydrogasification of Char," Ind. Eng. Chem. 52, 590 (1960).
211. Shultz, E. B. Jr. "High-Pressure Thermal Hydrogenolysis of Hydrocarbons," PH. D. Dissertation, Illinois Institute of Technology, Chicago, June 1960.
212. Kleppa, O. J., "A New Turn High Temperature Reaction Calorimeter. The Heats of Mixing in Liquid Sodium Potassium Nitrates." J. Phys. Chem. 64, 1937 (1960).

213. Becker, F. and Spalink, F. "Investigation of the Time Slope of Chemical Reactions by Calorimetric Measurements." Z. Physik Chim. None Folge 26, 1 (1960).
214. Novohradsky, M. "Synteza Metanu z Vodiku a Kyslicniku Uhelmateho Popripade Uhliciteho," Prace Ustavu Vyzkum Paliv No. 1 1 153-76 (1960).
215. Bienstock, D. et al. "Synthesis of High Btu Gas From CO and H₂ Using a Hot Gas Recycle Reactor," Paper No. CEP-60-14 in Proceedings of American Gas Association Operating Section New York (1960).
216. Heffner, W. H. et al. "Pipeline Gas From Bituminous Coal Via Suspension Gasification and Catalytic Synthesis of Methane," Study CE-60-207. M. W. Kellogg Co., New York (1960).
217. Hiteschue, R. W., Lewis, P. S. and Friedman, S. "Gaseous Hydrocarbons From Coal," A.G.A. Oper. Sect. Proc. - 1960, CEP-60-69.
218. Johnson, H. S. and Anderson, A. H. "Process for Preparation of Hydrocyanic Acid," U. S. Patent 2,958,584 (November 1, 1960).
219. Welinsky, I. H. (assigned to Consolidation Coal Co.), "Fluidized Carbonization Process for Agglomerative Coals," U. S. Patent 2,955,077 (1960) October 4.
220. Birch, T. J., Hall, K. R. and Urie, R. W. "Gasification of Brown Coal With Hydrogen in a Continuous Fluidized-Bed Reactor," J. Inst. Fuel 33 422-35 (1960) September.
221. Hiteschue, R. W., Anderson, R. B. and Friedman, S. "Gaseous Hydrocarbons by Hydrogenation of Coals and Chars," Ind. Eng. Chem. 52 577-79 (1960) July.
222. Maggs, F. A. P., Schwabe, P. H. and Williams, J. H. "Adsorption of Helium on Carbons: Influence on Measurement of Density," Nature 186, 956-58 (1960) June 18.
223. Wasilewski, J. C. "Bonding Metals at 15,000 P. S. I. G. and 1800°F," Ind. Eng. Chem. 52, 61A-62A, 64A (1960) June.
224. Nathan, M. F. (assigned to M. W. Kellogg Co.), "Fluidized Carbonization," U. S. Patent 3,032,477 (1962) May 1.
225. Neavel, R. C. and Miller, L. V. "Properties of Cutinite," Fuel 39, 212-22 (1960) May.
226. Kohl, A. L. and Buckingham, P. A. "Fluor Solvent CO₂ Removal Process," Pet. Refiner 39, 193-96 (1960) May.
227. Phinney, J. A., Consolidation Coal Co., letter of April 6, 1960.

1959

228. Batchelor, J. D., Yavorsky, P. M., Gorin, E. "Measurement of the Thermal Properties of Carbonaceous Materials," J. C. E. D. 4, 241-6 (1959).
229. Duff, A. W. "Physics," Blakiston's 8th ed. (1959).
230. Fuji, S. and Yokoyama, F. "Infrared Absorption Spectra of Air-Oxidized Coal," Nenryo Kyokai-shi 38, 98-106 (1959) (Japanese text with English summaries).
231. Veslovskii, V. A., Terpogosova, E. A. and Aleksuva, N. D. "The Phase of Low-Temperature Oxidation of Coal," Probl. Rudn. Aerol. Akad. Nauk U. S. S. R. Inst. Gorn. Dela. 311-22 (1959) (Russian text).
232. von Fredersdorff, C. G. and Vandaveer, F. E. "Manufacture of Substitute Natural Gas From Coal," A. G. A. Oper. Sect. Proc. - 1959, CEP-59-8.
233. Grosskinsky, O., Huck, G. and Lange W. "The Oxidation of Bituminous Coal With Air Formation, Composition and Properties of Oxidized Coal and of Humic Acid," Brennst. -Chem. 40, 252-61 (1959) August 26 (German text).
234. Dirksen, H. A. and Linden, H. R. "Production of Pipeline Gas by Methanation of Synthesis Gas Over Raney Nickel Catalysis." ACS Preprints September 1959, 37-57; also, as "Pipeline Gas by Methanation of Synthesis Gas Over Raney Nickel Catalyst," Industrial and Engineering Chemistry 52, 584-89 (1960) July.
235. von Fredersdorff, C. G. "Process Analysis of Coal Hydrogasification With Steam and Recycled Hydrogen," ACS Preprints September 1959, 70-99; also as "Process for Coal Hydrogasification," Ind. Eng. Chem. 52, 595-98 (1960) July.
236. Pyrcioch, E. J. and Linden, H. R. "Production of Pipeline Gas by High-Pressure, Fluid-Bed Hydrogasification of Char," ACS Preprints September 1959, 59-69; also as "Pipeline Gas by High-Pressure Fluid-Bed Hydrogasification of Char." Ind. Eng. Chem. 52, 590-94 (1960) July.
237. Linden, H. R. and Pyrcioch, E. J. "Pipeline Gas From Coal - Hydrogenation," A. G. A. PB-23a, Report No. 3, May 1959.
238. Blackwood, J. D. "The Reaction of Carbon With Hydrogen at High Pressure," Aust. J. Chem. 12, 14-28 (1959) February.
239. Mason, D. McA., and Hakewill, Henry, Jr. with Newmann, A. E. S., Ed. IGT Research Bulletin No. 5: Identification and Determination of Organic Sulfur in Utility Gases, Institute of Gas Technology, Chicago (1959) January.

1958

240. Oriani, R. S. and Murphy, W. K. "Differential Calorimeter for Heats of Formation of Solid Alloys. Heats of Formation of Alloys of the Noble Metals," J. Phys. Chem. 62, 327 (1958).
241. Kubaschewski, O. and Evans, E. Metallurgical Thermochemistry, Pergamon Press, 234 (1958).
242. Lacker, J. R. et al. Trans. Faraday Soc. 52, 1500 (1956).
243. Komiya, T. "The Formation of Organic Acids from Bituminous Coal by Oxygen Oxidation in Sodium Carbonate Solution," Kogyo Kagaku Zasshi 61, 197-200 (1958) (Japanese text).
244. Brosn, J. E. et al. "Reactions of Aliphatic and Aromatic Systems in Coals," Proc. Conf. on Science in the Use of Coal, Sheffield (Inst. Fuel, London) A43-47 (1958).
245. Kharitonov, G. V. and Purikoua, V. L. "Determination of the State of Oxidation of Coals by Their Total Content of Phenolic, Carboxylic, and Hydroxylic Groups," Okisleniei Khranenie Tverd. Gorvuch. Iskop. Akad. Nauk. U. S. S. R. Inst. Goriuch. Iskop. 130-36 (1958) (Russian text).
246. Yamasaki, T. and Murai, I. "The Oxidation of Coal. III. Characteristic Curve of Oxidation of Coal," Nippon Kogyo Kaishi 74, 81-86 (1958) (Japanese text).
247. Karl, A. (assigned to Heinrich Koppers G. m. b. H.), "Gasification of Bituminous Fuels," Ger. Patent 1,041,192 (1958) October 16.
248. May, W. G., Mueller, R. H. and Sweetser, S. B. "Carbon-Steam Reaction Kinetics From Pilot Plant Data," Ind. Eng. Chem. 50, 1289-96 (1958) September.
249. McCartney, J. T. and Ergun, S. "Optical Properties of Graphite and Coal," Fuel 37 272-82 (1958) July.
250. Channabasappa, K. C. and Linden, H. R. "Fluid-Bed Pretreatment of Bituminous Coals and Lignite - Direct Hydrogenation of Chars to Pipeline Gas," Ind. Eng. Chem. 50, 637-44 (1958) April.
251. Blackwood, J. D. and McCarthy, D. J. "The Mechanism of Hydrogenation of Coal to Methane," Aust. J. Chem. 19, 16 33 (1958) February.
252. Blackwood, J. D. and McGrory, F. "The Carbon-Steam Reaction at High Pressure," Aust. J. Chem. 11, 16-33 (1958) February.

1957

253. Dainton, F. S. et al. Trans. Farraday Soc. 53 1269 (1957).
254. Kini, K. A., Ganguli, N. C. and Lahiri, A. "The True Surface Area of Coal," Proc. 2nd Intern. Congr. Surface Activity 2 330-48. London: Butterworth (1957).
255. Shultz, E. B., Jr. and Linden, H. R. "Batch Hydrogenolysis Reactions of Pure Compounds Related to Petroleum Oils," Ind. Eng. Chem. 49 2011-16 (1957) December.
256. Hiteschue, R. W., Anderson, R. B. and Schlesinger, M. D. "Hydrogenating Coal at 800°F," Ind. Eng. Chem. 49, 2008-10 (1957) December.
257. Ellington, R. T., et al. IGT Research Bulletin No. 14: The Absorption Cooling Process - A Critical Literature Review, Institute of Gas Technology, Chicago (1957) August.
258. Weil, S. A., et al. IGT Research Bulletin No. 15: Fundamentals of Combustion of Gaseous Fuels - A Critical Literature Review, Institute of Gas Technology, Chicago (1957) April.
259. Lawson, G. J. "Chemical Constitution of Coal V - Optimum Conditions for the Hydrogen Peroxide Oxidation of Humic Acid to Sub-humic Acids," Fuel 36 182-90 (1957) April.
260. Smith, J. W. and Mapstone, G. E. "The Alkaline Permanganate Oxidation of Coal," Fuel 36 191-204 (1957) April.
261. Linden, H. R. and Channabasappa, K. C. "Fluid-Bed Pretreatment of Bituminous Coals and Lignite and Direct Hydrogenation of Chars to Pipeline Gas," A. G. A. PB-23a, Report No. 2, April 1957.
262. Zielke, C. W. and Gorin, E. "Kinetics of Carbon Gasification," Ind. Eng. Chem. 49 396-403 (1957) March.
263. Long, E. W., Smith, H. G. and Bordenca, C. "Carbonization of Agglomerating Coals in a Fluidized Bed," Ind. Eng. Chem. 49 355-59 (1957) March.
264. von Fredersdorff, C. G., Pyricioch, E. J. and Pettyjohn, E. S. IGT Research Bulletin No. 7: Gasification of Pulverized Coal in Suspension, institute of Gas Technology, Chicago (1957) January.

1956

265. Weller, S. "Analysis of Kinetic Data for Heterogeneous Reactions," A. I. Ch. E. J. 2 59-62 (1956).
266. Rossini, F. D. "Experimental Thermochemistry," Interscience, Vol. I, 309 (1956).

267. Furukawa, G. T. et al. "Thermal Properties of Aluminum Oxide From 0° to 1200°K," J. Res. of National Bureau of Standards 57, 67-82 (1956).
268. Schlesinger, M. D., Demeter, J. J. and Greyson, M. "Catalyst for Producing Methane from H₂ and CO," I&EC Prod. Process Develop. 48, 68-70 (1956).
269. Greyson, M. "Methanation," In Catalysis, Vol. IV, Emmet, P. H., Ed., 473-511. New York: Reinhold, 1956.
270. Boudart, M., "Kinetics on Ideal and Real Surfaces," A. I. Ch. E. J. 2, 62-64 (1956).
271. Benham, A. L. "Vapor-Liquid Equilibria of Light Hydrocarbon Systems Containing Hydrogen at Low Temperature," Ph. D. Thesis. Ann Arbor: University of Michigan, 1956.
272. Parry, V. F., Landers, W. S. and Wagner, E. O., "Low-Temperature Carbonization of Lignite and Noncaking Coals in the Entrained State," Min. Eng. 8 54-64 (1956).
273. Minet, R. G. and Mirkus, J. D. "Cost-Saving Techniques for Instrumenting a Fluidized-Bed Pilot Plant," Chem. Eng. Prog. 52 531-34 (1956) December.
274. Alpern, B. "The Anisotropy of Coke as Criterion for Its Classification," Brennst.-Chem. 37 194-98 (1956) July 18 (German text).
275. Terres, V. E. et al. "The Solution of the Problem of the Organization of Fibre Coal on the Ground of Its Specific Heats," Brennstoff-Chemie 269-73 (1956) June.
276. Shultz, E. B. Jr. and Linden, H. R. "Hydrogasification of Petroleum Oils and Bituminous Coal to Natural Gas Substitutes - Hydrogenolysis of Petroleum Oils," Ind. Eng. Chem. 48 894-905 (1956) May.
277. Channabasappa, K. C. and Linden, H. R. "Hydrogenolysis of Bituminous Coal," Ind. Eng. Chem. 48 894-905 (1956) May.
278. Channabasappa, K. C. "A Literature Survey of the Effects and Methods of Pretreatment of Coal," PB-23a, Report No. 1, March 1956.
279. Garbo, P. W. (assigned to Hydrocarbon Research, Inc.), "Rendering Solid Carbonaceous Materials Nonagglomerative," U. S. Patent 2,729,597 (1956) January 3.

1955

280. Greyson, M. et al. "Synthesis of Methane," Report No. 5137. Washington, D. C.: U. S. Dept. Interior, Bureau of Mines, 1955.

281. American Society for Testing and Materials, "D 271-48. Standard Methods of Laboratory Sampling and Analysis of Coal and Coke," in 1955 Book of ASTM Standards. Part 5: "Fuels, Petroleum, Aromatic Hydrocarbons, Engine Antifreezes." Philadelphia, 1955.
282. Reed, F. H., Jackman, H. W. and Henline, R. W. "Char for Metallurgical Coke," Ill. State Geol. Surv. Rep. Invest. No. 187 7-38. Urbana, Illinois, 1955.
283. Bukacek, R. F. IGT Research Bulletin No. 8: Equilibrium of Moisture Content of Natural Gases, and Supplement, Institute of Gas Technology, Chicago (1955) November.
284. Eakin, B. E., Ellington, R. T. and Gami, D. C. IGT Research Bulletin No. 26: Physical-Chemical Properties of Ethane-Nitrogen Mixtures, Institute of Gas Technology, Chicago (1955) July.
285. von Fredersdorff, C. G. IGT Research Bulletin No. 19: Reactions of Carbon With Carbon Dioxide and With Steam, Chicago (1955) May.
286. Zielke, C. W. and Gorin, E. "Kinetics of Carbon Gasification. Interaction of Hydrogen With Low Temperature Char at 1500° to 1700°F," Ind. Eng. Chem. 47 820-25 (1955) April.

1954

287. Wainwright, H. W., Egleson, G. C. and Brock, C. M. "Laboratory-Scale Investigation of Catalytic Conversion of Synthesis Gas to Methane," Washington, D.C.: U.S. Dept. of the Interior, Bureau of Mines, Report No. 5046 (1954).
288. Rosenqvist, T. "A Thermodynamic Study of the Iron, Cobalt, and Nickel Sulphides," J. Iron and Steel Inst. 37-57 (1954).
289. Hubbard, W. N., Katz, C. and Waddington, G. J. Phys. Chem. 58 142 (1954).
290. Bastick, M. "The Oxidation of Coal at Low Temperature," Bull. Soc. Chim. Fr. 1239-46 (1954) (French text).

1953

291. Goodman, J. B., Gomez, M. and Parry, V. F. "Determination of Moisture in Low-Rank Coals," U. S. Department of the Interior, Bureau of Mines Rept. of Inv. 4969, 1953.
292. Das, P. P. and Chatterjee, B. "The Nature of the Catalyst in the Decomposition of Carbon Monoxide in Presence of Iron," Trans. of the Indian Inst. of Metals 7 Vol. 7, 189-196 (1953).

293. Rossini, F. D. et al. Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, Pittsburgh: Carnegie Press, 1953.
294. Parry, V. F. et al. "Drying and Carbonizing Fine Coal in Entrained and Fluidized State," U. S. Department of the Interior, Bureau of Mines Rep. Invest. No. 4954 (1953).
295. Goring, G. E. et al. "Kinetics of Carbon Gasification by Steam Mechanism of Interaction of Low Temperature Char and Steam-Hydrogen Mixtures at 1600°F," Ind. Eng. Chem. 45 2586-91 (1953) November.
296. Riesz, C. H. et al. IGT Research Bulletin No. 6: Pilot Plant Catalytic Gasification of Hydrocarbons, Institute of Gas Technology, Chicago (1953) July.
297. Bloomer, O. T., Gami, D. C. and Parent, J. D. IGT Research Bulletin No. 22: Physical-Chemical Properties of Methane-Ethane Mixtures, Institute of Gas Technology, Chicago (1953) July.
298. Carr, N. L. IGT Research Bulletin No. 23: Viscosities of Natural Gas Components and Mixtures, Institute of Gas Technology, Chicago (1953) June.
299. Hunt, B. E. et al. "Reaction of Carbon With Steam at Elevated Temperatures," Ind. Eng. Chem. 45 667-80 (1953) March.
300. Dirksen, H. A., Linden, H. R. and Pettyjohn, E. S. IGT Research Bulletin No. 4: Cracking Catalyst Activity in the Presence of Hydrogen Sulfide, Institute of Gas Technology, Chicago (1953) February.

1952

301. Pursley, J. A., White, R. R. and Slipevich, C. "The Rate of Formation of Methane From CO and H₂ With a Nickel Catalyst at Elevated Pressures," Chem. Eng. Progr. Sym. Ser. 4 51-58 (1952).
302. Ticknor, L. B. and Bever, M. B. "Heats of Solution of Group 1B Metals in Liquid Tin," J. of Metals 4 941 (1952).
303. Barkley, L. W. et al. "Catalytic Reverse Shift Reaction," I&EC 44, 1066-71 (1952).
304. Rossini, F. D. et al. NBS Circular 500 386 (1952).
305. Japan. "Research on Carbon Monoxide Catalysis," Japan Gov't Chem. Ind. Research Inst. Report V. 46, 403-15 (1952).
306. Pettyjohn, E. S. and Linden, H. R. IGT Research Bulletin No. 9: Selection of Oils for Carbureted Water Gas, and Supplement, Institute of Gas Technology, Chicago (1952).

307. Riesz, C. H., Dirksen, H. A. and Pleticka, W. J. IGT Research Bulletin No. 20: Improvement of Nickel Cracking Catalysts, Institute of Gas Technology, Chicago (1952) October.
308. Bloomer, O. T. and Rao, K. N. IGT Research Bulletin No. 18: Thermodynamic Properties of Nitrogen, and Supplement, Institute of Gas Technology, Chicago (1952) October.
309. Bloomer, O. T. IGT Research Bulletin No. 13: Measurement of Gas Law Deviations with Bean and Burnett Apparatus, Institute of Gas Technology, Chicago (1952) May.
310. Goring, G. E. et al. "Kinetics of Carbon Gasification by Steam. Effect of High Temperature Pretreatment on Reactivity of Low Temperature Char to Steam and Carbon Dioxide," Ind. Eng. Chem. 44 1051-57 (1952) May.
311. Bloomer, O. T. and Parent, J. D. IGT Research Bulletin No. 17: Physical-Chemical Properties of Methane-Nitrogen Mixtures, Institute of Gas Technology, Chicago (1952) April.
312. Kinney, C. R. and Friedman, L. D. "Ozonization Studies of Coal Constitution," J. ACS 74, 57-61 (1952) January 5.

1951

313. Brysch, O. P. and Ball, W. E. IGT Research Bulletin No. 11: Expansion Behavior of Coal During Carbonization - A Literature Study, and Supplement, Institute of Gas Technology, Chicago (1951) October.
314. Riesz, C. H., Dirksen, H. A. and Kirkpatrick, W. J. IGT Research Bulletin No. 10: Sulfur Poisoning of Nickel Catalysts, Institute of Gas Technology, Chicago (1951) September.
315. Ergun, S. "Determination of Particle Density of Crushed Porous Solids - Gas Flow Method," Anal. Chem. 23 151-56 (1951) January.

1950

316. Binder, G. G. and White, R. R. "Synthesis of Methane From Carbon Dioxide and Hydrogen," Chem. Eng. Progr. 46, 563-74 (1950).
317. Stockman, C. H. and Bray, J. L. "The Hydrogenation of Coal at High Temperatures," Purdue Univ. Eng. Exp. Stn. Bull. Res. Ser. No. 111 (1950).
318. Gas Research Board. "Report of the Director for the Year 1949," Commun. GRB 55, London, 1950.
319. Clark, E. L. et al. "Hydrogenation of Coal in a Fluidized Bed," Ind. Eng. Chem. 42 861-65 (1950) May.

320. Ahmed, M. D. and Kinney, C. R., "Ozonization of Humic Acids Prepared From Oxidized Bituminous Coal," J. ACS 72 559-61 (1950) January.

1949

321. Dent, F. J. and Hebben, D. "The Catalytic Synthesis of Methane as a Method of Enrichment in Town Gas Manufacture," Gas Research Board Communication GRB 51 London, 1949.
322. Stickland-Constable, R. F. "The Synthesis of Methane From Carbon Monoxide and Hydrogen on a Nickel Catalyst," Gas Research Board Communication GRB 46 London, 1949.
323. Glendenin, J. D. et al. "Thermal and Electrical Properties of Anthracite and Bituminous Coals," Trans. 7th Annual Anthracite Conference of Lehigh Univ. Bethlehem, Pa. (1949) May 5-6.
324. Gas Research Board, "Report of the Director for the year 1948," Commun. GRB 45 London, 1949.

1948

325. Akers, W. W. and White, R. R. "Kinetics of Methane Synthesis," Chem. Eng. Progr. 44 553-66 (1948).
326. Gas Research Board, "Report of the Director for the year 1947," Commun. GRB 37 London, 1948.
327. Parent, J. D. and Katz, S. IGT Research Bulletin No. 2: Equilibrium Compositions and Enthalpy Changes for the Reactions of Carbon, Oxygen and Steam, Institute of Gas Technology, Chicago (1948) January.

