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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS RÉCU
A REACTOR DESIGN STUDY
FOR CHAR GASIFICATION KINETICS

by

VINCENZA M. ALLENGER

A thesis submitted to the School of Graduate Studies
in partial fulfillment of the requirement for the
degree of

MASTER OF APPLIED SCIENCE

in the
Department of Chemical Engineering
University of Ottawa

September 1982

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ABSTRACT

A critical review of the char gasification literature revealed that many researchers fail to account for concentration and temperature gradients which may exist at three levels in gas-solid systems: within a single reacting particle, in the film surrounding the particle, and in the reactor as a whole. Furthermore, in many of the gasification studies, the fluid mixing state has not been clearly defined. Theoretical and experimental tests for evaluating these effects are summarized. The use of 'gradientless' reactors, to alleviate these problems in studying gasification reactions is discussed. The potential of gradientless internal recirculation flow reactors in studying gasification kinetics was investigated by designing and constructing such a reactor. The degree of gas-phase mixing in the reactor was determined from step-response data using a novel approach to remove the intrusion of measurement device dynamics which prevents unambiguous evaluation of the mixing in bench scale reactors commonly having short residence times.
ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor, Dr. David D. McLéan for his guidance, advice and constructive criticism throughout the project.

I would also like to extend my appreciation to D. Lefebvre for his technical and analytical assistance during the early stages of this project.

Thanks are due to Dr. D. P. C. Fung for granting me permission to use his facilities to prepare coal char and G. Lett for analyzing the char samples.

The financial assistance received from the Natural Sciences and Engineering Research Council and from the Graduate School at the University of Ottawa is gratefully acknowledged.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>2. CHAR GASIFICATION</td>
<td>7</td>
</tr>
<tr>
<td>3. EXPERIMENTAL DESIGN</td>
<td>14</td>
</tr>
<tr>
<td>3.1 Features of System Design</td>
<td>14</td>
</tr>
<tr>
<td>3.1.1 Intraparticle Gradients</td>
<td>14</td>
</tr>
<tr>
<td>3.1.2 Interphase Gradients</td>
<td>25</td>
</tr>
<tr>
<td>3.1.3 Interparticle Gradients</td>
<td>31</td>
</tr>
<tr>
<td>3.1.4 Residence Time Distribution</td>
<td>35</td>
</tr>
<tr>
<td>3.1.5 Additional Features</td>
<td>38</td>
</tr>
<tr>
<td>3.1.6 Summary</td>
<td>39</td>
</tr>
<tr>
<td>3.2 Analytical Criteria for System Design</td>
<td>41</td>
</tr>
<tr>
<td>3.2.1 Intraparticle</td>
<td>42</td>
</tr>
<tr>
<td>3.2.2 Interphase</td>
<td>45</td>
</tr>
<tr>
<td>3.2.3 Interparticle</td>
<td>48</td>
</tr>
<tr>
<td>3.2.4 Summary</td>
<td>53</td>
</tr>
</tbody>
</table>
### TABLE OF CONTENTS (CONT'D)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3 Experimental Tests for System Design</td>
<td>53</td>
</tr>
<tr>
<td>3.3.1 Intraparticle</td>
<td>54</td>
</tr>
<tr>
<td>3.3.2 Interphase</td>
<td>54</td>
</tr>
<tr>
<td>3.3.3 Interparticle</td>
<td>55</td>
</tr>
<tr>
<td>3.4 Determination of Residence Time Distribution</td>
<td>56</td>
</tr>
<tr>
<td>3.4.1 Age Distribution Functions</td>
<td>56</td>
</tr>
<tr>
<td>3.4.2 Mathematical Models for Pseudo-Homogeneous Systems</td>
<td>67</td>
</tr>
<tr>
<td>3.4.3 Mathematical Models for Heterogeneous Systems</td>
<td>73</td>
</tr>
<tr>
<td>3.4.4 Mathematical Model Parameter Estimation</td>
<td>75</td>
</tr>
<tr>
<td>3.4.5 Summary</td>
<td>78</td>
</tr>
<tr>
<td>4. Evaluation of Reactor Systems</td>
<td>79</td>
</tr>
<tr>
<td>4.1 Systems Reported in the Literature</td>
<td>79</td>
</tr>
<tr>
<td>4.1.1 Tubular Fixed Bed Reactor: Integral Mode</td>
<td>80</td>
</tr>
<tr>
<td>4.1.2 Tubular Fixed Bed Reactor: Differential Mode</td>
<td>89</td>
</tr>
<tr>
<td>4.1.3 Thermogravimetric Balance</td>
<td>94</td>
</tr>
<tr>
<td>4.1.4 Fluidized Bed</td>
<td>105</td>
</tr>
<tr>
<td>4.1.5 Transport Reactor</td>
<td>117</td>
</tr>
<tr>
<td>4.1.6 Miscellaneous Reactors</td>
<td>124</td>
</tr>
<tr>
<td>4.1.7 Summary</td>
<td>129</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS (CONT'D)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2 Alternative Systems Available</td>
<td>129</td>
</tr>
<tr>
<td>4.2.1 External Recycle Reactor</td>
<td>136</td>
</tr>
<tr>
<td>4.2.2 Continuous Stirred-Tank Reactor</td>
<td>139</td>
</tr>
<tr>
<td>4.2.3 Internal Recycle Reactor</td>
<td>142</td>
</tr>
<tr>
<td>4.2.4 Summary and Conclusions</td>
<td>145</td>
</tr>
<tr>
<td>5. TESTING AN INTERNAL RECYCLE REACTOR</td>
<td>147</td>
</tr>
<tr>
<td>5.1 Introduction</td>
<td>147</td>
</tr>
<tr>
<td>5.2 Experimental Equipment and Materials</td>
<td>147</td>
</tr>
<tr>
<td>5.2.1 The Reactor</td>
<td>149</td>
</tr>
<tr>
<td>5.2.2 The Feed System</td>
<td>155</td>
</tr>
<tr>
<td>5.2.3 Product Analysis</td>
<td>156</td>
</tr>
<tr>
<td>5.2.4 Materials</td>
<td>162</td>
</tr>
<tr>
<td>5.3 Mixing Tests</td>
<td>162</td>
</tr>
<tr>
<td>5.3.1 Experimental Apparatus</td>
<td>165</td>
</tr>
<tr>
<td>5.3.2 Experimental Procedure</td>
<td>169</td>
</tr>
<tr>
<td>5.3.3 Modelling Approach</td>
<td>174</td>
</tr>
<tr>
<td>5.3.4 Measurement Device Model</td>
<td>176</td>
</tr>
<tr>
<td>5.3.5 Reactor Model</td>
<td>183</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS (CONT'D)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3 Mixing Tests (cont'd)</td>
<td></td>
</tr>
<tr>
<td>5.3.6 Parameter Estimation</td>
<td>192</td>
</tr>
<tr>
<td>5.3.7 Results and Discussion</td>
<td>198</td>
</tr>
<tr>
<td>5.4 Other Tests</td>
<td></td>
</tr>
<tr>
<td>5.4.1 Gas Flow Pattern</td>
<td>205</td>
</tr>
<tr>
<td>5.4.2 Temperature Profile</td>