1947

328. Montell, C. L. "Industrial Carbon," D. VanNostrand Co., Inc., N. Y. 2nd Ed. 1947, p. 432.
329. Howard, H. C. "Low Temperature Reactions on Bituminous Coal," Trans. AIME 177 523-34 (1947).
330. Kinney, C. R. "The Source of Acetic Acid Obtained by Oxidation of Coal," J. ACS 69 284-89 (1947) February.
331. Rossini, F. D. and coworkers, American Petroleum Institute, Research Project 44, National Bureau of Standards (1947).

1946

332. Nicolai, J., D'hont, M. and Jungers, J. C. "The Synthesis of Methane From Carbon Monoxide and Hydrogen on Nickel," Bull. Soc. Chim. Belgium 55 160-76 (1946).
333. Swietosjowski, W. "Microcalorimetry," Reinhold, N. Y. (1946).

334. Gas Research Board "8th Annual Report of the Council of the Gas Research Board, 1946," Commun. GRB 30. London, 1948.

335. Gas Research Board "7th Annual Report of the Council of the Gas Research Board, 1945-46," Commun. GRB 24. London 1947.

1945

336. Dent, F. J. et al. "An Investigation Into the Catalytic Synthesis of Methane for Town Gas Manufacture," Gas Research Board Communication GRB 20. London, 1945.

337. Jones, R. E. and Townsend, D. T. A. "Mechanism of the Oxidation of Coal," Nature 155 42A-45 (1945).

338. Lowry, H. H., Chemistry of Coal Utilization (2 vols) 1868 pp, John Wiley & Sons, N. Y., 1945.

339. Gas Research Board, "6th Annual Report of the Council of the Gas Research Board, 1944-1945," Commun. GRB 18. London, 1945.

1944

340. Dent, F. J. "The Production of Gaseous Hydrocarbons by the Hydrogenation of Coal," Gas J. 244 502-05, 507 (1944) October 18.

341. Gas Research Board, "5th Annual Report of the Council of the Gas Research Board, 1943-44," Commun. GRB 11. London, 1944.

342. Bray, J. L. and Morgal, P. W. "Hydrogenation of Coal at High Temperatures," Purdue Univ. Eng. Exp. Stn. Res. Ser. No. 93 3-36 (1944).

1943

343. Meller, A. "Catalytic Hydrogenation of CO - Methane Synthesis From Water Gas," Aust. Chem. Inst. J. Proc. 10 100-14, 123-29 (1943).

344. Bray, J. L. and Howard, R. E. "Hydrogenation of Coal at High Temperatures," Purdue Univ. Eng. Exp. Stn. Bull. Res. Ser. No. 90. Lafayette, Ind., 1943.

345. Haldane, J. S. and Makgill, R. H. "The Spontaneous Oxidation of Coal and Other Organic Substances," J. Soc. Chem. Ind. 53 359-67T (1943); also, Gas World 102 14 (1938) January 5.

1941

346. Yohe, G. R. and Harman, C. A. "The Oxidizing Power of Illinois Coal. I. The Reaction With Titanous Chloride," J. ACS 63 555-56 (1941) February.

1940

347. Mellor, J. W. Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. V, 767, Longmans, Green, London (1940).
348. Fritz, V. W. and Moser, H. "Specific Heat, Thermal Conductivity and Thermal Diffusivity of Mineral Coal, Charcoal and Coke," Feneringstechnik 5 97-107 (1940).
349. Bagham, D. H. and Bennett, J. G. "The Chemistry of Gasification With Reference to Small Producers," Fuel 19 95-101 (1940).
350. Warren, T. E., Bowles, K. W. and Gilmore, R. E. "Hydrogenation of Peat Char," Fuel 19 72-76 (1940) April.
351. Chowdhury, J. K., Bose, S. C. and Karim, Md. A. "Chemical Composition of Coal. I. Oxidation With Chlorine Dioxide," J. Indian Chem. Soc. Ind. News Ed. 3 1-12 (1940).
352. Chuhanov, Z. "The Burning of Carbon. I. The Sequence of Processes in the Combustion of Air Suspensions of Solid Fuels," Fuel 18, 292-302 (1939) October; Part II. Fuel 19, 17-20 (1940) January-February and 49-50 (1940) March.

Prior to 1940

353. Smith, R. C., Tomarelli, R. C. and Howard, H. C. "Oxidation of Carbonaceous Materials to Organic Acids by Oxygen at Elevated Pressures," J. ACS 61 2398-402 (1939) September.
354. Dent, F. J., Blackburn, W. H. and Millett, H. C. "43rd Report of the Joint Research Committee. The Investigation of the Use of Oxygen and High Pressure in Gasification. Part III. Synthesis of Gaseous Hydrocarbons at High Pressure," Trans. Inst. Gas Eng. 88 150-217 (1938-39).
355. Newall, H. E. "The Influence of Inorganic Compounds on the Combustion of Coal. Part II. Their Effect on the Oxidation and Ignition," Fuel 17 292099 (1938) October.
356. Scott, G. S. and Jones, G. W. "Oxidation of Anthracite: Effect of Time of Contact on the Concentration of Oxygen in the Effluent Gases," U. S. Department of the Interior, Bur. Mines Rep. Invest. No. 3405 (1938).
357. Speakman, J. B. and Stott, E. Trans. Faraday Soc. 34 1203 (1938).
358. Dewey, P. H. and Harper, D. R., 3rd, "Heat of Combustion of Anthracite Cokes and of Artificial and Natural Graphites," Contribution 71, Carnegie Institute of Tech. and NBS 21, October 1938.
359. Gas Times 17 "Complete Gasification Under Pressure. Hydrogenation of Coal," 19-21 (1938) October 22.

360. Scott, G. S. and Jones, G. W. "Composition and Inflammability of Gaseous Distillation Products From Heated Anthracite," U. S. Department of the Interior, Bur. Mines Rep. No. Invest. 3378 (1938).
361. Dent, F. J., Blackburn, W. H. and Millett, H. C. "41st Report of the Joint Research Committee. The Investigation of the Use of Oxygen and High Pressure in Gasification. Part II. Synthesis of Gaseous Hydrocarbons at High Pressure," Trans. Inst. Gas Eng. 87 231-87 (1937-38).
362. Neigishi, G. R. "The Heat of Fusion and Vapor Pressure of Stannic Iodide," J. Am. Chem. Soc. 58, 2293 (1936).
363. Schuster, V. F., Panning, G. and Bulow, H. "Methanation in Gas Mixtures Containing Carbon Monoxide and Carbon Dioxide With Various Nickel Catalysts," Brennst. Chem. 14 306-7 (1935).
364. Schuster, V. F., Panning, G. and Bulow, H. "Die Methanbildung in Kohlenoxyd- und Kohlendioxydhaltigen Gasgemischen and Verschiednen Nickelkatakysatoren," Brennstoff-Chemie, Vol. 16, 368-9 (1935).
365. Smith, R. C. and Howard, H. C. "Equivalent and Molecular Weights of Humic Acids From a Bituminous Coal," J. ACS 57, 512-16 (1935) March.
366. Weiler, J. F. "The Reaction of Bromine With a Coking Coal, Including a Study of Its Unsaturation," Fuel 14, 190-96 (1935) July.
367. Asbury, R. S. "Action of Solvents on Coal. Extraction of Edenborn Coal by Benzene at Elevated Temperatures," Ind. Eng. Chem. 26 1301-06 (1934).
368. Bunte, K., Bruckner, H. and Simpson, H. G. "Changes in the Constitution and the Caking Power of Coal During Heating to the Plastic Stage," Fuel 12 222-32 (1933) July.
369. Coles, G. and Graham, J. I. "The Effect Upon Oxidisability of the Heat Treatment (Partial Distillation) of Fine and Lump Coal," Fuel 12 304-12 (1933) September.
370. Lilly, V. G. and Garland, C. E. "The Regeneration of Humic Acids From Coal by Nitric Acid Oxidation," Fuel 11 392-400 (1932) November.
371. Lynch, C. S. and Collett, A. R. "The Electrolytic Oxidation of Coal," Fuel 11 408-15 (1932) November.
372. Francis, W. and Morris, H. M. "Relationship Between Oxidizability and Composition of Coal" U. S. Department of the Interior, Bur. Mines Bull 340. Pittsburgh, 1931.
373. LaMer, V. K. and Read, C. L. "Rapid Reactions, Velocity and Heat Effects Involved in the Neutralization of Sodium Dichromate by Sodium Hydroxide," J. Am. Chem. Soc. 52 3098 (1930).

374. Bone, W. A., Horton, L. and Ward, S. G. "Researches on the Chemistry of Coal. VI. Its Benzinoid Constitution as Shown by Its Oxidation With Alkaline Permanganate," Proc. R. Soc. (London) 127A 480-510 (1930).
375. Donnelly, J. T., Foott, C. H. and Reilly, J. "The Effect on the Primary Distillation Products of Coal. V. Examination of the Cokes and Gases Obtained by Distillation at 600°," J. Soc. Chem. Ind. 48 38-40T (1929); "VI. Examination of the Tars," ibid. 101-05T.
376. Barrett, W. J., Foott, C. H. and Reilly, J. "The Effect of Pre-Oxidation on the Primary Distillation Products of Coal. III. The Effects of Carbon Dioxide, Carbon Monoxide, Hydrogen and Nitrogen on Coal at Temperatures up to 200°," J. Soc. Chem. Ind. 47 142-43T (1928).
377. Donnelly, J. T. et al. "The Effect of Pre-Oxidation on the Primary Distillation Products of Coal. I. The Preliminary Oxidation of the Coal," J. Soc. Chem. Ind. 47 1-4T (1928); IV. The Distillation at 600° of the Oxidized Coal Samples," ibid. 189-92T.
378. Herd, J. T. et al. The Effect of Pre-Oxidation on the Primary Distillation Products of Coal. II. Controlled Preliminary Oxidation of Coal," J. Soc. Chem. Ind. 47 139-42T (1928).
379. Haslam, G. S. "A Study of the Action of Coal on a Photographic Plate in the Dark," Fuel 7 253-57 (1928) June.
380. Coles, G. and Graham, J. I. "The Absorption of Oxygen by Preheated Coal," Fuel 7 21-27 (1928) January.
381. Francis, W. and Wheeler, K. U. "The Reaction Between Oxygen and Coal," J. Chem. Soc. 2958-67 (1927).
382. Kreulen, D. J. W. "The Effect of Concentrated Sulphuric Acid on Different Coal Types. I." Brennst.-Chem. 8 149-54 (1927) May 15 (German text).
383. Kreulen, D. J. W. "The Change in Weight of Coal During Prolonged Oxidation at Low Temperatures," Fuel 5 345-46 (1926) August.
384. Parr, S. W. and Milner, R. T. "The Oxidation of Coal at Storage Temperatures," Fuel 5 298-301 (1926) July.
385. Parr, S. W. and Milner, R. T. "Storage of Coal and Spontaneous Combustion. Round Table Discussion. The Oxidation of Coal at Storage Temperatures," Ind. Eng. Chem. 17 115-17 (1925).
386. Pearson, A. R. "Some New Derivatives of Bituminous Coal," J. Soc. Chem. Ind. 42 68-72T (1923).
387. Coles, G. "The Specific Heat of Coal and Its Relation to Composition," J. of the Soc. of Chem. Industry, XLII 435-9 (1923).

388. Tideswell, F. V. and Wheeler, R. V. "The Oxidation of Coal," J. Chem. Soc. 115 895-902 (1919).
389. Wheeler, R. V. "Oxidation and Ignition of Coal," J. Chem. Soc. 113 945-55 (1918).
390. Fischer, F. Gesammelte Abhandlungen zur Kenntnis der Kohle 1 26-29. Berlin: Gebruder Borntraeger, 1915-16. ibid 2, 1917.
391. Porter, H. C. and Ralston, O. C. "A Study of the Oxidation of Coal," U. S. Department of the Interior Bur. Mines Tech. Paper No. 65. Pittsburgh, 1914.
392. Hoffman, K. A., Ehrhart, O. and Schneider, O. "Activation of Chlorate Solution by Means of Osmium. II. Communication," Dtsch. Chem. Ges. Berlin 46 1665 (1913) (German text).
393. Porter, H. C. and Taylor, G. B. "The Specific Heat of Coal and Its Relation to the Presence of Combined Water in the Coal Substance," I. E. C. 5 289-93 (1913).
394. Habermann, J. "An Experiment on the Auto-oxidation of Coal," J. Gasbeleucht. Verw. Beleuchtungsarten Wasserversorg. 49 419-22 (1906) (German text).
395. Hart, F. "Contribution to the Chemistry of Coals," Chem. Ztg. 97 1204 (1906) (German text).
396. Fischer, F. "Storage Loss and Spontaneous Combustion of Bituminous Coal," Z. Angew. Chem. 12 764-67 (1899) August 8 (German text).
397. Heumann, K. and Kochliss, P. "Behavior of Chlorosulfonic Acid to Several Metalloids and Tin," Dtsch. Chem. Ges. Berlin 15 416-20 (1882) (German text).
398. Ditte, A. "Chemical Society. March 18th Session," Dtsch. Chem. Ges. Berlin 3 325 (1870) (German text).

1.11 Associated Invention Disclosures

Invention disclosures associated with the work of OCR Contracts Nos. 14-01-0001-381, -381(1), and -381(2) are listed below; each listing starts with the OCR case number.

- OCR-1100: "Treatment of Coal to Prevent Agglomeration," B. S. Lee and F. C. Schora. U.S. Patent No. 3, 632, 479 issued January 4, 1972. (Assigned to United States of America.)
- OCR-1101: "Device for Dewatering and Feeding Slurry to a High-Pressure Reactor," B. S. Lee. Disclosed to OCR.
- OCR-1102: "Improved Methods of Coal Pretreatment," B. S. Lee. Disclosed to OCR.
- OCR-1175: "Methanation Process Utilizing Split Cold Gas Recycle," D. J. Tajbl, B. S. Lee, F. C. Schora and H. W. Lam. U.S. patent application filed. (ERDA Case No. S-46, 138.)
- OCR-1781: "Production of Carbon," W. W. Bodle. Disclosed to OCR.
- OCR-1817: "Electro-Chemical-Oxygen Gasifier," J. Huebler, F. C. Schora, and B. S. Lee. Disclosed to OCR.
- OCR-2051: "Electrode Assembly," F. C. Schora, C. W. Matthews, and T. M. Knowlton. U.S. patent application filed by U.S. Government. (ERDA Case No. S-46, 141.)
- OCR-2052: "Methanation Process," C. W. Matthews. U.S. patent application filed by U.S. Government. (ERDA Case No. S-46, 139.)
- OCR-2053: "Ammonia Destruction," C. W. Matthews. Disclosed to OCR. (ERDA Case No. S-46, 100.)

PART II
HYDROGASIFICATION IN 4-INCH PDU

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2.0 Summary of Hydrogasification in the 4-Inch PDU

During the contract period reported in this document, starting in 1964 and ending in 1972, more than 250 coal hydrogasification tests were performed under a variety of conditions and utilizing many types of coal in combination with a variety of gaseous feeds.

The work was performed in a 4-inch-diameter reactor termed the hydrogasification process development unit (PDU), which is described in its various configurations herein. The results of this PDU hydrogasification work helped to confirm early HYGAS concepts and played a significant role in shaping criteria for design of the HYGAS pilot plant reactors.

In the early phases of operation and shakedown of the demonstration unit, a low-temperature bituminous coal char of uniform composition was used. During the investigative phase of the hydrogasification program, 14 different coals were evaluated for the effect of pretreatment operations and/or char composition on the hydrogasification results. The coals were selected to give a range in rank from a lignite to a low-volatile bituminous as well as for three different high-volatile bituminous coals to determine variation in performance of coals due to origin. FMC Corporation Project COED char was also investigated for comparison.

Early moving-bed experiments were conducted with -35+80 USS mesh char for low throughputs and -10+40 USS mesh for high throughputs of coal and gas feeds. The coarser feed allowed higher gas velocities without fluidizing the char bed. For fluid bed tests, the particle size was extended to cover the whole range of char feed. The -10+80 mesh size was used for all fluidized-bed tests.

Initially, the hydrogasification program utilized a moving-bed configuration which offers a number of advantages. At the top, highly reactive fresh coal is in contact with the product gas which results in high methane equilibrium concentrations in the product gas. Less reactive partially gasified char is in contact with hydrogen-rich feed gas at the bottom of the bed which promotes the rates of both the carbon-hydrogen and carbon-steam reactions.

Typically, hydrogasification of lightly pretreated Ireland Mine bituminous coal with hydrogen and steam in a moving bed resulted in up to 38.5% carbon gasification and a product gas of 495 Btu per standard cubic foot. Results with Montour No. 4 mine pretreated coal and a North Dakota lignite are 28% and 57% carbon gasified and 576 and 511 Btu per standard cubic foot of product gas, respectively.

It was found, using volatile matter content as an index of pretreatment severity, that pretreated coal with between 24 and 26% volatile matter can be processed without agglomeration in a 4-inch diameter reactor. It may be possible to feed coals with less pretreatment — or even raw coal — in a larger diameter reactor.

Experience was gained from these tests in adjustment of feed tube size, length and location; the amount of nitrogen purge-gas required to pass through the tube; and the start-up sequence necessary for a successful operation.

Two-stage hydrogasification was simulated in sequence, by feeding the pretreated coal in the low-temperature stage and partially gasified coal from the low-temperature stage to the high-temperature stage. This is realistic except that the partially gasified coal was fed to the second (high-temperature) stage at ambient temperature instead of at temperatures between 1200° and 1400°F. All the tests were conducted at minimum hydrogen/coal ratio to yield about 50% carbon gasification, which provides sufficient residual carbon for hydrogen generation in a subsequent operation.

Because of the low temperature in the first stage, steam-carbon reaction is not expected in the first stage. The carbon-oxides formed in this stage come from the organic oxygen in the coal. However, steam does play an active role in low-temperature gasification. Experimental results indicate that steam seems to suppress the release of oxygen from coal as water and forces it to leave as carbon oxides. This is desirable because it reduces hydrogen loss and carbon oxides can be further converted to methane by catalytic methanation.

It has been well established that the hydrogenation of the volatile matter in coal proceeds very rapidly and yields methane concentrations higher than the equilibrium value in a β -graphite-hydrogen system. The first-stage hydrogasification demonstrated this type of reaction as shown by the observed rapid rate of reaction and lack of equilibrium hindrance to methane formation in this stage. The partially gasified coal (in the high-temperature stage) was less reactive at temperatures from 1700° to 1900°F.

On comparing the integral methane formation rates with those reported by others, it was found that 1) the rate of methane formation for pretreated Pittsburgh coal is not slowed by the presence of methane in the feed gas; 2) the pretreated coal is quite reactive, probably due to its high volatile matter content as compared to others; and 3) in the high-temperature stage, partially gasified coal gave rate constants quite similar to those obtained with Disco char and residual Australian brown coal, both of which had very little volatile matter.

The carbon-steam reaction was significant only at temperatures above 1700°F, and reaction rate was found to increase with temperature. At the hydrogasification temperature utilized, this reaction is expected to be substantially removed from equilibrium. The carbon-steam reaction is important not only as a source of generating in situ hydrogen, but also as a built-in temperature controller since it absorbs the heat generated by exothermic carbon-hydrogen reaction.

Gas samples collected at different levels indicated that in the high-temperature test the reaction was practically complete in the lower half of the bed, whereas in the low-temperature test the bulk of the reaction took place in the free-fall zone and at the top of the bed. This is to be expected because the high-temperature reaction is equilibrium-limited and apparently attains its limit in a relatively short contact time, and the low-

temperature reaction is extremely rapid, requiring only a matter of seconds for completion (the residual carbon being less reactive at the low temperature). In view of this, a likely hydrogasifier configuration would incorporate a low-temperature zone for the rapid reactions followed by a high-temperature zone for the slower reactions.

Free-fall tests were conducted to study coal conversions at short residence times. The coal residence times varied from 8 seconds for 60 mesh to 41 seconds for 200 mesh particles. The coal feeds included medium and low-volatile-content bituminous coals, a subbituminous coal and two different lignites. The tests indicated:

1. Most of the steam reacts with char rather than gaseous hydrocarbons, and hence the steam decomposition is dependent on the char residence time.
2. It is possible to hydrogasify a highly caking coal (Pocahontas No. 4 Seam) in free-fall without agglomeration.
3. It is feasible to convert lignite (up to 37%) at high pressures by pyrolysis in a free-fall.

A major operational restriction to moving-bed operation was the limit it set on coal and gas feed rates. Fluidized-bed operation would overcome this and increase the hydrogasification capacity significantly. Fluidized-bed operation, with its solids backmixing, would also eliminate the reaction gradient and yield uniform temperature and composition for the char bed.

Fluidized-bed tests were conducted at selected conditions on eight bituminous coals, three subbituminous coals and two lignites. Two-stage hydrogasification was also simulated in two sequential tests, as in the previous moving-bed tests. The feed gas was varied from hydrogen-steam mixtures to synthesis gas plus steam, mixtures of hydrogen, methane and steam, and mixtures of synthesis gas, methane and steam to simulate the two-stage hydrogasifier.

The following conclusions can be drawn from the fluidized-bed tests in the 4-inch-diameter reactor:

1. As shown in the free-fall tests, high-, medium-, and low-volatile bituminous coals can be successfully hydrogasified in a lean-phase mode before direct injection into a fluidized bed. This indicates that pretreatment of these coals may be eliminated by a two-step lean-phase process followed by dense-phase fluidization. Lignite and subbituminous coals generally need no pretreatment; one subbituminous coal (Colcrado Laramie No. 3 seam subbituminous) performed marginally without a pretreatment. There is no significant difference in hydrogasification results for medium and high-volatile-content bituminous coals.
2. Subbituminous coals are more reactive than pretreated bituminous coals but somewhat less active than the lignites. For both the subbituminous coal and the lignite feeds, hydrocarbon yields were similar. The increased carbon gasification with lignite was due mainly to the increased yield of carbon oxides and oil products.

3. Hydrogasification of FMC Corporation's Project COED char showed that this char has a lower reactivity than pretreated or partially-gasified bituminous coal from Pittsburgh No. 8 seam, Ireland Mine.

The use of synthesis gas instead of hydrogen in the feed gas to the hydrogasifier is of interest as it would eliminate the need for carbon monoxide shifting and carbon dioxide removal following the hydrogen production step. Results of the tests using synthesis gas-steam mixtures show that for bituminous coals the reaction rates are quite sensitive to the hydrogen partial-pressure in the system. The use of synthesis gas in place of hydrogen requires operating adjustments in order to maintain the necessary conversion levels of carbon and steam. These adjustments may consist of 1) longer residence time, 2) higher steam concentration to increase water-gas shift reaction, 3) higher synthesis gas-to-coal ratio, 4) higher system pressure to increase hydrogen partial pressure, and/or 5) multistage contacting to improve countercurrency, or combinations thereof. However, with lignite, the full benefit of hydrogasifying with a synthesis gas instead of hydrogen can be realized without any offsetting penalty. A beneficial effect of using synthesis gas for lignite hydrogasification is the apparent suppression of oil production.

The reaction of subbituminous coal to hydrogasification with synthesis gas is similar to that exhibited by bituminous coals. In another test, FMC char also yielded lower carbon gasification with synthesis gas than that with hydrogen.

The principal advantages of operation at a lower pressure are reduced capital investment and easier solids handling. These have to outweigh the reduced methane production and carbon conversion to be expected at lower pressure. Tests with high-volatile bituminous coal at 500 psig indicate that the product gas does indeed have lower methane concentration at lower pressure (27.5% versus 36.9%) for similar carbon conversions. For lignite the hydrocarbon yield at 500 psig was only 86% of that at 1000 psig, while the carbon oxides yield was 115% of that at higher pressure. Sixty-four percent less carbon in lignite was converted to oil at 500 psig. The use of synthesis gas instead of hydrogen did not unduly affect the carbon conversion at lower pressure for lignite.

For subbituminous coal, the carbon gasification, hydrocarbon yield and product gas heating values were significantly greater at 1000 psig than at 500 psig. The carbon gasified at 500 psig compares favorably with that at 1000 psig when synthesis gas and steam are used as feed gas.

2.0.1 Product Gas Composition and Trace Components

The major constituents of the product gases produced by the hydrogasification of coal and lignite with hydrogen and steam in the PDU tests discussed are: methane, carbon oxides (carbon monoxide and carbon dioxide), and hydrogen. Methane yield is determined by the degree of coal conversion and may also be controlled by the reactor temperature that sets the equilibrium composition of the product gas. The amount of carbon oxides formed is dependent on the oxygen content of the coal feeds and the steam-to-coal ratio. Feeds high in oxygen content such as subbituminous coal and lignite, when gasified, produce more carbon oxides than bituminous coals produce at

similar conditions. In addition, the higher the steam-to-coal ratio, the greater will be the carbon oxides production, other conditions being equal. The ratio of carbon monoxide to carbon dioxide is set by the water-gas shift reaction, which is temperature controlled. The hydrogen content of the product gas is determined largely by the quantity of unreacted hydrogen remaining after the reaction. The concentration of hydrogen is related directly, but not linearly, to the feed hydrogen-to-coal ratio. As the stoichiometric hydrogen-to-coal ratio is increased, hydrogen concentration in the product gas tends to increase at a greater rate.

In addition to methane, small quantities of other saturated hydrocarbon are produced. Typical concentrations of these components are, ethane, 1.5%; propane, 0.5%; and butane, 0.2%. The principal aromatic in the product gas, generally less than 1%, is benzene.

A portion of the nitrogen in the coal is gasified and a substantial part, if not all, of it appears in the reactor product gas as ammonia, which hydrolyzes in the water condensate.

While there is considerable scatter in the data, it is evident that sulfur gasification tends to increase as gasification proceeds and that the sulfur is preferentially gasified, i. e. the percent conversion of feed sulfur is always higher than percent conversion of coal on a moisture- and ash-free basis. Most of the sulfur appears in the reactor product gas as hydrogen sulfide, accompanied by small amounts (probably less than 200 ppm) of carbonyl sulfide (COS) and traces of organic sulfur compounds.

2.0.2 Char Compositions

Char rates and compositions reflected the degree of conversion of the feeds to gaseous and liquid products. Volatile matter contents of bituminous coals were generally reduced to 3% or less, and to less than 7% for subbituminous coal and for lignite. The reduction in hydrogen content tended to parallel the reduction in volatile matter content. Hydrogen concentration in the residue was reduced to less than 1.5% for all feeds. Gasification of the bituminous coals resulted in nearly complete consumption of the oxygen in the coal to produce carbon oxides and water. The residues produced from subbituminous coal and lignite gasification still contained from 3 to 6% oxygen by weight. In general, sulfur concentrations were reduced up to 50% in bituminous coal chars, and more than 50% in subbituminous and lignite residues. Carbon concentration, in all cases, was significantly higher in the residue than in the feed.

There was no observable trend in the change in size distribution of the coal feeds after hydrogasification. Any breakdown in particle size due to attrition, or fracture, induced by the reaction, appeared to be balanced by particle growth due to coalescence.

Gasification of the coals and lignite resulted in a sizeable reduction in the bulk density. Lightly pretreated bituminous coal bulk densities were reduced from a range of 20 to 25 pounds per cubic foot, to a range of 15 to 20 pounds per cubic foot. Bulk densities of dried, untreated subbituminous coal and lignite were of the order of 45 pounds per cubic foot. After gasification, the subbituminous coal bulk density was reduced to 28 pounds per cubic foot, while the lignite bulk density was reduced to 20 pounds per cubic foot.

2.0.3 Liquid Products

Condensed liquids resulting from the hydrogasification of coals and lignite consisted mainly of water and a light oil fraction. Small quantities of ammonia and unidentified sulfur compounds were generally dissolved in the liquids. The relative quantities of water and oil were dependent mainly on the amount of steam fed and steam decomposed, and on the nature of the coal feed. Feeds high in volatile matter content, such as subbituminous coal and lignite, produced more oils than bituminous coals, other conditions being equal. Oil production was also influenced by reactor temperature, being higher at lower temperatures than at higher temperatures.

Specific gravity of the by-product oils was in the range of 1.001 to 1.010. Typically, the oil composition was 90 weight percent carbon and 6 weight percent hydrogen, the remainder being small quantities of oxygen, nitrogen, and sulfur. The principal compounds in the oil are benzene and toluene.

2.1 Introduction

During the contract periods reported in this document, starting in 1964 and ending in 1972, more than 250 coal hydrogasification tests were performed under a variety of conditions and utilizing many types of coal in combination with a variety of gaseous feeds.

The work was performed in a 4-inch-diameter reactor termed the Hydrogasification Process Development Unit (PDU) which is described in its various configurations herein. The results of this PDU hydrogasification work helped to confirm early HYGAS concepts and played a significant role in shaping criteria for design of the HYGAS Pilot Plant reactors.

2.2 Description of Hydrogasification Process Development Unit (PDU)

Design requirements of the hydrogasification process development unit were based on operational pressures up to 2000 psig and temperatures up to 2200°F. The high temperatures and pressures were employed to promote the formation of methane. The reactor tube length was sized to provide adequate residence time for free-fall hydrogasification studies and the tube diameter was set by coal-bed fluidization velocity requirements at acceptable gas rates. From these design considerations, a balanced-pressure concept of reactor construction evolved.

2.2.1 Design Features

The balanced-pressure concept of reactor construction, involving two concentric vessels, was dictated by the strength of material at high temperature and pressure and by the size of the reactor. For small reactors, a single vessel is satisfactory up to 2 inches inside diameter. The wall can be made thick enough to withstand the pressure up to 1700°F even with heat being directly supplied through the wall. For large units and at higher temperatures, however, the wall thickness required for a single-tube design becomes, at best, impractically high. As a result, a balanced-pressure reactor design was chosen involving a reactor tube with heating elements surrounding it and a pressure-containing shell that encloses the reactor-heater assembly. The shell is insulated from the heating elements and hence is designed as a low-temperature pressure vessel; the reactor, not being subjected to differential pressure across its walls, need only be designed to withstand the high temperature.

The balance of pressure between the shell and the tube is maintained through a differential pressure controller that controls the shell pressure as a slave to the reactor pressure, admitting gas to, or venting gas from the shell as required. Gases flowing to the shell and reactor are thus separate, with the shell pressurized by nitrogen and the reactor pressurized with whatever gaseous reactants are being used. While more complex than a simple pressure-equalization line between the shell and reactor, the arrangement described prevents the hot, corrosive, tar-containing reactor gas from contacting the shell and the heating element.

At the pressure involved, gas density becomes high; therefore, free convection in the insulation must be minimized to enhance temperature control.

Consequently, the annular space between the heating elements and the shell is tightly packed with Fiberfrax insulating fibers.

2.2.2 Flow Sheet

A schematic diagram of the whole system is shown in Figure 2-1. Coal or char feed is placed in the feed hopper before a run starts and is fed to the top of the reactor continuously by a variable-drive screw feeder. The product is discharged through a star valve into a residue receiver. Within the limitation of the capacity of the feed hopper and residue receiver, the operation is continuous.

Reactant gases enter the reactor at the bottom, countercurrent to the flow of solids, in order to obtain the highest utilization of the hydrogen and to directly produce pipeline-quality high-Btu gas. Process gases are stored in four banks of high-pressure storage tanks, each consisting of four 9-inch diameter by 20-foot long cylinders. Each cylinder bank can store 8800 standard cubic feet of gas at 3600 psig. These storage tanks are serviced by two 3000 standard cubic feet-per-hour, 3000 psig Ingersoll-Rand compressors.

With the original auxiliary equipment for moving-bed operation, hydrogen comes from high-pressure storage tanks, is metered through an orifice, and preheated in a 13-kilowatt electric resistance-heating furnace. The hydrogen line then joins the steam line and enters the reactor. The steam is generated and superheated in a separate 13-kilowatt electric resistance-heating furnace. With modified equipment for fluidized bed operation the hydrogen is preheated in the tube coil of a natural-gas-fired furnace. The steam is generated and superheated in a different coil in the same natural gas fired furnace. Preheated hydrogen and superheated steam are then premixed before flowing to the reactor.

The water for steam generation is weighed and pumped through a high-pressure pump. Instead of hydrogen, premixed gaseous mixtures of various compositions can be blended in storage tanks for simulation tests. The gases flow upward through the reactor and leave at the top, then pass through bayonet filters which remove solids carryover and liquid reaction product. The gases then pass through a water-cooled condenser followed by a knockout pot to remove moisture, tar, and oil. After undergoing a final cleanup through packed cartridge filters, the gases are released through back-pressure regulating valves. The low-pressure gases are then metered through a gas meter, sampled in a gasholder, analyzed for specific gravity and heating value, and finally flared.

Temperatures and pressures at various points are recorded or indicated. A thermocouple at the center of each heating element controls the power input to that zone. Additional thermocouples along the length of the reactor tube furnish data on the temperature profile. All thermocouples are chromel-alumel. Pressure taps are located as shown in Figure 2-1. The differential-pressure controller between the shell and the tube controls solenoid valves (on-off, normally closed) for either admitting or venting nitrogen to and from the shell. The taps leading to this controller are not purged (despite the fact that tarry material may accumulate in the reactor side) in order to avoid having the controller sense the purge gas pressure in the event of blockage in either of the taps.

To prevent overpressurization on the shell-side, rupture disks are installed. On the reactor side, parallel back-pressure regulating valves are loaded to the desired operating pressure. These valves release product gases when the actual pressure exceeds the set value.

2.2.3 Reactor Description

The first reactor was a double-walled unit consisting of a 2-inch ID, 0.25-inch-thick mullite tube inside a Type 310 stainless steel, Schedule 40 pipe. The annulus between the mullite tube and the pipe was packed with Fiberfrax. The refractory liner is intended to promote adiabatic operation along the length and to prevent failure of the 4-inch reactor tube in the event of runaway reaction temperatures. The reactor assembly is 25 feet long. The entire allowance for expansion is taken up by an expansion bellows at the bottom.

Heat is supplied to the unit through seven zones, each 31 inches long, that utilize electrical resistance heaters. Each zone is controlled by a thermocouple peened to the outside wall of the reactor. The power supply for each of the two terminal zones is rated at 7.5 kilowatts, and for each of the five zones between the ends at 5 kilowatts each. The control is of the saturable transformer type, which enables heating along the reactor to be controlled to within $\pm 20^{\circ}\text{F}$.

To minimize stress to the reactor tube due to thermal cycling at the end of each run, the heaters are not turned off completely, but are merely cut back to hold the system near 1300°F . The double-walled reactor tube failed after about 25 tests. The inner refractory tube cracked and spalled under repeated thermal stressing. This allowed coal particles to lodge in the annulus between the refractory tube and the metal tube. When reacted with hydrogen, these coal particles produced excessively high temperatures at the metal tube walls resulting in the tube failure.

The replacement reactor was a 4-inch Type 446 alloy steel, Schedule 40 tube without any refractory liner. This low-nickel alloy was chosen for its greater resistance to sulfur attack than the high-nickel Type 310 stainless steel. This unit performed well for about 30 runs, then was ruptured over a weekend by a pressure upset.

The reactor assembly is shown in Figures 2-2 and 2-3. The reactor tube is a 4-inch-diameter Schedule 40, Type 446 alloy steel pipe. Of the 21-foot length, 18 feet are in the heated zone as in previous arrangements. Thermocouples are located about 10 inches apart. A 4-inch-diameter expansion bellow is welded to the lower end of the tube. Grayloc flanges of 0.5 inch or larger are used for connections. The feed hopper and residue receiver capacity are approximately 8 cubic feet each. Because product char tended to stick in the star valve, bottom product discharge was converted to a screw; feed now is introduced at the top through a 1-inch screw feeder. Assisted by a constant nitrogen purge, the solids drop through a feed tube into the top of the heated section. By adjusting the discharge rate relative to the feed rate, the reactor can be operated as a free-fall reactor or as a moving-bed reactor. The entire reactor assembly is enclosed in a steel barricade for safety.

The position of the feed gas inlet within the reactor tube is variable and is set by the length of the feed gas tube projecting from the bottom of the reactor shell. Ordinarily, the gas inlet in the bottom of the reactor is at the lowest heating element in order to minimize the problem of condensation when steam mixtures are used, and to minimize heat losses.

The reactor-shell pressure balance control system is shown in Figure 2-5. A dual-bellows differential pressure unit measures the pressure differential between the reactor and the shell which is then transmitted via mechanical linkages to a pneumatic transmitter. This in turn transmits a pneumatic signal of from 3 to 15 psi to a bourdon tube gage with six photoelectric control switches activated by the position of the gage pointer. The six action points are set in this gage, as shown. Valves 1 and 3 are small solenoid valves for fine control. Valves 2, 4, 5, 6, 7 and 8 are shear-seal shut-off valves, pneumatically operated and solenoid actuated, and are much larger than valves 1 and 3. Valves 1, 2, 3, 4 and 5 are normally closed, whereas valves 6, 7 and 8 are normally open. In the event of failure, however, all valves close.

The control sequence is as follows: When the shell pressure is high, as during depressurization, the control gage pointer moves past the first control point which opens valve 3 to vent nitrogen from the shell. If this valve is not venting rapidly enough to bring the differential pressure back to zero, and the differential pressure continues to rise, then valve 4 would open when the pointer moves past the second control point. Valve 4 should seldom be required and is large enough to equalize pressures instantaneously. In the event of a major upset, however, where the differential pressure rises beyond the second control point, when the third control point is reached, valves 1, 2, 3, 4, 6, 7 and 8 all close, stopping all gas flows in and out of the system. Next, valve 5 opens, equalizing the pressure between the shell and reactor. In addition, a 40-psi rupture disk is installed in parallel with valve 5 so that, should valve 5 fail to open when required, the rupture disk would break and equalize pressure. Similar control action takes place when reactor pressure is high; in this case, instead of venting nitrogen from the shell, nitrogen is admitted into the shell. As a further aid in detecting the pressure differential, a dual-bellows differential pressure indicator is mounted in the panel board to indicate the true pressure differential between the reactor and the shell.

To improve the sensitivity of pressure response, distributor rings for both inlet and outlet gas flow are mounted inside the shell at several levels. These rings are perforated around the periphery. With this arrangement, pressure lags along the length of the reactor due to the shell being tightly packed with insulation, are practically eliminated.

To obtain data for studying the kinetics of the gasification reactions, internal gas sample probes and thermocouples have been inserted through the top. These probes provide data for establishing both a temperature and a conversion profile. The gas sample probes are stainless steel tubing of 0.125-inch OD by 0.0625-inch ID; the thermocouples are 0.0625-inch OD. The entire bundle is passed through the reactor top and sealed by special packing

glands. Life of these internal probes is limited by bends and kinks, formed through use, which eventually cause the probes to either crack or make their positions uncertain.

Among process variables, the accurate measurement of the bed level in the reactor is the most difficult to record. At the high pressures of operation that prevail, and with a low-density bed material such as coal or char, conventional means for measuring bed heights are not satisfactory. Differential pressure measurement across the bed fluctuates too much to be meaningful, because it represents a small difference between two large pressures, each of which tends to fluctuate individually. Devices such as a conductivity probe, which senses the difference in thermal conductivity between a bed of solids and a gas phase, are limited in life under the severe environmental conditions. A radiation-type sensor was found to be the most reliable and accurate means to sense and indicate bed level. The sensor utilized in the tests is manufactured by Nuclear-Chicago Corp.

The source of radiation is 2 curies of cesium-137. The source and the detector are mounted externally, 180° opposed, on a movable yoke outside the reactor shell. The density of the reactor contents is related to the degree of beam attenuation during beam transit through the reactor. In principle, the cesium sensor should indicate changes in bed density; actually, the unit is more reliably used as a bed-level sensor. It has the advantage of being external to the unit and thus can be located anywhere along the reactor; however, the unit must be calibrated at each location because the material in the path of the beam is not homogeneous.

2.2.4 Operation Sequence

Before each run, the system is first pressure tested to the full operating pressure with no solids in the system. Thus, without having to be concerned about solids being drawn into the reactor due to pressure surges, both pressurization and depressurization can proceed rapidly. Nitrogen, used for the pressurization, enters through either the top or bottom of the reactor tube; depressurization is through either the product gas line or the top of the feed hopper. When the test is satisfactory, the unit is depressurized and coal feed is charged to the hopper. The system is again pressurized for operation and power input to the heaters is adjusted to give the desired operating temperature. During the pressurizing, nitrogen is continuously purged through the solids feed tube to keep it clear and reasonably cool. Hydrogen flow is then established to the reactor, and solids feeding begins. If steam is to be admixed with the hydrogen, it is admitted to the reactor about a half hour after hydrogen flow is started. This procedure helps minimize the chances of condensation at cool spots.

Depending on whether the operation is to be free-fall or with a coal bed, the discharge screw rate is adjusted to either run the bed empty or permit the buildup of a bed. In moving-bed or fluidized-bed operation, the radiation bed-level sensor would indicate that the desired level has been reached. At this point, discharge rate is adjusted to maintain this bed level. Gas samples are taken regularly, and a composite gas sample is accumulated in a gas holder. Reactant and product gases are both metered for material balance.

After the run, solid samples are taken from the residue receiver. Temperatures, pressures, and flows are recorded or indicated on the panel board. Condensates from the product gases are drained periodically during the run, to be weighed, sampled, and analyzed.

At the end of the run, reactant gas and solids feed are turned off, and nitrogen is passed through the system for 30 minutes to purge the combustible gases. The system is then depressurized, disassembled and cleaned, particularly the product gas line which is always coated with tar and oil.

2.2.5 Equipment Modification and Addition Details

The broad scope and the complexity of the program for the study of the hydrogasification of coal made it necessary that the system for this study be adaptable to the processing conditions required by the program. To meet the needs of the processing conditions, to incorporate improvements as they evolved, and to replace components that failed, the hydrogasification system was modified in the course of the program. As these modifications have a bearing on the interpretation of the operating data, details of significant changes, additions, and modifications are discussed. To the degree possible, the time of the modifications is indicated relative to the run number of the hydrogasification test program.

2.2.5.1 Reactor Tube

In the early phase of the test program, when studies in the 4-inch diameter reactor tube had just begun, the expansion bellows attached to the bottom of the tube was damaged. The reactor expansion bellows was ruptured by an overpressurization of the reactor tube that resulted from a sudden and uncontrolled drop in the shell pressure that normally should be in balance with the reactor pressure. The upset occurred at a pressure of 250 psig when the reactor was being depressurized after run HT-43.

The rupture in the bellows occurred at a seam and was 0.25 inch long; faulty material did not appear to be a factor.

Following run HT-52, a routine pressure test of the pilot unit with nitrogen was started in preparation for the next scheduled hydrogasification test. To facilitate the pressure testing, 200-psig pressure was left unrelieved in the unit over the weekend, and the pressure-equalizing line between the reactor and the reactor shell remained open. During the weekend, however, an undetermined pressure disturbance caused the reactor-shell differential pressure controller to open the shell-pressurizing solenoid valve. However, a preferential flow of nitrogen to the reactor was caused by the higher resistance in flow to the shell as a result of piping and insulation. As a consequence, the reactor tube pressure rose above that in the shell and the tubes ruptured. The rupture occurred at the level of heating zone 5, as numbered from the top. The rupture damaged the heating elements in the lower section of the furnace. The heating elements in the upper section of the furnace were damaged in the process of removal of the ruptured reactor tube. The heating elements were replaced with new elements of similar design and construction as the original elements obtained from Marshall Products Company. A new

4-inch diameter reactor tube of type 446 stainless steel, and a new 4-inch diameter expansion bellows were installed. The change to the 4-inch diameter bellows was made to improve solids outflow from the bottom of the reactor by eliminating the restriction of the smaller diameter bellows. Before installation, the reactor tube was wrapped with a 0.50-inch-thick layer of Fiberfrax insulation so that temperature profiles could be clearly defined. The lower 31 inches of the reactor were left uninsulated to improve heat transfer to the tube in this zone where the heat loss is high, and where final preheating of the steam and hydrogen feed is accomplished.

The reactor tube was next replaced after run HT-137C. During post-run clean-up of the unit, it was found that the top of the feed tube and the upper portion of the thermowell extending into the solids bed had fused to the reactor tube. After the fused sections were removed a pressure test revealed a break in the reactor tube.