<td>206</td>
</tr>
<tr>
<td>5.5 Conclusion</td>
<td>211</td>
</tr>
<tr>
<td>6. CONCLUSIONS AND RECOMMENDATIONS</td>
<td>213</td>
</tr>
<tr>
<td>6.1 Conclusions</td>
<td>213</td>
</tr>
<tr>
<td>6.2 Recommendations for Future Work</td>
<td>214</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>216</td>
</tr>
<tr>
<td>APPENDICES</td>
<td>237</td>
</tr>
<tr>
<td>A. Compilation of Char Gasification Bench Scale Kinetic Studies</td>
<td>237</td>
</tr>
<tr>
<td>Table of Contents (Cont'd)</td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>B.</strong> Example of Interphase Temperature Gradient of an Integral Tubular Bed</td>
<td>250</td>
</tr>
<tr>
<td><strong>C.</strong> Example of Interphase Temperature Gradient for a Thermogravimetric Balance</td>
<td>252</td>
</tr>
<tr>
<td><strong>D.</strong> Experimental Tests for Absorption of CO/CO$_2$ on Drying Agent</td>
<td>259</td>
</tr>
<tr>
<td><strong>E.</strong> Chromatograph Calibration Procedure</td>
<td>266</td>
</tr>
<tr>
<td><strong>F.</strong> Devolutilization Procedure for Coal</td>
<td>274</td>
</tr>
<tr>
<td><strong>G.</strong> Derivation of Exit Age Distribution for $N$-tanks in Series Model</td>
<td>278</td>
</tr>
<tr>
<td><strong>H.</strong> Derivation of Mixed Model Step Response</td>
<td>280</td>
</tr>
<tr>
<td><strong>I.</strong> Derivation of Combined Model Step Response</td>
<td>282</td>
</tr>
<tr>
<td><strong>J.</strong> Computer Program for Parameter Estimation</td>
<td>284</td>
</tr>
<tr>
<td><strong>K.</strong> Void Volume Estimates for Packed Beds</td>
<td>297</td>
</tr>
<tr>
<td><strong>L.</strong> Pressure Drop Calculation for Internal Recirculation Reactor</td>
<td>298</td>
</tr>
<tr>
<td><strong>M.</strong> Experimental Data</td>
<td>300</td>
</tr>
<tr>
<td>TABLES</td>
<td>PAGE</td>
</tr>
<tr>
<td>--------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>1-1 Arrhenius factors and reaction orders</td>
<td>3</td>
</tr>
<tr>
<td>for some gasification reactions</td>
<td></td>
</tr>
<tr>
<td>2-1 Gasification reactions</td>
<td>8</td>
</tr>
<tr>
<td>2-2 Governing equations for tubular fixed</td>
<td>12</td>
</tr>
<tr>
<td>bed reactor</td>
<td></td>
</tr>
<tr>
<td>3-1 Gas phase molecular diffusion coefficients</td>
<td>17</td>
</tr>
<tr>
<td>3-2 Effective diffusivity of carbon at high</td>
<td>20</td>
</tr>
<tr>
<td>temperatures</td>
<td></td>
</tr>
<tr>
<td>3-3 Effective thermal conductivity of coal</td>
<td>23</td>
</tr>
<tr>
<td>3-4 Essential and desirable features of system design</td>
<td>40</td>
</tr>
<tr>
<td>3-5 An evaluation of tracer input signals</td>
<td>63</td>
</tr>
<tr>
<td>3-6 Moments of probability distribution functions</td>
<td>68</td>
</tr>
<tr>
<td>4-1 The effect of temperature deviations on reaction rate constants</td>
<td>85</td>
</tr>
<tr>
<td>4-2 Observed activation energies for Boudouard reaction</td>
<td>88</td>
</tr>
<tr>
<td>4-3 Thermogravimetric balance sample holders</td>
<td>102</td>
</tr>
<tr>
<td>4-4 Comparison of activation energies for steam-graphite reaction</td>
<td>107</td>
</tr>
<tr>
<td>4-5 An evaluation of bench-scale char gasification reactors</td>
<td>130</td>
</tr>
<tr>
<td>4-6 Alternative bench-scale char gasification reactors</td>
<td>146</td>
</tr>
<tr>
<td>5-1 Analysis of Byron Creek coal</td>
<td>163</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>5-2</td>
<td>Analysis of Byron Creek coal char</td>
</tr>
<tr>
<td>5-3</td>
<td>Range of operating variables</td>
</tr>
<tr>
<td>5-4</td>
<td>$2^3$ factorial design for mixing tests</td>
</tr>
<tr>
<td>5-5</td>
<td>Measurement device and combined reactor/measurement device step responses</td>
</tr>
<tr>
<td>5-6</td>
<td>Parameter estimates for combined reactor/measurement device model</td>
</tr>
<tr>
<td>5-7</td>
<td>Specific volumes of components of reactor mixed model</td>
</tr>
<tr>
<td>5-8</td>
<td>Comparison of free gas volume in the reactor</td>
</tr>
</tbody>
</table>
FIGURES

1-1 Effect of temperature and reactor type on hydrogasification

3-1 Effect of mixing (RTD) on conversion for 1st order kinetics

3-2 Internal and exit age distributions for plug flow reactor

3-3 Internal and exit age distributions for backmix reactor

3-4 Diagnosing dead space from an exit age distribution

3-5 Diagnosing fluid by-passing from an internal age distribution

3-6 Step responses for a) plug flow and b) complete mixing

3-7 Pulse responses for a) plug flow and b) complete mixing

3-8 Signal-Flow or circulation model

4-1 Schematic of fixed bed tubular flow reactor

4-2 Differential reactor used by Blackwood and McGrory

4-3 Schematic of thermogravimetric balance

4-4 Calculated intraparticle temperature difference as a function of temperature level

4-5 Comparison of isothermal and nonisothermal rates of reaction

4-6 Schematic of a fluidized bed

4-7 Performance of a fluidized bed as a function of bubble size
<table>
<thead>
<tr>
<th>FIGURES (cont'd)</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-8 Rate of reaction as a function of carbon bed weight</td>
<td>115</td>
</tr>
<tr>
<td>4-9 Schematic of a) entrained bed b) free fall reactor</td>
<td>118</td>
</tr>
<tr>
<td>4-10 Conversion data showing small effect of average reactor residence time</td>
<td>120</td>
</tr>
<tr>
<td>4-11 Schematic of spouted bed</td>
<td>125</td>
</tr>
<tr>
<td>4-12 Schematic of diffusion cell apparatus</td>
<td>128</td>
</tr>
<tr>
<td>4-13 Schematic of external recycle reactor</td>
<td>133</td>
</tr>
<tr>
<td>4-14 Schematic of continuous stirred tank reactor, two versions</td>
<td>134</td>
</tr>
<tr>
<td>4-15 Schematic of internal recycle reactor</td>
<td>135</td>
</tr>
<tr>
<td>4-16 Catalyst baskets used in CSTR</td>
<td>141</td>
</tr>
<tr>
<td>5-1 Schematic flow diagram of experimental apparatus</td>
<td>148</td>
</tr>
<tr>
<td>5-2 Reactor assembly</td>
<td>150</td>
</tr>
<tr>
<td>5-3 Reaction chamber internals</td>
<td>151</td>
</tr>
<tr>
<td>5-4 Impeller</td>
<td>152</td>
</tr>
<tr>
<td>5-5 Modified Magnedrive Assembly</td>
<td>154</td>
</tr>
<tr>
<td>5-6 Chromatographic system for product gas analysis</td>
<td>158</td>
</tr>
<tr>
<td>5-7 Typical gas separation and analysis</td>
<td>160</td>
</tr>
<tr>
<td>5-8 Schematic flow diagram of experimental apparatus for mixing studies</td>
<td>166</td>
</tr>
<tr>
<td>5-9 Instrument calibration curve</td>
<td>168</td>
</tr>
<tr>
<td>5-10 Schematic of bed packing</td>
<td>170</td>
</tr>
<tr>
<td>FIGURES (cont'd)</td>
<td>PAGE</td>
</tr>
<tr>
<td>----------------</td>
<td>------</td>
</tr>
<tr>
<td>5-11 Measurement device step response</td>
<td>177</td>
</tr>
<tr>
<td>5-12 F-curve for N tanks-in-series model</td>
<td>178</td>