The reactor had been in service for about 80 runs over 18 months. In the course of the operations, the thermocouples, peened to the reactor wall, had gradually burned out. Accurate monitoring and control of the wall temperature could not be maintained. Thus, fusion of the gas feed tube and the thermowell could have resulted from undetected local overheating. A further contributing factor, however, was oxidation of the reactor residual lig-nite that had adhered to the feed tube and thermowell in the course of emptying the reactor.

The 4-inch-diameter reactor tube was replaced. Like the previous tube, the new one was a type 446 stainless steel. Schedule 40 4-inch ID pipe (4.50-inch OD, 4.026-inch ID). A section of the reactor tube corresponding to heating zones 3,4 and 5 was insulated with a 1-inch-thick blanket of Fiberfrax insulation. This insulation helps keep a more nearly adiabatic condition in the region of the coal bed.

2.2.5.2 Reactor Furnace

All seven of the reactor furnace heating sections had to be replaced as a result of the reactor tube rupture following run HT-52. These sections were damaged either by the tube rupture, or in the process of removal of the ruptured tube from the shell. The replacement heating sections were of the same size and design as the original sections, and came from the same supplier. The space between the outside of the heating sections and the inside of the pressure shell was again packed with Fiberfrax insulation.

After run HT-108, reactor furnace heating section of zone 3 became shorted. It was repaired by installing new insulation on the power input electrode at the reactor shell wall. Similar repair work was done on the electrode of zone 6 furnace section following run HT-110.

Zone 7 furnace section, the lowest section in the furnace, stopped working after run HT-158. The heating element apparently failed because of the severe power output demands and high temperatures at the lower part of the reactor. It was not practical to get to this heating section for either repair or replacement, so that tests subsequent to run HT-158 were made with only six heating sections operating.

2.2.5.3 Feed Gas Tube

Feed gases, including reactant steam, were fed to the bottom of the reactor. Within the reactor, the level at which the gases contacted the coal bed was determined by the length the feed gas tube projected upward from the base of the char discharge housing. This level set the bottom of the coal bed, for calculation purposes, in moving- and fluid-bed operations. To meet changing operational needs the length of the feed gas tube was varied as was the configuration at the end of the tube setting the gas distribution at the bottom of the coal bed.

Up to run HT-72, dry feed gas and steam were fed to the reactor through separate tubes. Each feed tube was a 0.375-inch, Schedule 40 pipe capped with a sintered metal disk contacting the coal bed at the bottom level of the reactor furnace.

For run HT-72, in order to maintain a more uniform coal-bed temperature distribution, a porous gas-distribution disk was positioned 108.5 inches above the bottom of the reactor furnace. The bottom of the coal bed was at the distributing disk. The modification described essentially eliminated the effect of heat losses at the end of the tube. As a result, a uniform temperature was maintained along the entire length of the reaction bed. The feed gas distributor, also installed for eventual fluid-bed operations, was a 3-inch-diameter, 0.125-inch-thick porous, stainless steel disk, positioned near the midpoint of the reactor tube. The disk is supported by a sectional pipe column which rests on the bottom reactor closure. Two 0.375-inch-OD by 0.277-inch-ID gas feed tubes extend up through the support column and terminate in a conical section just below the porous disk. The gas distributor disk also acts as a coal-bed support plate to keep the bottom of the coal bed well within the heated section of the reactor tube. Coal is discharged from the bed by gravity, through the annulus between the gas distributor disk and the reactor wall, then is screw fed from the bottom of the reactor tube to the residue receiver.

Coal discharge difficulties were encountered repeatedly in tests following run HT-72, because coal particles lodged in the annulus between the gas distributor disk and the reactor walls. For run HT-76, the feed gas distributor disk was removed and the previously used feed gas tube was reinstalled. This is a 0.375-inch pipe that extends to only 16.5 inches above the bottom of the reactor furnace.

For run HT-79, the gas distributor disk was again installed, but only for a limited number of tests. Because of difficulty in discharging coal from the reactor through the annulus between the disk and the reactor walls in subsequent tests, the 3-inch-diameter feed gas distributor was removed and a 0.375-inch pipe feed-tube extending to 16.5 inches above the bottom of the reactor furnace was installed for run HT-82. The feed gas tube was again extended to 108.5 inches above the bottom of the reactor for run HT-86. The gas distributor at the end of the tube was a 3.5-inch diameter "Rigimesh" porous disk. After run HT-88 it appeared that poor coal flow through the annulus between the feed-gas distributor disk and the reactor tube walls was responsible for coal backup experienced in this run. To improve the flow of coal at

this point, the annular area was increased for run HT-89 by reducing the diameter of the feed-gas distributor disk from 3.5 to 3.3125 inches. Coal flow past the distributor disk remained erratic in subsequent tests. Temporarily, in order to avoid coal discharging problems, the 3.3125-inch-diameter feed gas distributor disk was changed to a 0.5-inch tube with its end capped by a porous disk prior to run HT-95.

For run HT-96, a 2.88-inch-diameter feed gas distributor disk was installed. This disk provided a reasonably large annular cross-section for coal discharging.

To obtain higher coal bed temperatures when hydrogasifying at fluidization throughput rates, additional heat transfer area was provided between reacted coal flowing downward from the reaction zone and the feed gas flowing up to the gas distributor. This was achieved by installing a 0.375-inch-diameter U-tube, 108 inches long, in the feed-gas line between the base of the reactor and the gas distribution disk. This change was made for run HT-100.

For the next test, run HT-101, an annular feed-gas distributor disk of 3.5-inch OD and 1.75-inch ID was installed to improve solids flow past the disk. With this ring-type distributor, coal could flow around the outer edges of the disk and through the core of the disk.

To increase the free-fall distance in the reactor and thereby provide for a higher rate of coal hydrogasification in suspension, the annular feed gas distributor disk for run HT-102 was lowered from 108.5 inches to 62 inches above the bottom of the furnace.

To minimize discharge problems around the distributor for run HT-103, the annular gas distributor disk was replaced by a capped 0.375-inch pipe with twelve one-sixteenth inch diameter ports through the walls in the upper 1 inch of the tube. To increase the free cross-sectional area of the reactor below the end of the feed gas tube, the internal U-bend heat exchange tube for feed gas superheat (installed for run HT-100) was removed.

For run HT-164, to lengthen the free-fall reaction time before the coal reached the coal bed, the top of the hydrogen-steam feed tube was lowered by 31 inches so that feed gas contacted the coal bed 31 inches above the bottom of the furnace.

The feed gas distributor was returned to its position 62 inches above the bottom of the furnace for run HT-169.

For run HT-179 we again lowered the hydrogen feed tube distributor by 31 inches from its normal position to obtain a longer effective free-fall reactor length.

2.2.5.4 Coal Feed Tube

Normally, coal was introduced into the reactor tube through an injection tube extending into the heated section of the reactor tube. For reported tests,

up to run HT-56C, the coal injection tube was a 1-inch OD tube with a 0.049-inch wall, discharging at a level 36 inches below the top of the reactor furnace. The tube was attached to an insert in the head of the reactor.

For run HT-56C, the coal feed tube was removed to allow coal feed directly into the 4-inch-diameter reactor tube. The coal feed tube that was removed for run HT-56C was reinstalled following that test, but with modifications so that the coal could be injected into the heated section of the reactor tube. The tube has an inside diameter of 1.380 inches and extends 6 inches below the top of the furnace level.

Following run HT-87, when equipment modifications for fluid-bed operation were made, a modified reactor head insert with a 1-inch-OD coal feed tube was installed. The end of the feed tube extended 6 inches below the top of the furnace.

Purge nitrogen was normally fed to the top of the insert. To promote the flow of coal through the tube, for run HT-94, the nitrogen was injected directly into the coal feed tube through a 0.125 inch-diameter nozzle.

To improve coal flow through the top of the reactor at high coal feed rates, the 1-inch-diameter coal injection tube was removed before run HT-107 so that the feed screw would discharge coal directly into the reactor.

The coal injection tube was reinstalled for run HT-109.

For run HT-120, a motor-driven magnetically coupled stirrer was installed in the coal injection tube to promote the flow of coal by breaking up any buildup in the tube. The stirrer, driven at between 5 and 10 rpm, extends the full length of the tube and about 1 inch beyond. It is a 0.125-inch stainless steel rod formed into a 0.75-inch spiral with a 3-inch pitch.

For run HT-144, a modified drive for the stirrer in the coal tube was installed increasing the stirrer rotation to the range of 50 to 60 rpm. A tachometer indicated the movement of the stirrer and any stoppage due to binding.

Toward the end of the hydrogasification development test program, the uppermost reactor heating section, Zone No. 1, became inoperative so that no heat was being supplied to the top of the reactor. For hydrogasification tests with untreated New Mexico subbituminous coal, loss of Zone 1 heating was compensated for by providing a more rapid heat-up of the coal as it entered the reactor. The faster heat-up was achieved by lengthening the 1-inch-diameter coal feed tube by 30 inches for run HT-252. With the longer feed tube, the coal entered the reactor at the top of heating Zone No. 2, instead of at its former entry point in Zone No. 1.

2.2.5.5 Coal Feed and Discharge

Following run HT-52, the original star feeder used for discharging reacted coal from the reactor to the residue receiver was replaced with a screw discharger in order to 1) improve the rate and the reliability of char

discharge, and 2) increase the discharge rate in proportion to the programmed increase in the coal-feed rate. Dimensions of the discharge screw were: flight diameter, 2 inches; shaft diameter, 0.75 inch; flight pitch, 1 inch.

Modifications for fluid-bed operation made following run HT-87 included the installation of a 1.875-inch-diameter coal-feed screw, replacing the original 0.875-inch-diameter feeder.

Coal-feed screw jamming in run HT-137B was caused either by binding of the screw in the housing or by biting of the flights into the housing or housing connector. To correct the problem described, the front edges of the flights were tapered back to remove the sharp corners over the first 18 inches of the screw. In addition, the outside diameter of two flights at the housing connector was reduced by 0.125 inch to increase the screw clearance.

2.2.5.6 Product Gas Offtake Line

Product gases were withdrawn from the reactor through a 0.25-inch OD x 16-gage open-end tube. The entry to this tube for reported tests up to run HT-57 was 27.75 inches above the outlet of the coal injection tube. To minimize possible interference of product gas outflow with coal injection, the product gas offtake tube was extended 2 feet below the end of the coal feed tube for run HT-57. Because of partial plugging of the product gas offtake tube, for the next test, run HT-58, the 0.25-inch diameter product gas offtake tube was replaced with a 0.5-inch diameter tube, and was made 6 inches shorter than the coal feed tube.

When the unit was modified for fluid-bed operation following run HT-87, an internal cyclone was installed to separate coal dust from the product gas.

Prior to run HT-99 the product gas cyclone at the top of the reactor was removed, and two 18-inch-long sintered metal bayonet filters were installed inside the reactor tube just above the heated zone. The previously used bayonet filters outside the reactor were bypassed; the product gas was piped directly to the condenser from the top of the reactor.

For run HT-108 the upper of the two porous metal product gas filters was removed to minimize heat exchange between the product gases and the coal feed.

During run HT-114, the bayonet filter failed. Thermal stresses had cracked the filter face, allowing coal dust to be carried into the product gas line and the condenser, and plugging the product gas offtake system. The damaged bayonet filter was replaced.

New product-gas bayonet filters were installed for runs HT-154 and HT-160, replacing those that had become plugged and could not be cleaned.

2.2.5.7 Product Gas Sample Probes

Product gas sample probes for sampling gases within the coal bed consisted of 0.125-inch-OD x 0.0625-inch-ID stainless-steel open-end tubing

projecting into the coal bed. Three probes were installed for run HT-52 to sample gases 4, 6 and 7 feet above the bottom of the coal bed. Prior to this run, one gas sample probe was used for sampling at the top of a 7-foot coal bed. Following run HT-52, the number of gas sample probes in the bed was increased to six to better establish the gaseous concentration profiles in the bed. Gas sampling points were at the 0, 2-, 5-, 7-, 10-, and 12-foot levels, as measured from the bottom of the reactor.

These probes were removed for run HT-57. Three probes were installed for run HT-86 to sample gases from points 6, 18 and 30 inches below the top of 3.5-foot coal beds. These were used till run HT-102 when three new probes were installed as the position of the bottom of the coal bed was changed from 108.5 inches to 62 inches above the bottom of the coal bed. These probes were removed for run HT-107 and were not replaced until run HT-111. In tests following run HT-137, no gas sample probes were used.

2.2.5.8 Coal Feed Hopper and Residue Receiver

A 7.7-cubic foot residue receiver was installed following completion of run HT-52. This larger capacity receiver replaced the original 5.1-cubic foot receiver. It was used until a coal residue receiver of 14.7-cubic foot volume was installed in the hydrogasification PDU as part of the modification program for handling larger throughput rates in fluidized-bed operation. Design details of the 24-inch-OD receiver are shown in Figure 2-4.

At the same time, the original coal-feed hopper of 8.3-cubic foot capacity was replaced with a 17.5-cubic foot capacity hopper.

2.2.5.9 Differential Pressure Control System

Following the reactor tube rupture after run HT-52, an improved reactor-shell differential pressure control system was installed to maintain pressure balance across the reactor tube and to reduce chances of tube overpressurization. With the modified control system the shell is pressurized and vented by dual flow lines, the secondary lines to be opened when the differential pressure exceeds the normal control differential. This shortens the time lag for balancing the reactor tube and the shell. At a third control point, that is set well below the critical differential pressure at which damage to the tube might result, all inlet and outlet valves to both the reactor tube and the shell are closed, and the equalizing line between the reactor tube and the shell is opened. A schematic diagram of this control system is shown in Figure 2-5.

2.2.5.10 Coal Bed-Level Sensors

Coal bed levels in the reactor had been sensed by differential pressure readings and also by a heated thermocouple. The heated thermocouple device sensed the position of the coal bed by a change in temperature due to a change in heat conduction when immersed in the coal bed. Because of corrosion by hydrogen sulfide and extreme temperature, however, the life of the relatively slender thermocouple was limited. An additional consideration is that the heated thermocouple is essentially a fixed-level sensor because of inherent restrictions in its mounting. To allow flexibility in sensing the char bed along the entire reactor, and to improve the closeness of sensing, a radiation-type bed-level sensor was procured.

This bed-level sensor, essentially a density gage, was obtained from Nuclear-Chicago Corp. It consists of a lead-shielded radioactive cesium 137 source of 2 curies, and a radiation detector. The radiation source and the radiation detector are mounted 180° opposed on a movable yoke, outside of the reactor shell. The radiation detector is connected by a wire cable to a radiation indicator mounted on a panel board.

Following adjustments and calibration, the radiation-gage bed-level sensor was put in operation following run HT-55.

2.2.5.11 Temperature Sensing

Reactor tube temperatures were sensed by chromel-alumel thermocouples peened to the outside wall of the tube. Thermocouple spacing and locations on the tube before its rupture after run HT-52 are shown in Figure 2-6. Twenty-one thermocouples were attached to the tube wall. The number of thermocouples on the tube was increased to 31 after run HT-52. These thermocouples were also peened to the outside wall of the tube. Thermocouple locations and spacing in the expanded array are shown in Figure 2-7.

Thermocouples sensing the tube wall temperatures became totally inoperative after run HT-130 and could not be repaired without removing the reactor tube.

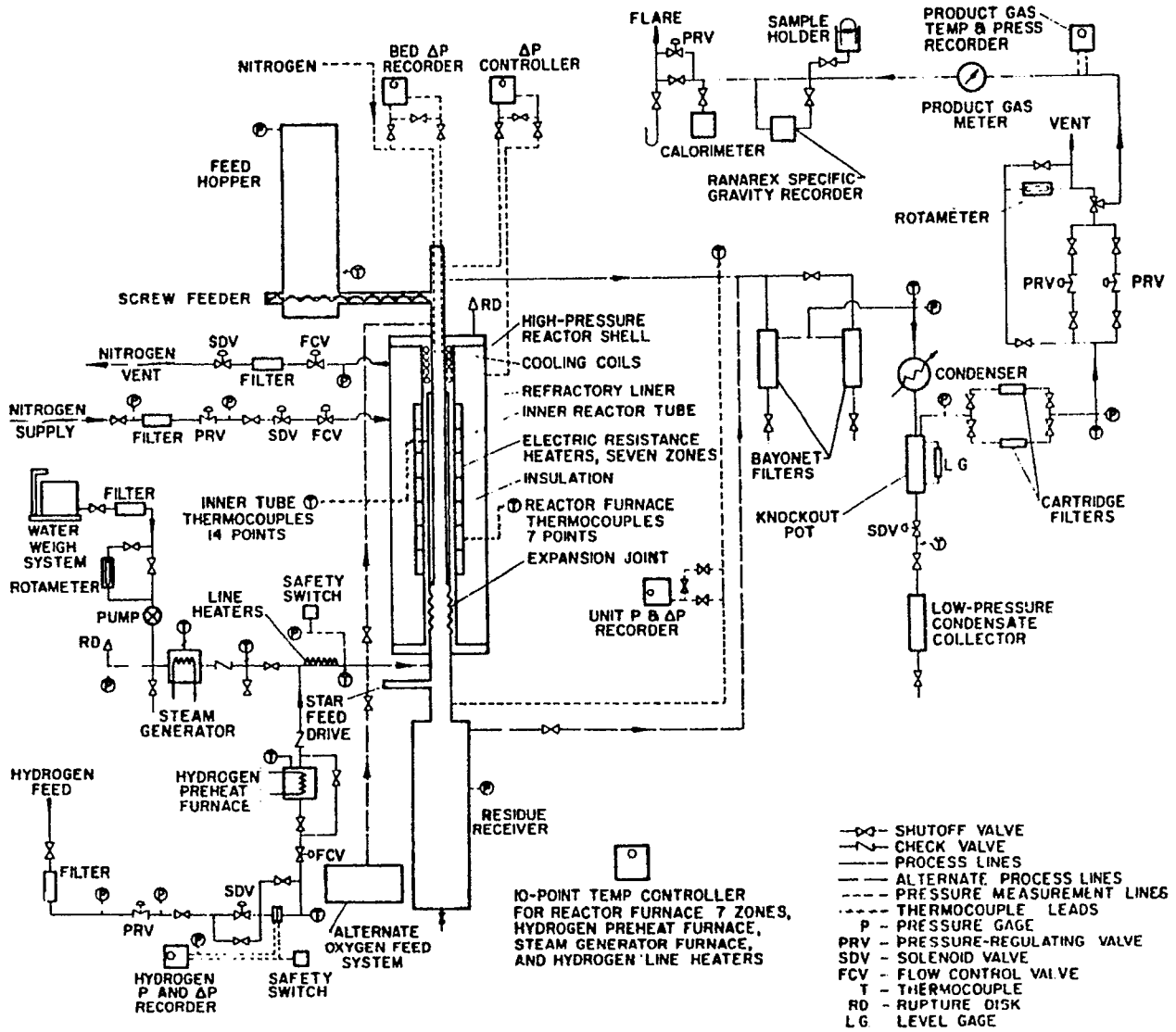
Reactor temperatures reported for runs HT-131, HT-132 and HT-135 are internal coal-bed temperatures. In these three tests, thermocouples sensed temperatures 72.5, 84.5 and 96.5 inches above the bottom of the reactor furnace.

A new reactor tube and thermocouples were installed for run HT-138. To sense tube-wall temperatures for preheat and operational control, a total of 32 thermocouples were peened to the outside tube wall along the length of the tube. The thermocouples were chromel-alumel with a 0.125-inch-diameter sheathing. Positions of the thermocouples on the tube are shown in Figure 2-8. Thermocouples were spaced at about 5-inch intervals along the lower 8 feet of the reactor tube, and at about 10-inch intervals above the 8-foot level. The closer thermocouple spacing at the lower end of the reactor tube provided more detailed temperature sensing in the region of the coal bed and in the region of the highest reactor-tube temperatures. Also, if some of the thermocouples at the lower end of the tube should have failed, the denser thermocouple spacing would still have provided adequate temperature sensing.

2.2.5.12 Auxiliaries

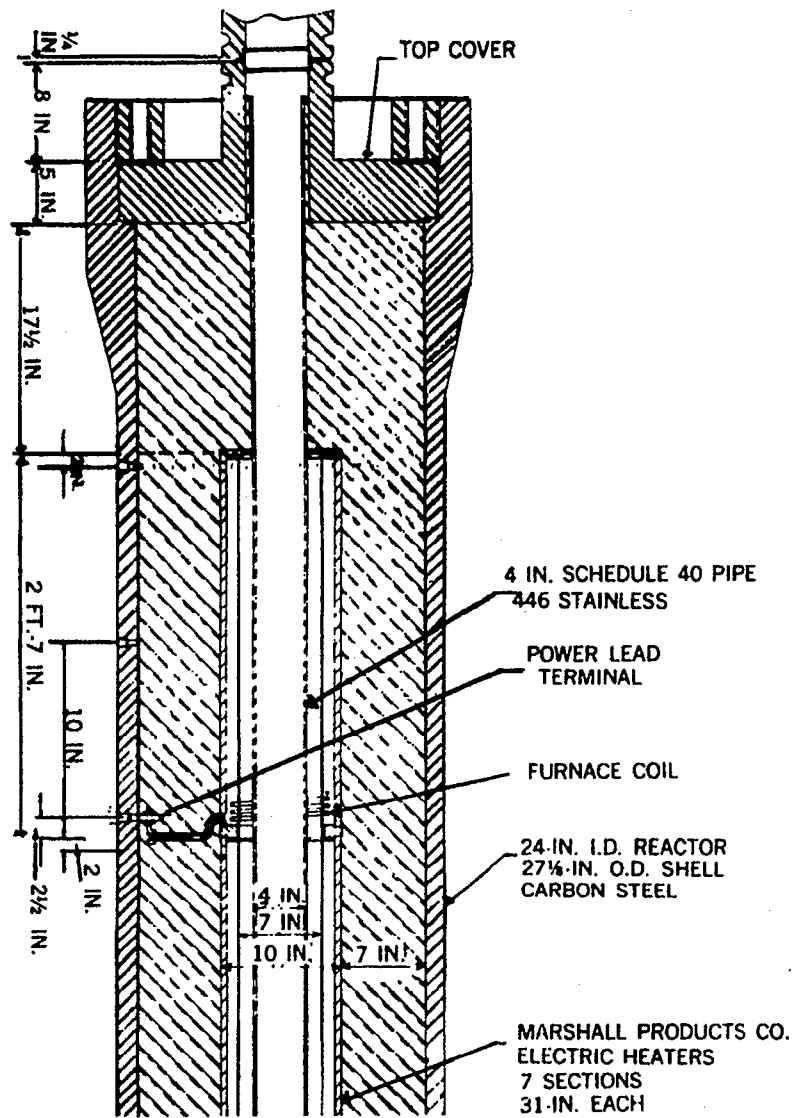
Major modifications of and additions to the auxiliary equipment of the hydrogasification unit were made when the unit was adapted for handling larger throughput rates in fluidized-bed operation.

A larger capacity, natural gas-fired, steam generating and hydrogen preheat furnace was fabricated. The heat-transfer tubes were fabricated



A7506 1400

Figure 2-L FLOW AND INSTRUMENTATION FOR HIGH-TEMPERATURE BALANCED-PRESSURE COAL GASIFICATION PROCESS DEVELOPMENT UNIT (PDU)



A7506 1401

Figure 2-2. FOUR-INCH REACTOR TUBE AND SHELL, UPPER PORTION

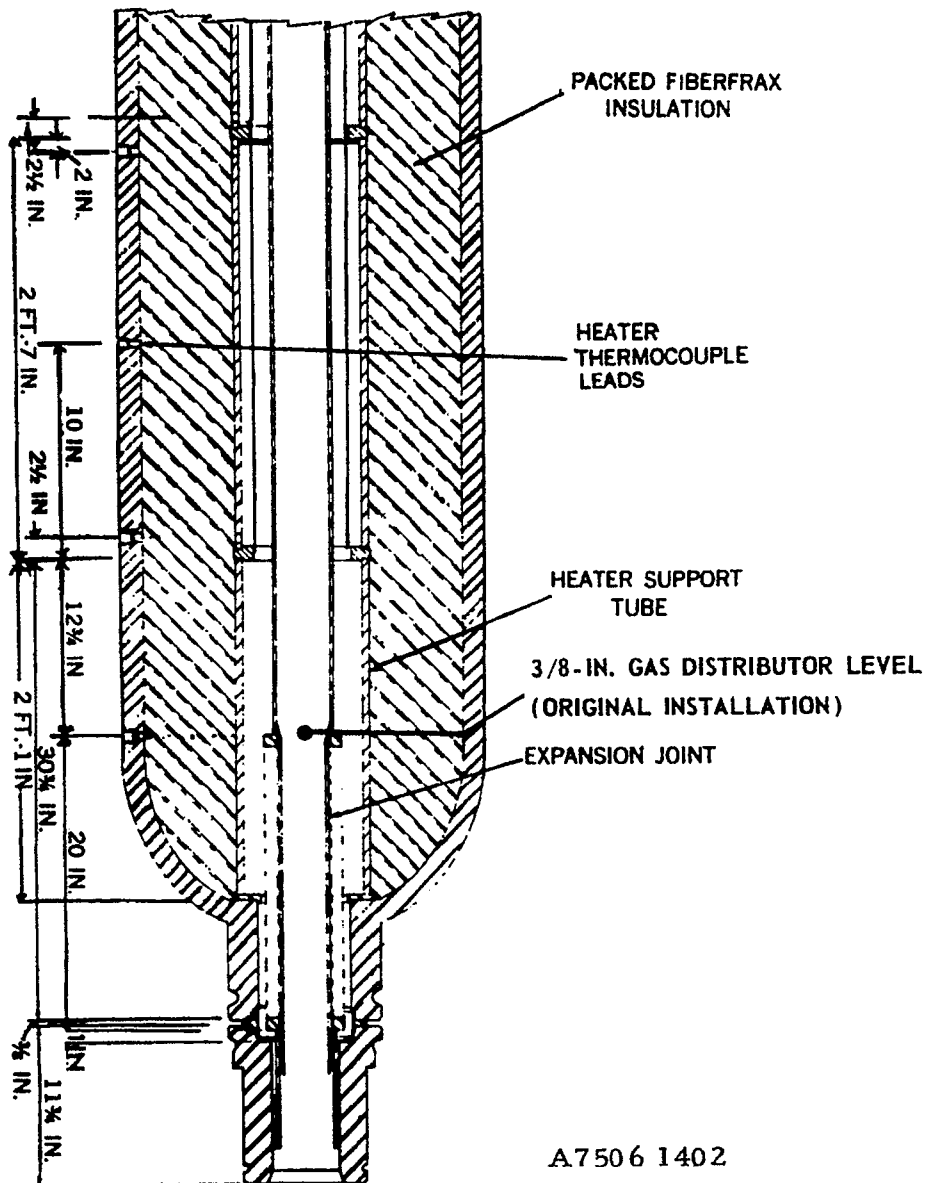


Figure 2-3. FOUR-INCH REACTOR TUBE AND SHELL, LOWER PORTION

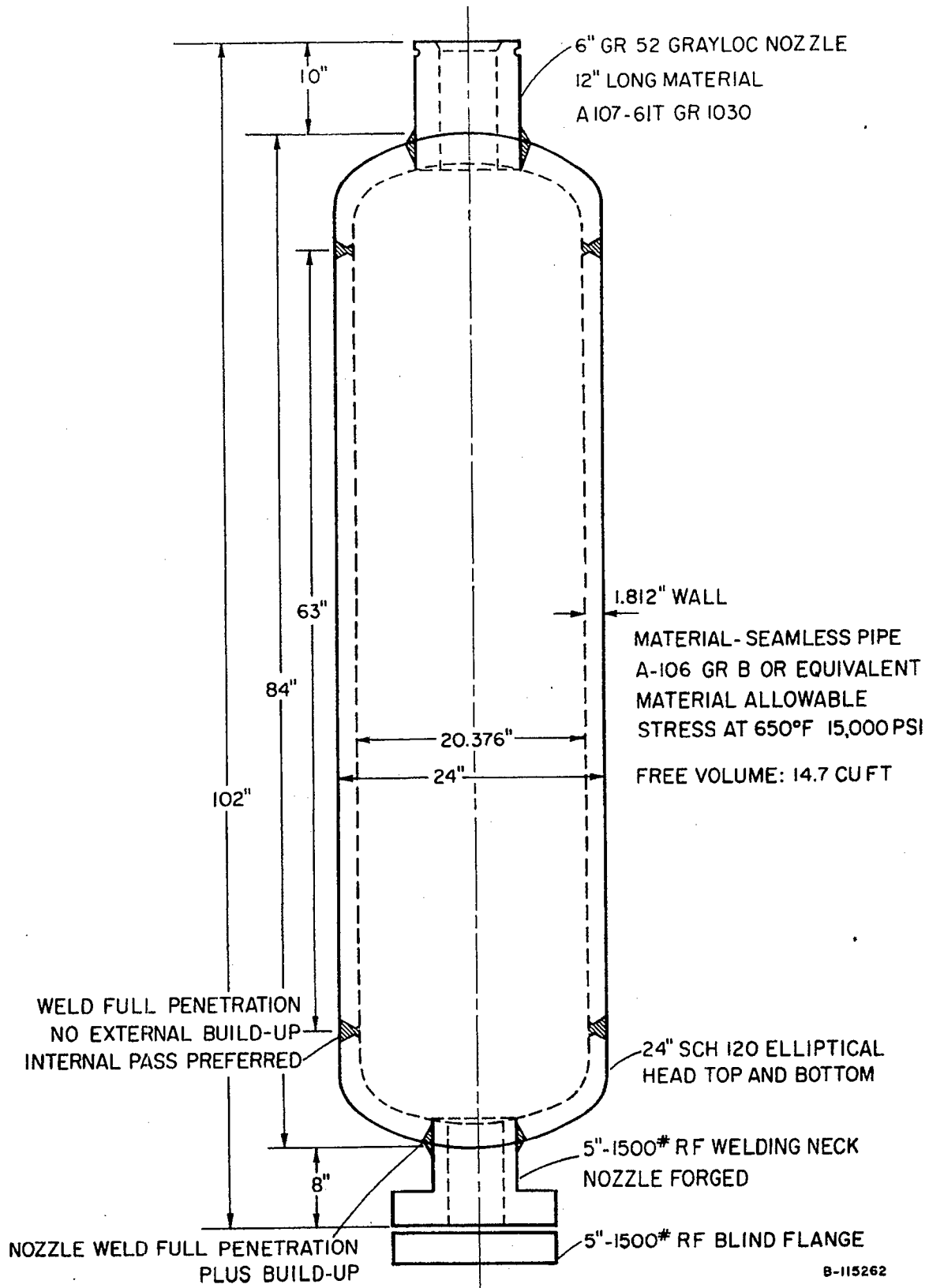
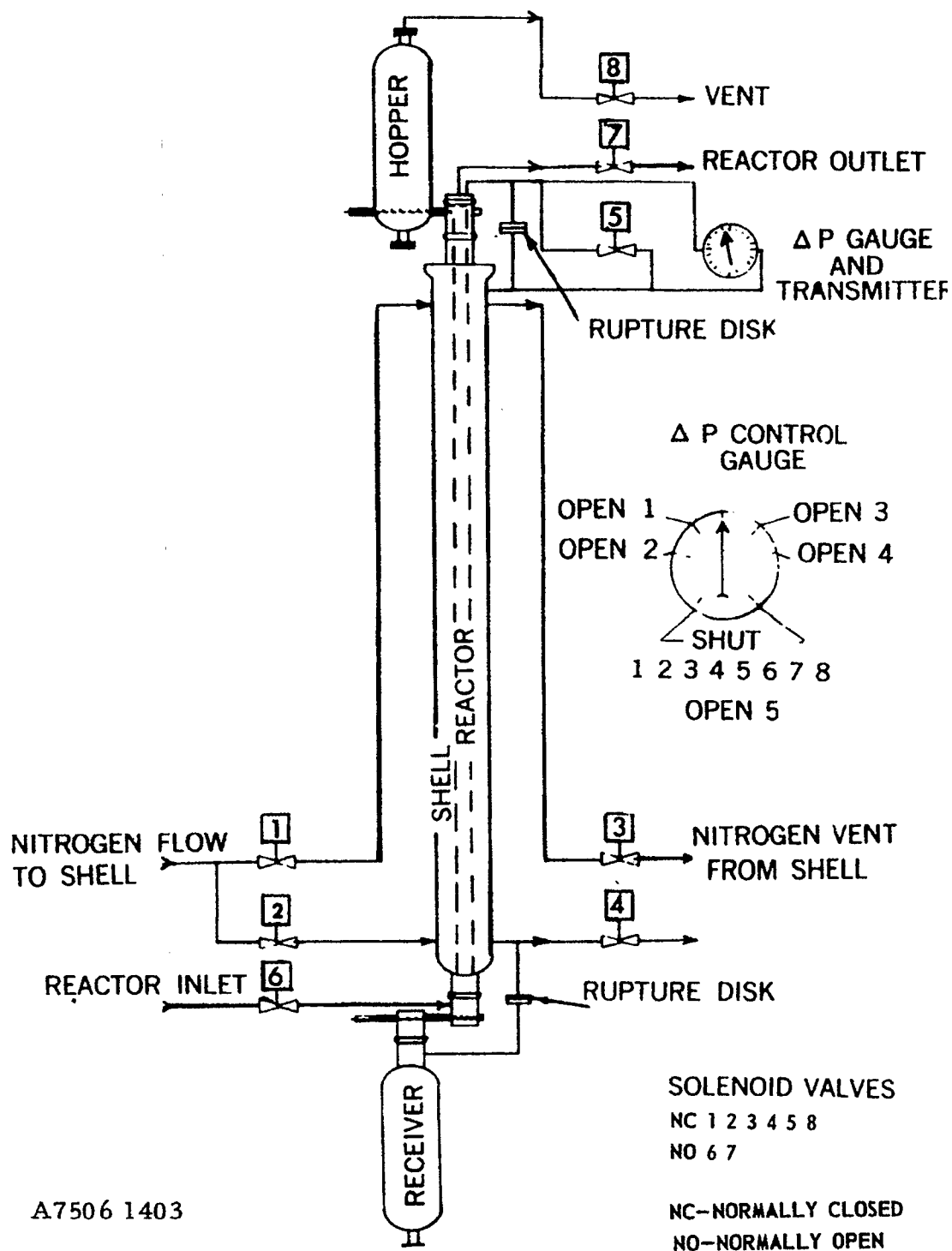
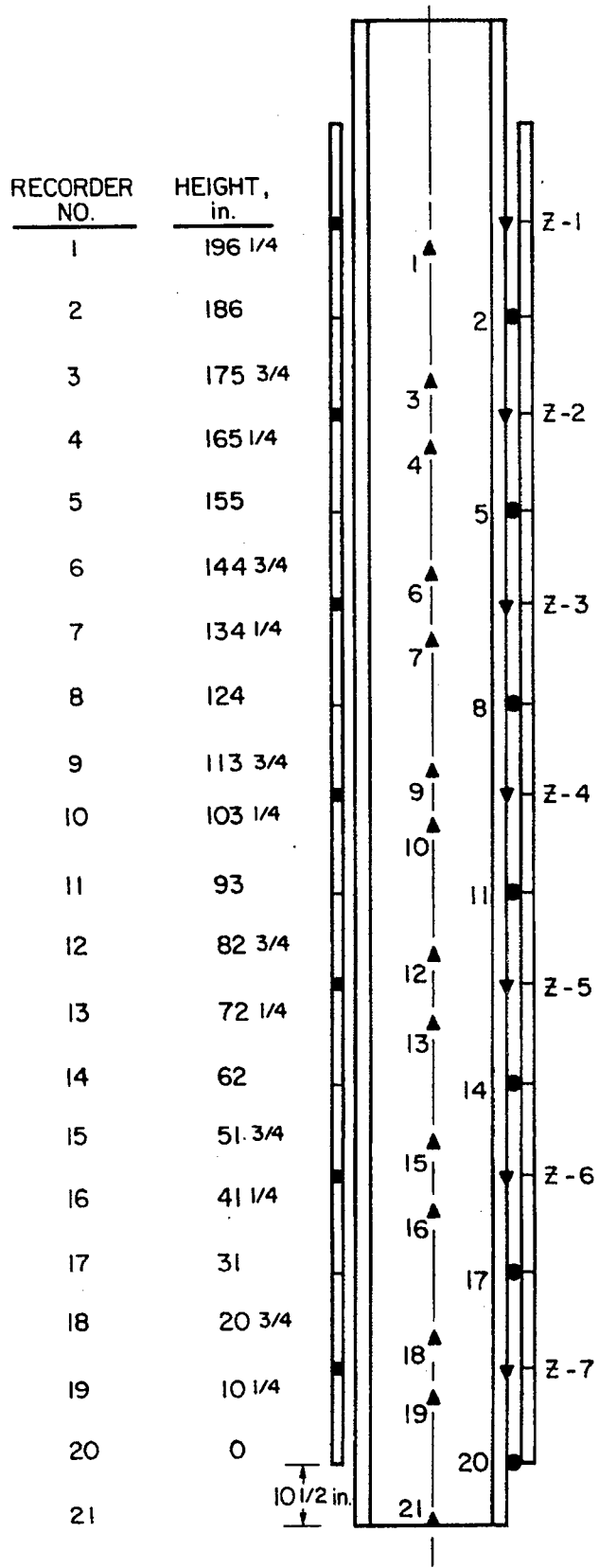


Figure 2-4. COAL RESIDUE RECEIVER



A7506 1403

Figure 2-5. SCHEMATIC OF REACTOR-SHELL DIFFERENTIAL PRESSURE CONTROL SYSTEM



CONSTRUCTION

4 in. SCH 40 PIPE, TYPE 446
 19 ft 3 in. LONG
 HEATED LENGTH : 18 ft 1 in.

HEATING ELEMENTS

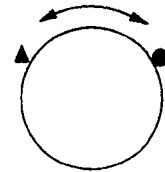
10 in. OD X 7 in. ID X 31 in. LONG (EACH)

THERMOCOUPLE DESIGNATIONS

- METAL TUBE, FURNACE ZONE BOTTOM
- ▲ METAL TUBE, 10 1/4 in. ABOVE AND 10 1/4 in. BELOW FURNACE ZONE BOTTOM
- HEATING ELEMENTS, ZONE CENTER
- ▼ OUTSIDE FIBERFRAX INSULATION, ZONE CENTER

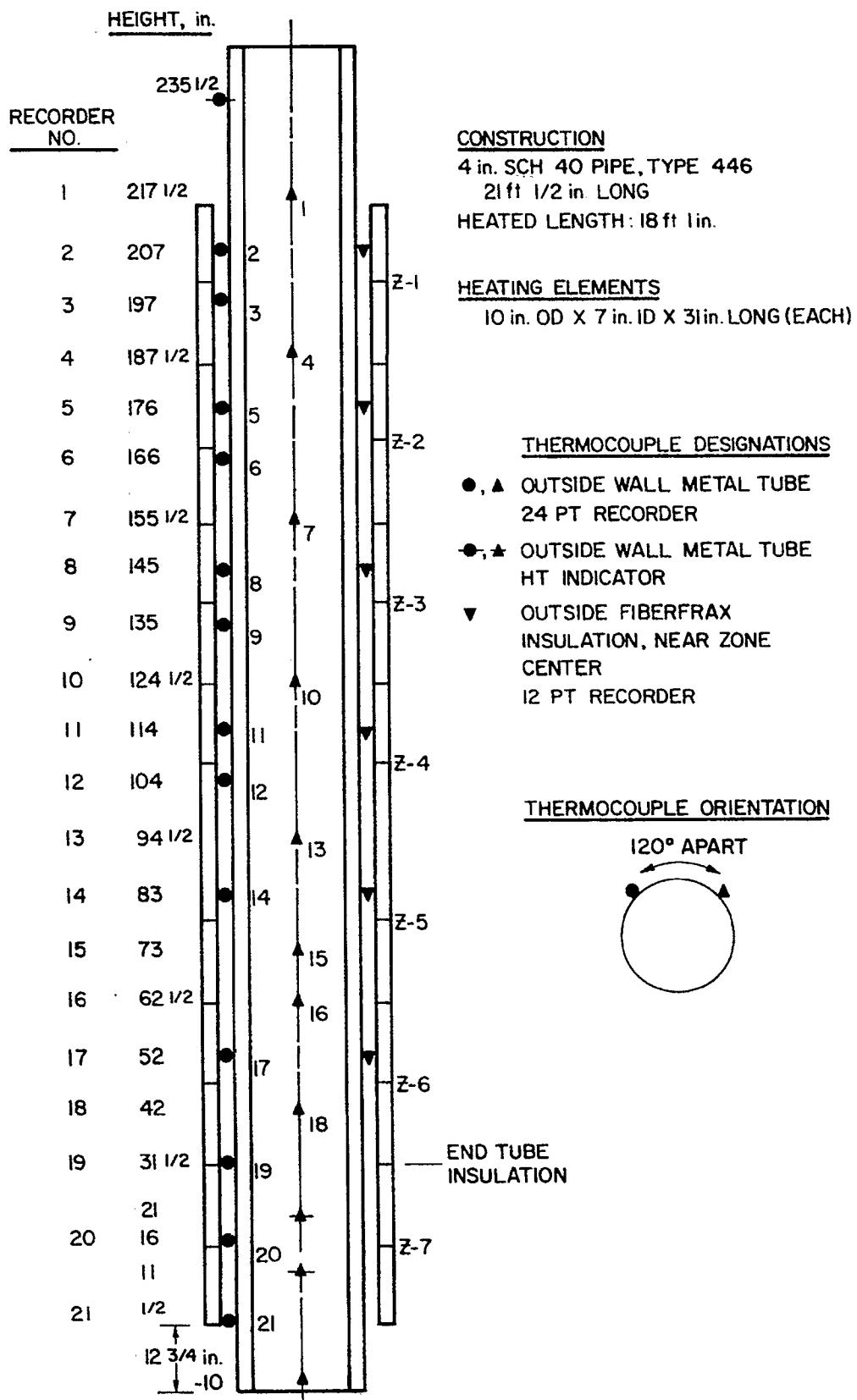
THERMOCOUPLE ORIENTATION

120° APART



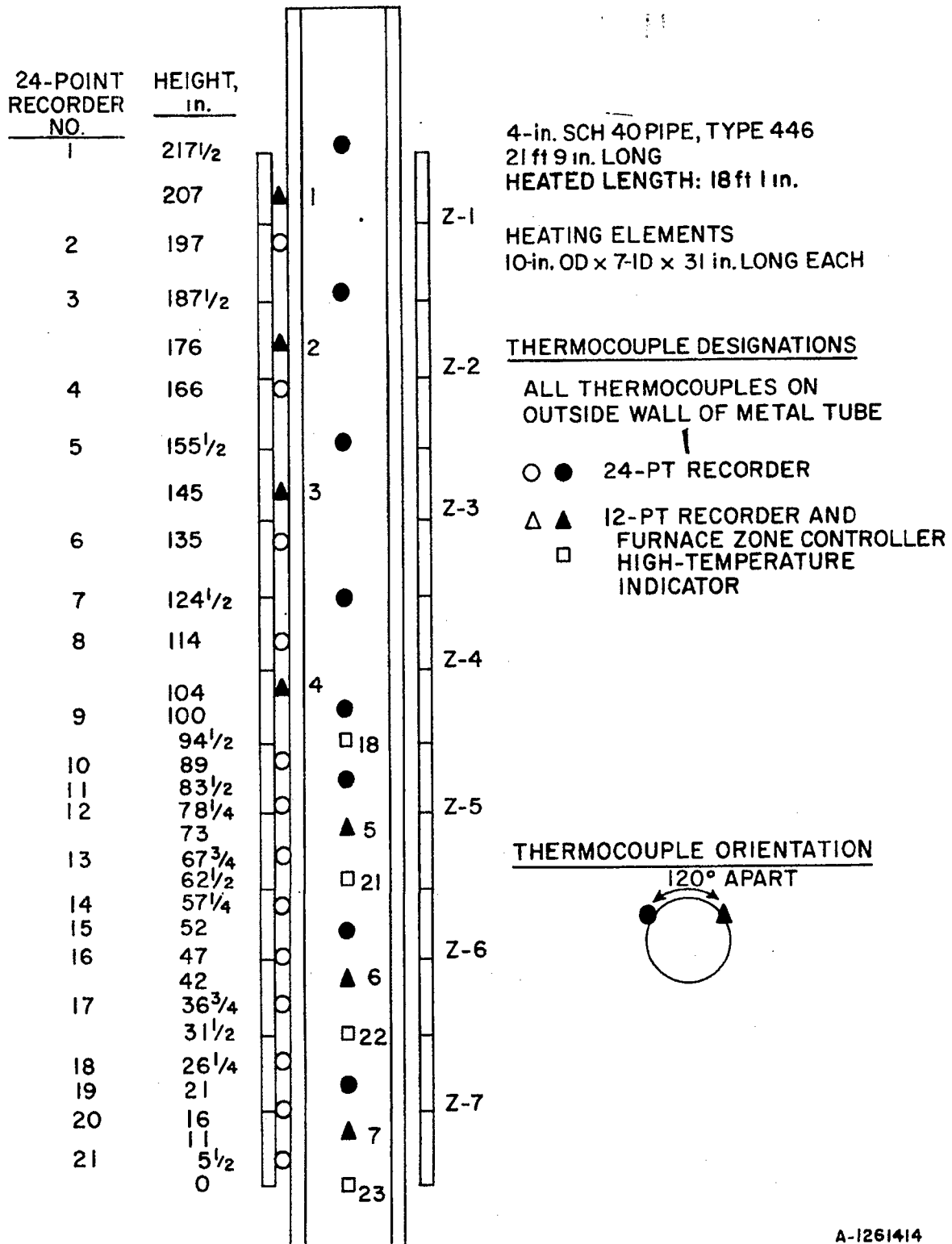
A-74-1290

Figure 2-6. BALANCED-PRESSURE REACTOR THERMOCOUPLE LOCATIONS (From Run HT-22 through HT-52)



A-74-1289

Figure 2-7. BALANCED-PRESSURE REACTOR THERMOCOUPLE LOCATIONS (Runs HT-53 through HT-130)



A-1261414

Figure 2-8. BALANCED PRESSURE REACTOR THERMOCOUPLE LOCATION
(After Run HT-138)

of type 316 stainless steel tubing and were 0.5-inch OD by 0.25-inch ID. Each set of tubes had 100 feet of tubing with a straight run of 6 feet between the return bends. Both sets of tubes were installed in a gas-fired furnace.

To provide increased feed gas storage capacity, necessary for high hydrogen feed rates in fluidized-bed hydrogasification tests, sixteen high-pressure gas storage cylinders were mounted in an outdoor support frame. Each of the cylinders was 21 feet long with an outside diameter of 9.625 inches. The inside free volume of each cylinder was 8.2 cubic feet. Other modifications designed to allow hydrogasification operations at feed gas and steam throughputs of from 3 to 5 times the rates used in moving-bed tests, with proportional increases in coal feed rates, included a new water-feed pump for steam generation, and a larger capacity product gas meter.

A high-capacity, high-pressure water-feed pump with a positive displacement piston was installed. The pump is capable of feeding up to 80 pounds per hour of water at pressures up to 3000 psig.

A large-capacity diaphragm-type dry-gas meter with positive displacement was procured and installed. Rated for 3000 cubic feet per hour, it metered product gases leaving the hydrogasification PDU.

2.2.6 Electrical Heat Input to Reactor

During a hydrogasification test, the furnace around the reactor tube serves to control the heat losses from the reactor tube walls and to maintain a reasonably fixed temperature in the reactor. The electrical heat input to the furnace varies, dependent upon 1) the heat release due to the hydrogasification reaction in the reactor, 2) the conductive and radiative heat losses from the reactor tube, through the insulation inside the outer pressure shell, and 3) the convective and radiative heat losses from the outside of the pressure shell. In order to gage the level of electrical heat input to the furnace under better controlled conditions than are possible in a coal hydrogasification test, a special test was performed in the PDU.

In this special heat input test, technicians measured the electrical heat input required to maintain the reactor tube at typical hydrogasification temperatures in the range of 1300° to 1700°F. For this test, the reactor was pressurized with nitrogen to 1000 psig and held at that pressure with no gas flow through the reactor. There was no coal bed in the reactor, and no coal was fed. Wattmeter readings measuring the electric power input to the reactor furnaces were taken over a 5-hour period as the reactor was controlled to a nearly constant temperature profile. The objective of this test was to establish the level of heat loss from the reactor shell for use in heat balance calculations of hydrogasification runs. The average electric power input to the reactor furnaces for the nearly steady temperature level was 10 kilowatt, corresponding to a heat input of 34,000 Btu per hour. This heat input represents the heat losses to the atmosphere from the pressurized shell of the reactor. The average room temperature near the bottom of the reactor shell during the test was 83.5°F. The temperature profile along the outer wall of the reactor tube is indicated by the temperatures at different levels in Table 2-1. The lowest level temperature corresponds to the bottom of the coal bed in hydrogasification tests.

Table 2-1. HEAT INPUT TEST IN HYDROGASIFICATION DEVELOPMENT UNIT BALANCED-PRESSURE REACTOR

Reactor Pressure: 963 psig

Pressurizing Gas: Nitrogen

<u>Inches From Bottom</u>	<u>Reactor Temperature, °F</u>
62.5	635
67.75	1260
73.0	1580
78.25	1710
83.5	1800
89.0	--
94.5	1620
100.0	1755
104.0	1695
114.0	1690
124.5	1530
135.0	1535
145.0	1375
155.5	1450
166.0	1435
176.0	1290
187.5	1305
197.0	1280
207.0	1180
217.5	<u>1020</u>
Average:	1430

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2.3 Hydrogasification Tests in Process Development Unit

2.3.1 Coal Feedstocks

In the early phases of the operation of the balanced-pressure hydrogasification process development unit (PDU) the coal feed was a low-temperature bituminous coal char supplied by the Consolidation Coal Company. This char was first used in laboratory and the original continuous flow hydrogasification studies. It was used in the demonstration unit to facilitate operation during the unit shakedown period and the program definition phase. Because it was available in adequate quantities with a generally uniform composition, hydrogasification tests in the demonstration unit were not dependent on pretreatment operations, or on differences in char composition due to varying pretreatment conditions.

During the investigative phase of the hydrogasification program, fourteen different coal feeds were used. These selected coals were chosen 1) to give a range in rank from a low-volatile content bituminous coal to a lignitic-type, and 2) to enable evaluation of three different high-volatile bituminous coals to determine variation in performance of coals due to origin as well as rank.

Coals tested and their origin are as follows:

<u>Type</u>	<u>Seam</u>	<u>Mine</u>	<u>Location</u>
High-volatile Bituminous	Pittsburgh, No. 8	Montour No. 4	Lawrence, Washington Co., Pa.
High-volatile Bituminous	Pittsburgh, No. 8	Ireland	Moundsville, Marshall Co., W. Va.
High-volatile Bituminous	Ohio No. 6	Broken Aro	Coshocton, Coshocton Co., Ohio
High-volatile Bituminous	Illinois No. 6	Crown	Farmersville, Mont- gomery Co., Illinois
High-volatile Bituminous	Indiana -- Sixth Vein	Minnehaha	Sullivan, Sullivan Co., Indiana
High-volatile Bituminous	No. 5 Block	---	Kanawha Co., W. Va.
Low-volatile Bituminous	Sewell	Lochgelly No. 2	Mount Hope, Fayette Co., W. Va.
Low-volatile Bituminous	Pocahontas No. 4	Stotesbury No. 10	Helen, Raleigh Co., W. Va.
Subbituminous	Laramie No. 3	Eagle	Erie, Weld Co., Colorado
Lignite	---	Glenharold	Stanton, Mercer Co., No. Dakota
Medium- Volatile Bituminous	Sewell	Sewell No. 1	Nicholas Co., W. Va.
Subbituminous	---	Colstrip	Rosebud Co., Montana
Subbituminous	A	---	Navaho Indian Lease, Farmington, New Mexico
Lignite	---	Savage	Savage, Montana

Most of the hydrogasification tests were performed with Pittsburgh No. 8 seam bituminous coal from the Ireland mine. The other coals were used in selected tests to establish how coal type affected hydrogasification results. Only one test was completed with Pittsburgh No. 8 seam bituminous coal from the Montour No. 4 mine because additional supplies of this coal were no longer available at the time of the program reported here. Light pretreatment of all the bituminous coals, and of the subbituminous coal was necessary to destroy agglomerating tendencies before they could be used for hydrogasification tests. The North Dakota and Montana lignites were hydrogasified without pretreatment, but required drying to insure uniform feeding. Analyses of the coal feedstocks are given in the tabulations of coal and residue analyses of each run.

HYGAS researchers also studied the reactivity to hydrogasification of a bituminous coal char produced by the FMC Corporation Project COED (Char Oil Energy Development). This char was produced from an Illinois No. 6 seam, Crown mine, high-volatile C bituminous coal. The COED process involves a multistage fluidized-bed pyrolysis of high-volatile bituminous coals to produce oil, gas, and char.

2.3.2 Coal Particle Size

Coal and char feeds for all hydrogasification tests were screened to a specific size range. Three different particle size distribution ranges were used to meet the changing operational needs. Early moving-bed tests were conducted with -35+80 USS mesh char. This range was satisfactory for low throughputs but was changed to -10+40 USS mesh size when coal and gas feed rates were increased. The purpose of switching to this coarser feed was to allow operation at high linear gas velocities without fluidization of the char, and to enable a more uniform flow of gas through the char bed. With moving-bed tests scheduled at increasing hydrogen/char ratios, continued use of -35+80 mesh particle size would limit operations to about 50 percent of stoichiometric at solids feed rates of between 10 and 15 pounds per hour in order to prevent the bed from fluidizing.

When hydrogasification studies were extended to fluidized-bed operation the fine size of the coal particles was extended to include those down to +80 mesh size. Coarse particles were still controlled to no larger than 10 mesh size. The -10+80 mesh sieve range was used for all coal feeds in fluidized-bed operation.

At the hydrogasification conditions investigated, there was no evidence that coal particle size significantly affected the hydrogasification results.

2.3.3 Results of Operations

2.3.3.1 Moving Bed Hydrogasification Tests

The first part of the hydrogasification investigative program in the balanced-pressure demonstration unit utilized a moving coal bed configuration. Coal, fed to the top of the reactor, moved downward in plug flow, being contacted with upward flowing feed gas in countercurrent fashion. Highly reactive fresh coal was contacted in the upper part of the bed with a reactant gas-product gas mixture having a low hydrogen concentration, while the less reactive partially gasified coal was contacted in the lower part of the bed with undiluted feed gas. Plug flow of the coal enabled researchers to maintain 1) a temperature gradient across the coal bed, 2) high temperatures at the bottom of the bed, to promote the rate of reaction, and 3) a lower temperature at the top of the bed, for high methane equilibrium concentrations. Moving bed operation also allowed flexibility in the range of coal and reactant gas feed rates, important because operational experience was being acquired. As minimum linear gas velocities were not an operational factor, tests could be conducted at low hydrogen/coal ratios in order to study limited coal conversions.

For the most part, the moving-bed tests were conducted with Pittsburgh No. 8 seam bituminous coal from the Ireland mine. When two-stage hydrogasification operation was simulated in sequence, pretreated coal was the feed in the low-temperature stage simulation, and partially gasified coal from the low-temperature stage was the feed to the high-temperature stage simulation. Selected moving bed tests were also conducted with Consolidation Coal Company low-temperature bituminous coal char, pretreated Montour No. 4 mine bituminous coal, pretreated Ohio No. 6 seam, Broken Aro mine bituminous coal, and North Dakota lignite. The moving bed was operated at a height of either 7 or 3.5 feet. In some tests, where bed-level sensing was marginal, there were variations from these heights.

2.3.3.1.1 Pretreated Bituminous Coal Results

Typical results of the moving-bed hydrogasification tests conducted with Montour No. 4 mine and Ireland, both Pittsburgh seams, and Broken Aro mine, Ohio seam, high-volatile content bituminous coals are shown in the appended Table 2-A1. Reported coal residence times are based on measured bulk densities of the reactor residues and the coal-bed volume. Time in free fall was negligible compared to time in the bed. Feed gas residence times are based on the flow rate at average bed conditions and coal bed volume. Time in the free-fall section is not included. Typically, hydrogasification of lightly pretreated Ireland mine bituminous coal with hydrogen and steam in a moving bed resulted in up to 38.5% carbon gasification and a product gas of 495 Btu per standard cubic foot. When processing Montour No. 4 mine pretreated coal, 28% of the carbon was gasified as a product gas of 576 Btu per standard cubic foot was produced.

2.3.3.1.2 Coal Pretreatment

The proximate and ultimate analyses of the three pretreated high-volatile content bituminous coals used in the moving-bed tests are shown in Table 2-A2 (appendix). These coals were pretreated to various extents and then hydrogasified. Using volatile matter content as an index of severity of pretreatment, HYGAS researchers found that pretreated coal with between 24 and 26% volatile matter can be processed without agglomeration. Raw coal was tested but it swelled badly during the reaction, stuck to the reactor, and caused bridging. It is entirely possible that in larger size reactors in which the coal feed would not contact reactor walls immediately, coals with less pretreatment – or even raw coal – could be fed successfully. However, the capability to feed pretreated coal with as much as 24 to 26% volatile matter is considered a significant achievement. Factors that were learned through this experience included adjustment of feed tube size, length, and location; the amount of nitrogen purge-gas required to pass through the tube; and the startup sequence.

2.3.3.1.3 North Dakota Lignite Results

Hydrogasification of a dried – but otherwise untreated – North Dakota lignite from the Glenharold mine was successfully conducted in a 3.5-foot moving bed (run HT-135, Table 2-A1, appendix). Carbon conversions were comparatively high; 57% of carbon was converted to gaseous products, and 6.8% of carbon was converted to liquid products. The heating value of the product gas was 511 Btu per standard cubic foot.

2.3.3.1.4 Two-Stage Simulation

The stage-by-stage simulation procedure used is realistic except that the partially gasified coal was fed to the second stage at ambient temperature instead of at temperatures between 1200° and 1400°F. Because hydrogen represents the largest share of the total pipeline gas cost, practically all the runs were conducted at the minimum hydrogen/coal ratio that would produce a total carbon gasification of about 50%. At this degree of gasification, sufficient residual carbon would be available for generating the necessary hydrogen. These figures resulted from an overall system analysis based on existing data on equilibrium, kinetics and heat and material balances.

Key results obtained in two-stage simulations are summarized in Figure 2-9 with pretreated Pittsburgh seam coal, and in Figure 2-10 with pretreated Ohio seam coal. Product gas analyses were adjusted to a nitrogen-free basis because of the high nitrogen purge rates actually used in the tests. The purge gas was needed to prevent hot reactor gases from entering the coal-feed tube.

High concentrations of unreacted hydrogen in the product gas from the low-temperature stages limited the heating value to about 700 Btu per standard cubic foot. To obtain a high-Btu gas (900 Btu per standard cubic foot) requires catalytic methanation of the carbon oxides. Note the absence of carbon oxides in the feed gas in the first stage. Because of the low temperature in the first stage, no steam-carbon reaction was expected. Thus, carbon monoxide is considered an inert insofar as methane formation is concerned. Therefore, to simplify preparation of the simulation gas mixture, carbon monoxide was not included in this feed. This assumption appears valid, judging from the low carbon oxide concentration in the first-stage effluent; the amount measured came from the organic oxygen in the coal rather than from the steam-carbon reaction.

Apparently, however, steam plays an active role in the low-temperature gasification. Two runs were made, one with a steam-natural gas-hydrogen mixture (run HT-84) and the other with a nitrogen-natural gas-hydrogen mixture (run HT-85, Table 2-A1, appendix). Significantly greater amounts of carbon oxides were formed and significantly less water was released from the coal when steam was used. Steam, then, seems to suppress the release of organic oxygen from coal as water, but forces the oxygen to leave as carbon oxides. This phenomenon seems plausible from the mass-action standpoint. From a process standpoint, the release of organic oxygen in coal as carbon oxides is more desirable than as water. In the latter case, hydrogen (either from coal or from external sources) is lost by being combined with the oxygen to form water. In contrast, when the oxygen is released as carbon oxides, these can be converted to more hydrocarbon by subsequent catalytic methanation.

2.3.3.1.5 Methane Formation

2.3.3.1.5.1 Equilibrium

It has been well established that the hydrogenation of the volatile matter in coal proceeds very rapidly and yields methane concentrations higher than the equilibrium value in a β -graphite-hydrogen system. This excess is

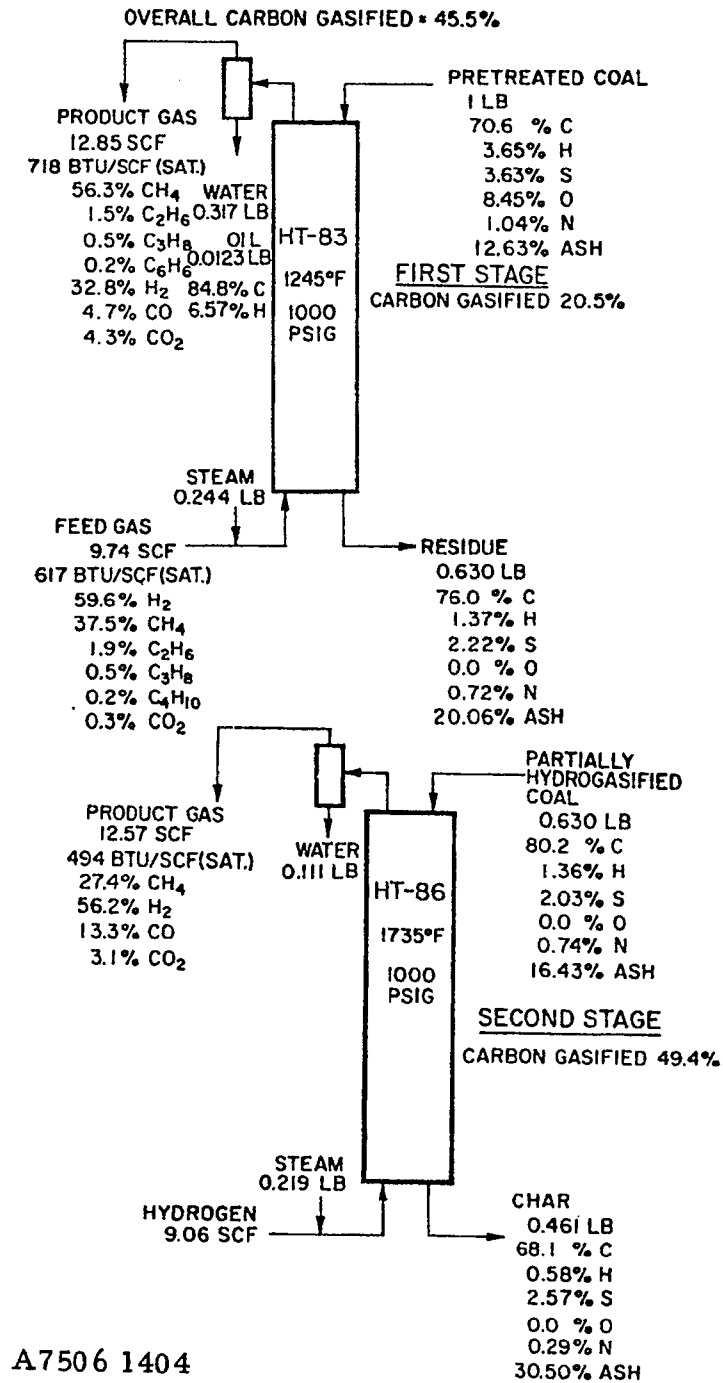


Figure 2-9. STAGE-BY-STAGE SIMULATION IN HYDROGASIFYING PRE-TREATED PITTSBURGH SEAM COAL

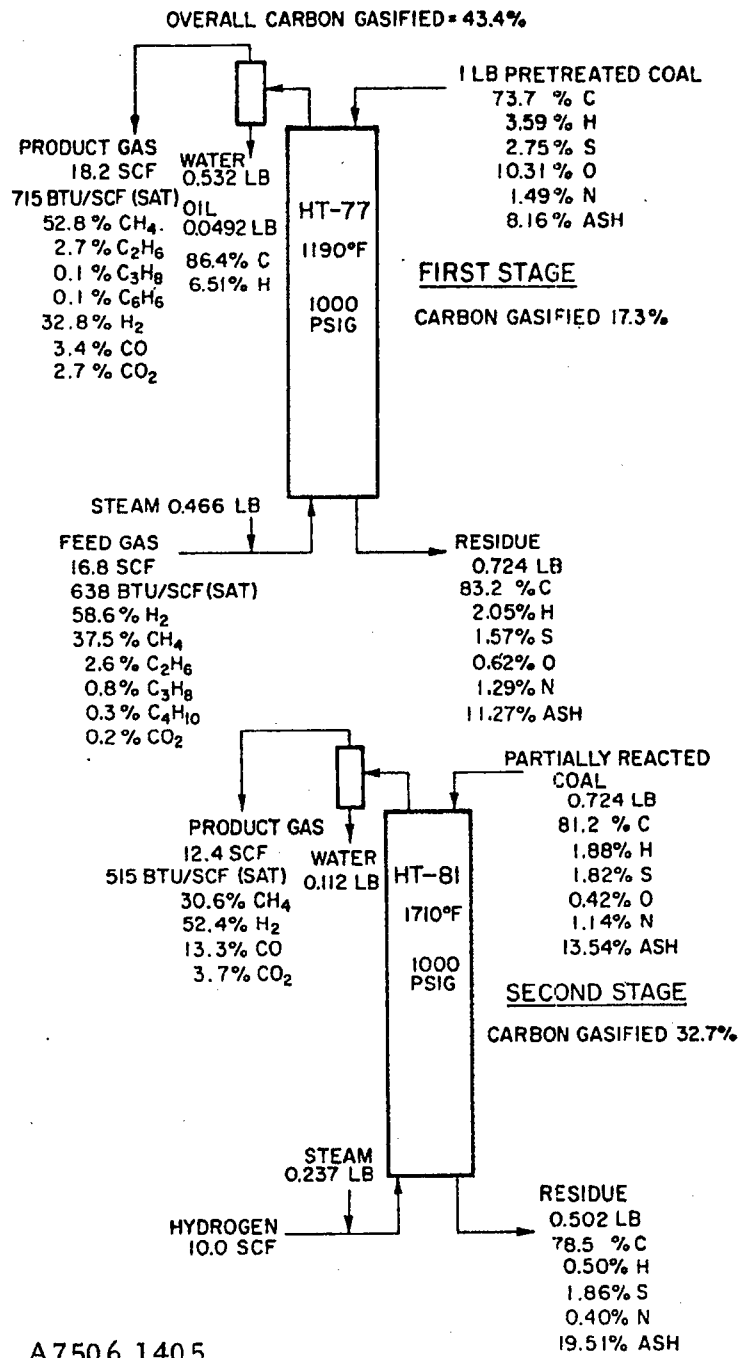
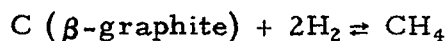


Figure 2-10. STAGE-BY-STAGE SIMULATION IN HYDROGASIFYING PRETREATED OHIO SEAM COAL

conveniently attributed to a greater-than-unity coal activity in reference to β -graphite activity. In fact, the hydrogenation of the reactive carbon groups proceeds by splitting off the carbon chains and functional groups rather than by reacting with graphitic carbon. Such reactions lead to methane formation because methane is the predominant stable hydrocarbon at the temperature and pressure in question. The first-stage hydrogasification demonstrates this type of reaction as shown, for example, by the predominance of methane versus other hydrocarbons or carbon oxides in the effluent gas (Figure 2-9).

Figure 2-11 presents the calculated "equilibrium ratio", obtained from the PDU tests, as a function of the maximum bed temperatures. The curve represents true equilibrium ratio for the reaction:



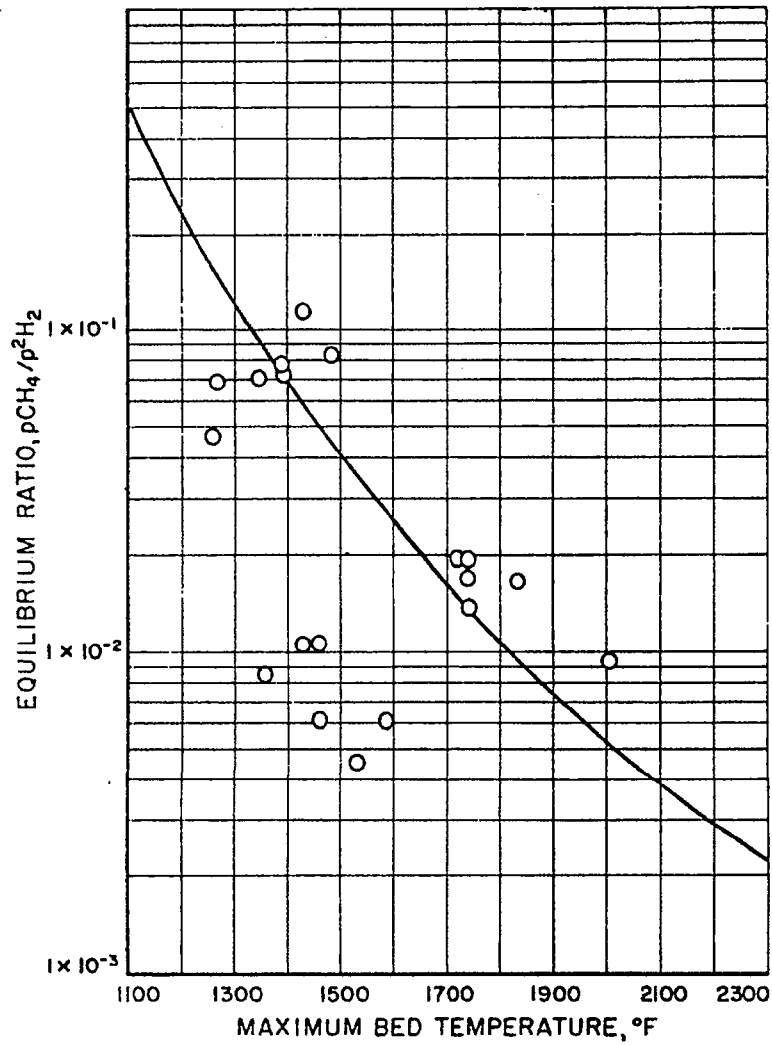
Note the many runs yielding equilibrium ratios higher than the curve. The group of points below the curve between 1450° and 1550°F came from runs in which a high hydrogen/coal ratio was used, resulting in low methane concentration.

Initial gasification was found to be rapid. There appears to be little equilibrium hindrance in view of the mechanism of methane formation discussed above. Once the reactive carbon is gone, however, the remaining fixed carbon reacts much more slowly in the second stage. Here we check the approach to β -graphite equilibrium to see if the coal, after the first stage, still has sufficient reactive carbon left to show activity greater than unity. Because methane formation is exothermic, from the process standpoint, the more methane that is formed in the second stage, the more heat there would be available to furnish the endothermic heat for the steam-carbon reaction; the steam-carbon reaction, in turn, would produce hydrogen *in situ* and reduce the external hydrogen requirement. With partially gasified Pittsburgh No. 8 seam coal, the carbon activity observed ranged between 1 and 2 at from 1700° to 1950°F.

2.3.3.1.5.2 Reaction Rate

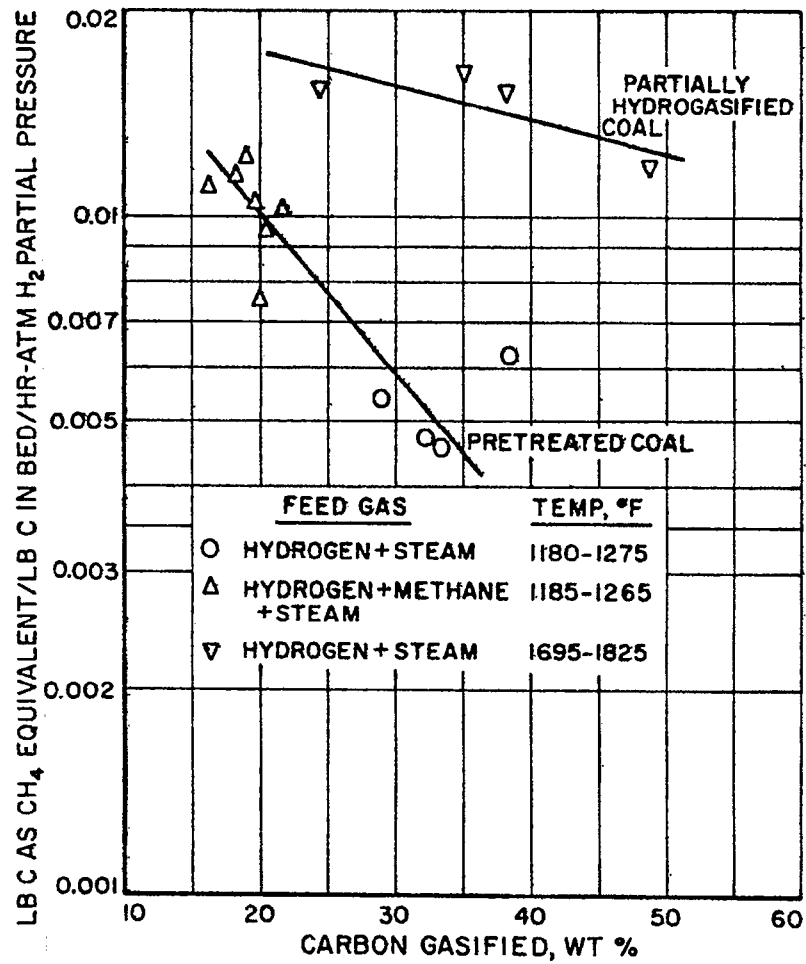
The integral methane formation rates from PDU tests were compared with those reported by others. In order to perform the comparisons, the reaction rate was considered to be pseudo-first order with respect to the hydrogen partial pressure. The calculated reaction rate constant for each run is plotted against carbon gasification in Figure 2-12. Several observations can be made:

- 1) The rate of methane formation for pretreated Pittsburgh coal is not slowed by the presence of methane in the feed gas. This is in agreement with Zielke and Gorin in their study of hydrogasification of Disco char.
- 2) The pretreated coal is quite reactive. For example, at between 25 and 30% carbon gasification with steam-hydrogen mixtures, the rate constant is more than twice that reported by Feldkirchner and Linden in reacting low-



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Figure 2-11. APPROACH TO CARBON-HYDROGEN REACTION EQUILIBRIUM FOR PRETREATED PITTSBURGH SEAM BITUMINOUS COAL



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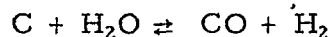
Figure 2-12. INTEGRAL METHANE FORMATION RATE FOR PRE-TREATED PITTSBURGH SEAM BITUMINOUS COAL

temperature bituminous char with hydrogen. The greater reactivity is most likely attributable to the higher volatile content of the pretreated coal utilized (24 to 26%) than that of their char (17%).

3) Partially hydrogasified coal, upon further reaction in the high-temperature second stage, gave rate constants quite similar to those obtained with Disco char and residual Australian brown coal, both containing very little volatile matter.

2.3.3.1.6 Steam-Carbon Reaction

The reaction



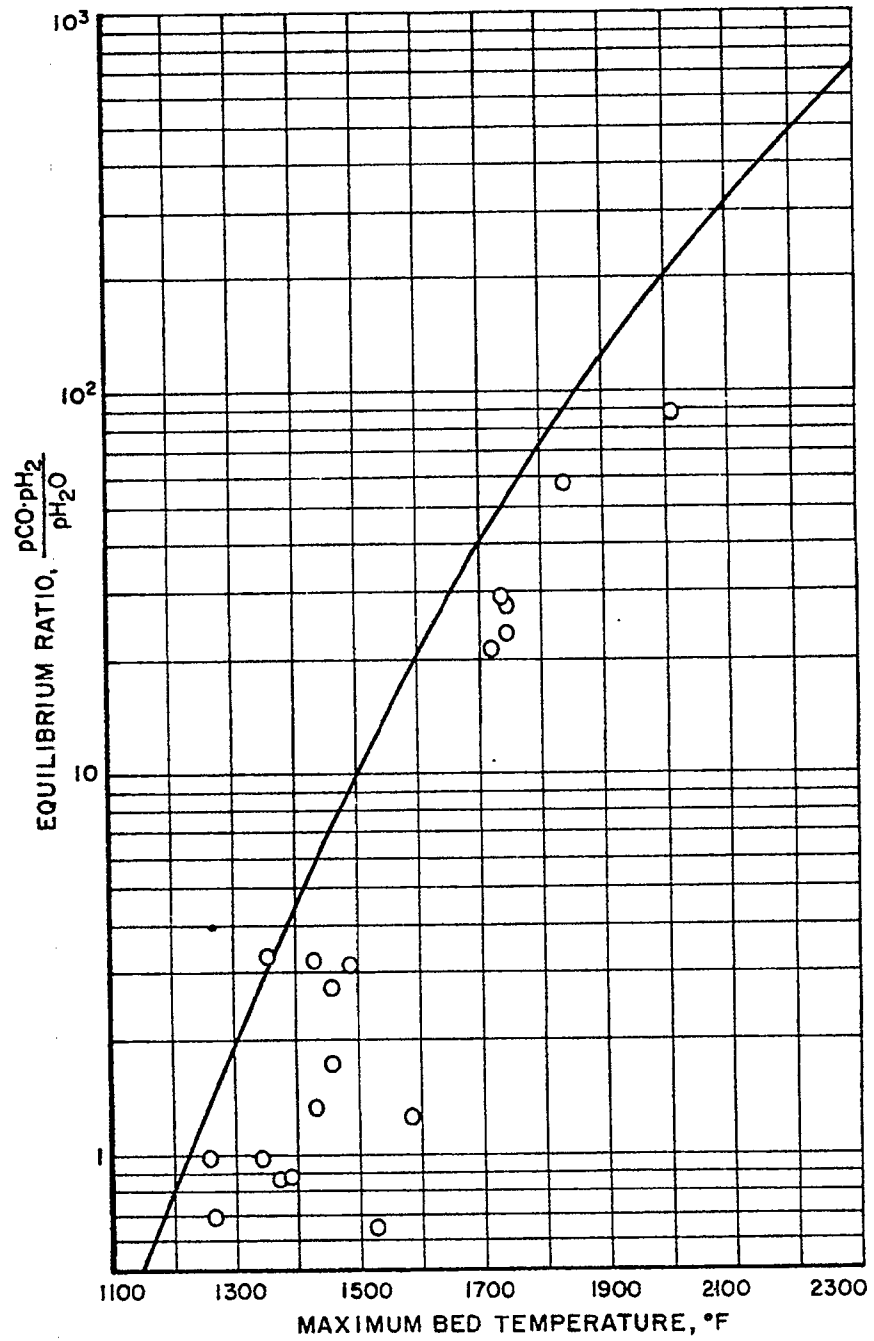
was significant only at temperatures above 1700°F, and was found to increase with temperature. For example, at 1695°F (run HT-80), 50% of the feed steam decomposed, but at 1825°F (run HT-72), 70% was decomposed (Table 2-A1, appendix). Carbon oxides formation was related directly to the steam fed and to the steam decomposition. As much as 5.5 standard cubic feet of carbon oxides per pound of coal were produced at the maximum 70% steam decomposition. With little or no feed steam decomposition, carbon oxides formation was about 1 standard cubic foot, or less, per pound of coal. In the low-temperature first stage, the presence of steam in the feed gas is responsible, through the laws of mass action, for converting a major fraction of the oxygen in coal to carbon oxides. This oxygen is converted to water when steam is omitted from the feed; in other words, when only hydrogen is fed.

The rate at which the steam-carbon reaction proceeds is highly temperature-dependent, requiring heat above 2000°F to approach equilibrium. Because hydrogasification tests are conducted at less than 2000°F, in order to preserve the methane formed, the carbon-steam reaction is expected to be substantially removed from equilibrium. This fact is shown in Figure 2-13 where calculated "equilibrium ratios" are plotted against maximum bed temperature. The curve represents true equilibrium for comparison.

The carbon-steam reaction is important from the process standpoint not only as a source of generating in situ hydrogen, but also as a temperature controller. When pure hydrogen is the gasifying medium, the strong heat release by the methane-forming reaction causes runaway temperatures. In a hydrogen-steam mixture, this released heat is absorbed by the carbon-steam reaction, thereby stabilizing temperatures.

2.3.3.2 Reaction Profile-Gas Sample Probes

To gain some insight into the path of reaction in free-fall or moving-bed zones, gas sample probes were located at several levels in the bed. In Table 2-2, compare the probe gas analyses from low-temperature run HT-67 with those from high-temperature run HT-72. Both runs were made with a 7-foot-deep moving bed. Note that, in the high-temperature test, the reaction was practically complete in the lower half of the bed, with very little reaction in the upper half of the bed and in the free-fall zone above the bed. On the



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Figure 2-13. APPROACH TO STEAM-CARBON REACTION EQUILIBRIUM FOR PRETREATED PITTSBURGH SEAM BITUMINOUS COAL

Table 2-2. GAS SAMPLE PROBE ANALYSES (Nitrogen- and Water-Free Basis)

Run No.	HT-67		HT-72		HT-86	
	42	18	42	18	30	6
Bed Height, ft	7.0		7.0		3.5	
Reactor Temp, max., °F	1395		1835		1740	
Bed Sampling Point, in. below top of bed	42	18	42	18	30	6
Gas Composition, mole %	Feed Gas	Product Line	Feed Gas	Product Line	Feed Gas	Product Line
CO	0.0	0.0	18.0	18.7	7.0	11.5
CO ₂	0.1	0.2	0.0	3.5	1.6	3.6
H ₂	58.0	55.8	97.30	57.4	72.7	59.7
Ar	1.14	1.27	2.70	1.66	0.61	0.36
CH ₄	36.6	39.2	0.0	18.9	18.1	24.9
C ₂ H ₆	2.5	3.3	0.0	0.0	0.0	0.0
C	1.7	0.5	0.0	0.0	0.0	0.0
H ₂ S	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.04	100.07	100.00	99.96	100.01	100.03
		100.06		100.09		100.06
		100.04		99.96		100.03
		100.04		100.09		99.97

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other hand, in the low-temperature test, the reverse is true: The bulk of the reaction took place in the free-fall zone and at the top of the bed, with very little reaction in the rest of the bed. It follows, then, that at both temperatures the bed height could be reduced to 3.5 feet without any loss of gasification. This is in fact the case as shown in Table 2-2 by the probe samples from HT-86, a high-temperature run using a 3.5-foot-deep bed.

The high-temperature reaction is apparently equilibrium-limited; it attains its limit in a relatively short contact time, in a short bed. The low-temperature reaction is extremely rapid, requiring only a matter of seconds to complete. The reactive portion of coal is quickly gasified, after which the remainder of the carbon is not reactive at the low temperature. In view of these facts, a likely hydrogasifier configuration would incorporate a low-temperature free-fall zone followed by a shallow high-temperature stage.

2.3.3.3 Free-Fall Tests

Hydrogasification tests with coal in free fall were performed to study conversions of the coal at short residence times. The coal was gasified as it fell through the 18.02-foot heated portion of the reactor tube, with reactant gases flowing upward. The gasified coal residue was immediately removed from the bottom of the reactor tube, preventing bed buildup anywhere in the reactor. Residence time of the coal was determined by the length of the reactor and the settling velocity of the coal particles. The settling velocity of the coal particles is a function of the particle size, and the linear velocity, density, and viscosity of the reactant gases. At typical test conditions, and at normal coal and reactant gas feed rates, coal residence times could vary from 8 seconds for 60-mesh coal particles, to 41 seconds for 200-mesh coal particles.

The types of coal used in the free-fall gasification tests included medium- and low-volatile content bituminous coals, a subbituminous coal, and two different lignites. Operating results of all of the free-fall tests are given in Table 2-A4 in the appendix. Chemical and screen analyses of the feeds and residues of these tests are appended in Table 2-A5. Composition of the liquid products from these tests are appended in Table 2-A6.

Bituminous coal and char conversion in free fall was studied in two tests. In run HT-48 the feed was the low-temperature bituminous coal char from the Consolidation Coal Company pilot plant, and in run HT-60 the feed was a lightly pretreated bituminous coal from the Ireland mine. A short char residence time of from 4.8 to 16.7 seconds was obtained in run HT-48; the residence time affect on hydrogasification results is shown in the table below, where key operating conditions and results of the test are summarized:

<u>Run No.</u>	<u>HT-48</u>
Average Reactor Temperature, °F	1645
Bed Height, ft	free-fall
Char Feed Rate, lb/hr	10.16
Char Bed Residence Time, s	4.8-16.7
Steam Rate, lb/hr	7.16
Hydrogen/Char Ratio, % of stoichiometric	77.7
Steam in Feed Gas, mole %	30.9
Steam Decomposition:	
% of steam fed	nil
lb/lb	--
lb/lb char	--
MAF Char Gasified, %	20.6
Measured Carbon Gasified, %	24.8
Hydrocarbon Yield, SCF/lb	4.69
Carbon Oxides Yield, SCF/lb	0.87

The char residue time of HT-48 is based on the terminal settling velocities of char particles in the range of 40 to 100 mesh, and a heated reactor tube length of 18.02 feet.

The low carbon oxides yield of run HT-48 reflects the low steam decomposition in this test; this is an indication that most of the reacted steam reacts with char rather than with gaseous hydrocarbons, and therefore is controlled by the solids residence time.

In run HT-60 (Table 2-A4, appendix), an additional objective was to establish the feasibility of operation with lightly pretreated coals. Only hydrogen was used for feed gas in this test. Steam was not used in order to avoid the possibility of condensing steam interfering with coal discharge. The hydrogasified coal residue was as free-flowing as the feed. This test established the feasibility of discharging hydrogasified pretreated coal from the bottom of the reactor.

Run HT-60, conducted with coal in free-fall, was the first completely successful attempt to hydrogasify a lightly pretreated coal. Because of the relatively short 4-second coal residence time, the carbon conversion to gas was only 20.0%.

Free-fall tests were also performed with two low-volatile content bituminous coals, a West Virginia, Sewell seam coal from the Lochgelly No. 2 mine, and a Pocahontas No. 4 seam coal from the Stotesbury No. 10 mine.

Run HT-165, (Table 2-A4, appendix), with West Virginia Sewell seam bituminous coal was conducted for about 1 hour with the coal gasification in free fall (Part A), and then for over 2 hours with the coal gasification in a 2-foot fluidized bed (Part B). The free-fall and fluidized-bed combination used prevented the recurrence of agglomeration encountered in previous tests. The results show that the carbon gasified increased from 15 to 23% when the operation was changed from free-fall to a 2-foot fluidized bed. The 8% increase was due primarily to the increase in methane production, as shown by the product gas composition and the product gas rate.

Run HT-167, (Table 2-A4, appendix), with low-volatile-content Pocahontas No. 4 seam bituminous coal, represents the only successful hydrogasification of this highly caking coal in the hydrogasification PDU. Gasification of the coal, without agglomeration, was accomplished with the coal in free-fall. When the operation was changed to a fluidized coal bed, the coal agglomerated in the reactor. In general, results of this test are similar to those of the free-fall operation of run HT-164, indicating only minor differences in the performance of the Pocahontas and the Sewell seam coals.

Untreated Colorado subbituminous coal was processed with only partial success in a fluidized bed. Completely successful hydrogasification was obtained in run HT-179, (Table 2-A4, appendix), when the coal was hydrogasified entirely in free fall. No agglomeration of the untreated coal occurred anywhere in the reactor. Two steady-state operating conditions, at coal feed rates of 29 and 55 pounds per hour, were achieved in this test. With the increase in coal feed rates, the hydrogen/coal ratio was reduced from 47 to 35% of stoichiometric. There was only a small decrease in carbon gasified with the increase in coal feed rate - from 29.3 to 27.7%.

To study the feasibility of limited lignite conversion at high pressures by thermal treatment with no reactant gas, run HT-229 (Table 2-A4, appendix), a high-temperature free-fall carbonization test, using as feed a dried lignite from Savage, Montana was performed in the PDU. Conversion of the lignite took place during free fall through a 15.5-foot heated portion of the reactor tube with only a nitrogen sweep gas flowing countercurrent to the falling lignite particles. The lignite was fed at a nominal rate of 20 pounds per hour to the top of the hydrogasification reactor, allowing the lignite to be thermally converted while in free-fall. The top 7.5 feet of the reactor tube was heated to 1300°F; the lower section of the 15.5-foot heated portion of the reactor was controlled to a temperature of 1500°F. Nitrogen sweep gas was fed to the bottom of the reactor at a rate of 250 standard cubic feet per hour. The test lasted nearly 5 hours; 4.5 hours of this time was at steady-state.

The results of this test show that 37% of the lignite was converted, based on the lignite residue recovery of 0.628 pound per pound of lignite fed. About 13% of the lignite was converted to liquid products (0.1293 pound liquids per pound lignite fed). Twenty-four percent of the lignite fed, was converted to gaseous products based on the mass of gas produced and also by feed weight loss. Carbon gasification was limited to 15.2% of the carbon in the lignite. The hydrocarbon yield was 0.923 standard cubic feet per pound of lignite, while the carbon oxides yield was nearly twice as large at 1.808 standard cubic feet per pound of lignite. The large carbon oxides yield reflects, of course, the large oxygen content (20.46%) of the lignite feed.

A lignite particle residence time for 10-mesh particles, the largest size range in the lignite feed, was calculated based on Newton's law for free-falling solid particles through a fluid. Residence time for the 10-mesh particles was

2.5 seconds. This is for a 15.5-foot reactor length, corrected for the upward velocity of the nitrogen sweep gas. Residence times of particles smaller than 10 mesh are, of course, higher because of their lower settling velocities.

Limited conversion of a dried North Dakota lignite from the Glenharold mine was studied in run HT-234 by thermal treatment of the lignite while in free-fall through the reactor tube with no feed gas (Table 2-A4, appendix). Operating conditions for this test were similar to those of run HT-229, performed with a Montana lignite. The lignite was fed at a nominal rate of 20 pounds an hour and gasified in the 15.5-foot heated section of the reactor tube. To keep the lignite from hanging up on the walls of the reactor tube, we fed 185 standard cubic feet per hour of sweep nitrogen to the bottom of the reactor. The test lasted just over 3.25 hours. During this period, lignite feeding was interrupted four times by minor plugs at the top of the reactor. Because of these lignite feed stoppages, the steady-state operating period was less than 1 hour. The thermal treatment of North Dakota lignite in free-fall during run HT-234 resulted in the gasification of 24.5% of the lignite on a moisture- and ash-free basis. Only 13.7% of carbon in the lignite was gasified, including the formation of hydrocarbons (primarily methane), carbon monoxide, and carbon dioxide. Additional lignite was converted to liquid products with 7.11% going into the formation of water and 1.91% producing oils. The carbon appearing in the oil represents 2.41% of the carbon in the lignite. Based on an ash balance, 0.728 lb of partially gasified lignite was recovered for each pound of lignite fed. The volatile matter content of the lignite was reduced from 40.0 to 11.9%, while the ash content increased from 7.66 to 10.54% as a result of the carbonization (Table 2-A5, appendix). The results of this test are similar to those obtained in run HT-229 performed with a Montana lignite at similar conditions, but at a system pressure of 1004 psig.

2.3.3.4 Fluidized Bed Tests

The hydrogasification test program in the development unit was started with moving coal-bed operations. A major operational restriction on moving-bed operation was the limit it set on coal and feed gas rates. Gas rates could not exceed those resulting in fluidization velocities. Coal rate, at the same time, was limited so that desired hydrogen-to-coal ratios were maintained. From a processing standpoint, the plug flow of the moving coal bed resulted in a reaction gradient and in a steep temperature profile characterized by a temperature peak near the top of the coal bed.

Fluidized-bed operation removed the limitation on coal and feed gas throughputs, significantly increasing the hydrogasification capacity of the unit. Solids backmixing, inherent in a fluidized bed, minimized the hydrogasification reaction gradient and reduced the temperature profile peaks by a more uniform distribution of the heat of reaction.

The evaluation of coals of different origins to hydrogasification was performed with fluidized coal-bed operation. In these evaluations, tests were conducted at selected conditions on eight bituminous coals, three subbituminous coals, and two lignites. Tests simulating two-stage hydrogasification, similar to those conducted with moving coal beds, were also conducted with two bituminous coals at fluidized bed conditions. Most of the

fluidized-bed tests were made at a system pressure of 1000 psig. Selected tests were performed at pressures of 1500 psig and 500 psig. Operating results of all of the fluidized-bed hydrogasification tests are given in Table 2-A7 in the appendix. Chemical and screen analyses of the feeds and residues of these tests are appended in Table 2-A8. Compositions of the liquid products from these tests are appended in Table 2-A9.

2.3.3.4.1 Pittsburgh No. 8 Seam Bituminous Coal

Initial gasification tests with Pittsburgh No. 8 coal were performed using hydrogen plus steam as the gasifying medium. In a later series of tests, the coal was gasified with a synthesis gas plus steam feed gas. The coal was also gasified in tests, at selected conditions, with mixtures of hydrogen, methane and steam, and with mixtures of synthesis gas, methane, and steam, to simulate a two-stage hydrogasifier.

This Ireland mine coal was gasified, after light pretreatment, in 7.0 and 3.5-foot fluidized beds with hydrogen and steam. A carbon gasification of 37.3% was obtained with a hydrogen-to-coal ratio of 32.1% of stoichiometric and a steam concentration of 49.5 mole percent while producing a product gas of 581 Btu per standard cubic foot (run HT-129). These results were obtained in a 3.5-foot bed at an average coal bed temperature of 1650°F, and a reactor pressure of 1502 psig. Carbon conversions in a 7.0-foot bed were not significantly different from those in a 3.5-foot bed when conducted at similar conditions.

In a test simulating the upper, low-temperature zone of a two-temperature zone hydrogasifier, 20.5% of the carbon in the coal was gasified with a feed gas containing 67.3% hydrogen and 32.7% methane, plus higher hydrocarbons, and steam (run HT-106). Hydrogen-to-coal ratio was 27.9% of stoichiometric, and steam concentration in the feed gas was 33.8 mole percent. A product gas having a heating value of 670 Btu per standard cubic feet was produced in the 3.5-foot fluidized bed at an average temperature of 1480°F and a reactor pressure of 1009 psig.

In run HT-111A, the partially hydrogasified bituminous coal from the low-temperature zone test (run HT-106) was gasified with hydrogen and steam. The test simulated the lower, high-temperature zone in which 20.9% of the carbon remaining in the coal was converted to gaseous products. Hydrogen-to-coal ratio was 36.9% of stoichiometric, and steam concentration in the feed gas was 51.3 mole percent. Temperature of the 3.5-foot coal bed averaged 1715°F while producing a product gas of 413 Btu per standard cubic foot heating value. Overall carbon gasification in these two tests was 38.7% based on the original carbon content of the coal.

Hydrogasification results of Pittsburgh seam bituminous coal with synthesis gas-steam feed gas, and with synthesis gas-methane-steam mixtures, are discussed in a later section that presents the effect of synthesis gas on coal gasification. Results of the gasification of the coal at a nominal pressure of 500 psig are discussed in a later section that presents the effect of this pressure on hydrogasification results.

2.3.3.4.2 Ohio No. 6 Seam Bituminous Coal

Coal from the Broken Aro mine was gasified in a 3.5-foot fluidized bed with hydrogen and steam at an average temperature of 1685°F to yield a product gas with a heating value of 562 Btu per standard cubic foot (run HT-130). To produce this gas, 29.7% of the carbon in the coal was gasified. This conversion was obtained with a hydrogen-to-coal ratio of 19.8% of stoichiometric and a steam concentration of 51.7 mole percent in the feed gas.

2.3.3.4.3 West Virginia No. 5 Block Seam Bituminous Coal

The best carbon conversion and product gas heating value were obtained with this coal in run HT-147 when 31.5% of the carbon was gasified, and a product gas with heating value of 572 Btu per standard cubic foot was produced. These results were obtained at 1700°F with a hydrogen-to-coal ratio of 20.2% of stoichiometric and a steam concentration of 31.5 mole percent in the feed gas.

2.3.3.4.4 Pocahontas No. 4 Steam Low-Volatile Bituminous Coal

Tests revealed this coal is significantly different in operating characteristics from those of high-volatile bituminous coals.

The evaluation of the hydrogasification performance of Pocahontas low-volatile-content bituminous coal was made in two tests. In run HT-150, the lightly pretreated coal was reacted at a nominal feed rate of 46 pounds per hour with 530 standard cubic feet per hour of hydrogen and 25 pounds of steam per hour. This run was terminated after 1 hour because of excessive coal agglomeration in the reactor tube. Agglomeration of the coal prevented flow through the reactor and discharge to the residue receiver. The reactor residue from this test was screened to determine the extent of agglomeration. Approximately 10% of the coal was of 4 mesh size (0.187 inch) or larger. The feed size for this test, as in all fluidized-bed tests, was 10 to 80 mesh. Laboratory evaluations of the pretreated coal feed used showed that it remained free-flowing at conditions simulating those in hydrogasification.

Run HT-151, conducted at flow conditions similar to those of run HT-150, lasted 1.5 hours before coal agglomeration in the reactor forced a shutdown. This coal was processed successfully in free-fall, run HT-167, as discussed earlier. Carbon gasification was 14.1% as a product gas of 441 Btu per standard cubic foot was produced.

No tabulated operating data for runs HT-150 and HT-151 are given in Table 2-A7 (appendix) because of the limited duration of these tests.

2.3.3.4.5 Illinois No. 6 Seam Bituminous Coal

The three tests with lightly pretreated Illinois bituminous coal — runs HT-155, HT-156, and HT-157 — exhibited a range of carbon gasifications similar to those of the tests with West Virginia bituminous coal, which were conducted at similar conditions. The highest carbon gasification (34.4%) was obtained with a hydrogen/coal ratio of 25.5% of the stoichiometric ratio

and a steam concentration of 51.3%; the lowest carbon gasification (29.0%) was obtained with a hydrogen/coal ratio of 17.5% of the stoichiometric ratio and a steam concentration of 53.4%. When 34.4% of the carbon was gasified, a product gas with heating value of 551 Btu per standard cubic foot was produced; with the lower carbon conversion of 29.0%, a product gas of 549 Btu per standard cubic foot was generated.

2.3.3.4.6 Indiana No. 6 Vein Bituminous Coal

Both operational performance and results in hydrogasification of the Indiana coal were similar to those of the Illinois coal.

The carbon gasification of 31.9% obtained with lightly pretreated Indiana bituminous coal in run HT-161 is only somewhat lower than the 34.4% obtained with Illinois bituminous coal in run HT-155 at generally similar conditions. However, this is explained in part to the lower hydrogen/coal ratio of run HT-161, which was 22.0% of stoichiometric, compared to the 25.5% of stoichiometric of run HT-155. The difference in hydrogen/coal ratio also accounts for the higher product gas heating value of 560 Btu per standard cubic foot in the test with Indiana coal. The concentration of unreacted hydrogen was lower in the product gas.

2.3.3.4.7 West Virginia Sewell Seam Low-Volatile Bituminous Coal

Three hydrogasification tests were conducted with this coal after it was lightly pretreated (runs HT-170, HT-172 and HT-174). The best carbon gasification of 28.5% was obtained with a hydrogen-to-coal ratio of 24.5% of stoichiometric and a steam concentration of 24.5 mole percent in the feed gas, run HT-170. The product gas with the highest heating value (520 Btu per standard cubic foot) was also obtained at the same time. From an operational standpoint, the performance of this coal was significantly better than that of the other low-volatile-content bituminous coal tested from the Pocahontas No. 4 seam.

2.3.3.4.8 Colorado Laramie No. 3 Seam Subbituminous Coal

Initial hydrogasification studies with this coal from the Eagle mine were conducted without pretreatment after only drying the coal. The coal was dried from a moisture content of 19.5% (as received) to 3.1%. Only minimal agglomeration tendencies were detected when the coal was tested in the laboratory. In the first test the dried coal was reacted in a 3.5-foot fluidized bed with a hydrogen/coal ratio of 25% of stoichiometric and with 50 mole percent steam in the feed gas. The run was only partially successful, being terminated shortly after the 3.5-foot coal bed was established when the coal began to agglomerate in the reactor tube and would not discharge. The agglomeration of the coal appeared to start near the top of the feed gas distributor.

The performance of untreated Colorado subbituminous coal in six other fluidized-bed tests continued to be marginal. The only completely successful operation was when the coal was hydrogasified in free-fall (runs HT-179

and HT-138, Table 2-A4, appendix. In a fluidized-bed operation the coal agglomerated after 1 to 3 hours and prevented discharge of the coal bed. In some cases, agglomeration of the coal near the top of the reactor choked off the coal-feed tube.

Partially successful operation with the untreated Colorado subbituminous coal was achieved in a fluidized bed during run HT-182 (Table 2-A7, appendix). The hydrogasification data of this run represent operation with a fixed coal bed at an average bed height of 4.75 feet. The coal bed increased in height as coal was fed to the top of the reactor, but agglomeration prevented the discharge of residue at the bottom of the reactor. Carbon gasification was comparatively high at 40%, based on a hydrogen/coal ratio of 28% of the stoichiometric ratio. Carbon in the oil products was 4.4% of the carbon in the coal. This is a significant fraction, but is of the order expected with a low-rank coal of this type. A product gas with a heating value of 581 Btu per standard cubic foot was produced.

To destroy the agglomerating tendencies of this coal and make it suitable for hydrogasification use, the coal was pretreated with air in the fluidized bed PDU pretreater. Following pretreatment, the coal successfully hydrogasified in a 3.5-foot fluidized bed during three tests (runs HT-184, HT-185 and HT-187). A carbon gasification of 38% was obtained in two of the tests when the hydrogen-to-coal ratio was 19 to 21% of the stoichiometric ratio and the steam concentration in the feed gas was 51 mole percent. Product gas heating values for these tests were in the range of 539 to 542 Btu per standard cubic foot. When the coal was hydrogasified with a hydrogen-to-coal ratio of 24% of the stoichiometric ratio, and a steam concentration of 31 mole percent, 40% of the carbon was gasified and a product gas of 599 Btu per standard cubic foot was produced.

2.3.3.4.9 North Dakota Lignite

Dried, but otherwise untreated, lignite had been first processed successfully in a moving bed in run HT-135, as discussed in the section on moving bed tests.

This lignite was also thermally gasified in free-fall in run HT-234, as discussed in the section on free-fall tests.

Run HT-139 (Table 2-A7, appendix), was the first successful fluidized-bed test conducted in the balanced-pressure PDU with North Dakota lignite. The high reactivity of the lignite is illustrated by the 46% carbon gasification when hydrogasifying with a hydrogen/lignite ratio of only 24% of stoichiometric. In addition, about 6.6% of the carbon in the lignite was converted to liquid hydrocarbons as a product gas of 534 Btu per standard cubic foot was produced. Steam concentration in this test was 51.3 mole percent. In another test (run HT-145) a gas of 574 Btu per standard cubic foot heating value was produced with a carbon gasification of 42.1%. To get these results the hydrogen-to-coal ratio was 24.7% of the stoichiometric ratio, and the steam concentration in the feed gas was 31.2 mole percent.

Compared to moving-bed hydrogasification of the lignite when 57% of carbon was gasified at similar operating conditions (run HT-135), the carbon gasification in fluidized bed tests was significantly less. This difference is

most readily explained by the longer residence time of the lignite in moving-bed operation as the lignite feed rate was about one-half of that in fluidized-bed operation.

Fluidized-bed gasification tests of this lignite were also made using synthesis gas plus steam feed gases, at selected conditions. Results of these tests are discussed in a section which discusses how synthesis gas affects coal gasification.

2.3.3.4.10 Montana Subbituminous Coal

The feasibility of successfully gasifying Montana subbituminous coal from the Colstrip mine with no prior pretreatment was demonstrated in a series of tests. The dried, but otherwise untreated coal was gasified in a fluidized bed with hydrogen and steam feed gases, and with synthesis gas and steam mixtures. Tests with both gases were performed at nominal reactor pressures of 1000 psig and 500 psig (Table 2-A7, appendix).

More than 48 percent of the carbon in the subbituminous coal was gasified in test run HT-212, when the coal was treated in a 3.5-foot fluidized bed at an average reactor temperature of 1595°F and a reactor pressure of 1082 psig. The hydrogen-to-coal ratio was 37.2% of stoichiometric, and the steam concentration in the hydrogen-steam mixture was 51.4%. In test run HT-216 using a significantly lower hydrogen-to-coal ratio of 24.8% of stoichiometric, but with otherwise similar conditions, the carbon gasification was 43.1%.

The hydrogasification tests made with the dried, but unpretreated Montana subbituminous coal have shown that this coal is more reactive than pretreated bituminous coal, but somewhat less reactive than lignite, judging from the degree of gasification.

Results of the hydrogasification of Montana subbituminous coal with synthesis gas and steam are presented in the section on the effect of synthesis gas on coal gasification. How pressure affects gasification of this coal is discussed in the section on 500 psig Hydrogasification Tests.

2.3.3.4.11 Montana Lignite

The hydrogasification behavior of a Montana lignite was studied in the balanced-pressure, high-temperature PDU to extend the evaluation of coals of different ranks in order to determine variation in performance due to origin as well as rank. It was not necessary to pretreat the lignite for hydrogasification use.

The Montana lignite was supplied by the Knife River Coal Co. from its mine at Savage, Montana. The feed for the tests was prepared by first pulverizing the as-received 1.5- to 3-inch particles in a swing hammer mill to -10+80 mesh size. After crushing and screening, the lignite was dried with air at 240°F in the PDU fluidized-bed coal pretreatment unit. The moisture content was reduced by drying from the as-received level of 35% to 3.5%. After drying, the lignite was again screened to remove particles of minus 80 mesh size not removed in the first screening.

The hydrogasification performance of the dried lignite with hydrogen and steam was studied in three tests, runs HT-217, HT-218 and HT-219, (Table 2-A7, appendix) performed in a 3.5-foot fluidized bed controlled to 1700°F, and at a nominal reactor pressure of 1000 psig. In these tests, the hydrogen-to-lignite ratio was varied from 20 to 25% of stoichiometric, and the steam concentration from 30 to 50 mole percent in the feed gas. No difficulties were experienced in feeding the lignite or in discharging the lignite residue from the reactor in any of the tests. Lignite flow through the free-fall section of the reactor tube and through the fluidized bed was generally smooth with no evidence of holdup.

Hydrogasification test HT-217, the first with Montana lignite, was performed with a hydrogen/lignite ratio of 19.1% of stoichiometric, and a steam concentration of 53.9 mole percent in the feed gas. At these conditions, 60% of the moisture- and ash-free lignite was converted, 43% of the carbon in the lignite was gasified, and a product gas of 534 Btu per standard cubic foot (nitrogen-free basis) was produced.

Key results of run HT-217 are shown in Table 2-3 with those of run HT-213 to show the comparative hydrogasification behavior of Montana lignite and Montana subbituminous coal. Run HT-213 was conducted at conditions similar to those of run HT-217.

The lignite shows a higher degree of reactivity than the subbituminous coal based on the larger fraction of carbon, and moisture- and ash-free feed that was gasified. For both feeds, hydrocarbon yields are similar. The increased carbon gasification with lignite was due mainly to the increased yield of carbon oxides. A greater conversion of feed carbon to oil products was also obtained with the lignite feed. Of the carbon in the subbituminous coal, 5.8% was converted to oil, whereas 8.8% of the carbon in the lignite appeared as oil. In general, both feeds produced gases of similar compositions. The somewhat lower heating value of the gas produced from the lignite feed shows that the carbon oxide concentrations are higher and that the methane concentrations are lower than those of the gas produced from the subbituminous coal feed.

In the second test, run HT-218, the lignite was fed at a nominal rate of 69.5 pounds per hour, the hydrogen at a rate of 463 standard cubic feet per hour, and the steam at a rate of 11.9 pounds per hour. At these flow conditions, the hydrogen/lignite ratio was 20.2% of the stoichiometric ratio; the steam concentration in the feed gas was 35 mole percent.

At these conditions, 51.3% of the moisture- and ash-free lignite was converted, 38.5% of the carbon in the lignite gasified, and a product gas of 581 Btu per standard cubic foot (nitrogen-free basis) was produced. The lignite conversion of run HT-218 is lower when compared to that of run HT-217. The product gas heating value, however, is higher in run HT-218 than in run HT-217. The reason for this is that run HT-217 was conducted at a higher steam concentration (50 mole percent) which resulted in higher carbon oxides production, but in lower hydrocarbon production than in run HT-218.

The third Montana lignite hydrogasification test with hydrogen and steam (run HT-219), was performed with a hydrogen/lignite ratio of 28.1% of

Table 2-3. COMPARISON OF MONTANA SUBBITUMINOUS COAL AND LIGNITE TEST RESULTS

<u>Run No.</u>	<u>HT-213</u>	<u>HT-217</u>
Feed	<u>Montana Subbituminous</u>	<u>Montana Lignite</u>
OPERATING RESULTS		
Reactor Pressure, psig	1068	1020
Coal Bed Temp., average, °F	1605	1605
Coal Bed Height, ft	3.5	3.5
Coal Feed Rate, lb/hr	69.11	75.44
Hydrogen Feed Rate, SCF/hr	489.2	462.8
Steam Feed Rate, lb/hr	25.62	25.75
Steam/Coal Ratio, lb/lb	0.371	0.341
Hydrogen/Coal Ratio, % of stoichiometric	20.8	19.1
Steam Concentration Feed Gas, mole %	52.4	53.9
Steam Decomposed, % of steam fed	18.8	6.16
Steam Decomposed, % of total equivalent steam fed	50.7	45.5
Carbon Gasified, %	38.3	42.7
MAF Coal Gasified, %	46.6	60.1
Hydrocarbon Yield, SCF/lb	4.317	4.232
CO + CO ₂ Yield, SCF/lb	3.089	3.643
Carbon in Oil Products, % of carbon in coal	5.85	8.82
PRODUCT GAS PROPERTIES		
Gas Composition (nitrogen-free), mole %		
Carbon Monoxide	11.8	12.6
Carbon Dioxide	14.4	16.8
Hydrogen	36.8	36.1
Methane	34.1	32.0
Ethane	1.6	1.4
Propane	0.8	0.6
Benzene	0.5	0.5
Total	100.0	100.0
Product Gas Heating Value (nitrogen-free), Btu/SCF	564	534