</tr>
<tr>
<td>5-13 Instrument step response fit with independent data</td>
<td>180</td>
</tr>
<tr>
<td>5-14 Instrument step response fit with correlated data</td>
<td>181</td>
</tr>
<tr>
<td>5-15 Sum of squares surface as a function of N</td>
<td>182</td>
</tr>
<tr>
<td>5-16 Measurement device model fitted to uncorrelated data, gas flowrate 500 cm³/min</td>
<td>184</td>
</tr>
<tr>
<td>5-17 Measurement device model fitted to uncorrelated data, gas flowrate 750 cm³/min</td>
<td>185</td>
</tr>
<tr>
<td>5-18 Measurement device model fitted to uncorrelated data, gas flowrate 1000 cm³/min</td>
<td>186</td>
</tr>
<tr>
<td>5-19 Schematic representation of reactor mixed model</td>
<td>187</td>
</tr>
<tr>
<td>5-20 Schematic representation of combined reactor/measurement device model</td>
<td>191</td>
</tr>
<tr>
<td>5-21 Combined reactor/measurement device step response</td>
<td>201</td>
</tr>
<tr>
<td>5-22 Residuals for combined reactor/measurement device model</td>
<td>202</td>
</tr>
<tr>
<td>5-23 Schematic of solid packing for gas flow determination</td>
<td>207</td>
</tr>
<tr>
<td>5-24 Thermocouple arrangement</td>
<td>208</td>
</tr>
<tr>
<td>5-25 Axial temperature profile in char bed</td>
<td>209</td>
</tr>
<tr>
<td>SYMBOL</td>
<td>DEFINITION</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$a_m$</td>
<td>external surface/unit mass ( [m_p^2 \text{ kg}^{-1}] )</td>
</tr>
<tr>
<td>$a_v$</td>
<td>external surface area/unit reactor volume ( [m_p^2 m_r^{-3}] )</td>
</tr>
<tr>
<td>$b$</td>
<td>dilution ratio</td>
</tr>
<tr>
<td>$b'$</td>
<td>molar stoichiometric coefficient</td>
</tr>
<tr>
<td>$\dot{C}_A$</td>
<td>concentration of gaseous component ( [\text{kmol} \ m_f^{-3}] )</td>
</tr>
<tr>
<td>$\bar{C}_A$</td>
<td>mean concentration of reactant leaving vessel ( [\text{kmol} \ m_f^{-3}] )</td>
</tr>
<tr>
<td>$C_{AB}$</td>
<td>concentration of species A in bulk stream ( [\text{kmol} \ m_f^{-3}] )</td>
</tr>
<tr>
<td>$C_{AS}$</td>
<td>concentration of species A at surface ( [\text{kmol} \ m_f^{-3}] )</td>
</tr>
<tr>
<td>$C_b$</td>
<td>bulk fluid concentration ( [\text{mol} \ m_f^{-3}] )</td>
</tr>
<tr>
<td>$c_p$</td>
<td>fluid heat capacity at constant pressure ( [\text{kJ} \ \text{kg}^{-1} \text{K}^{-1}] )</td>
</tr>
<tr>
<td>$c_s$</td>
<td>molar concentration of fluid reactant in front of solid surface ( [\text{kmol} \ m_f^{-3}] )</td>
</tr>
<tr>
<td>$d_p$</td>
<td>particle diameter ( [\text{m}] )</td>
</tr>
<tr>
<td>SYMBOL</td>
<td>DEFINITION</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$D_{12}$</td>
<td>binary molecular diffusion coefficient [cm$^2$ s$^{-1}$]</td>
</tr>
<tr>
<td>$D_a$</td>
<td>mixing dispersion coefficient for axial dispersion model</td>
</tr>
<tr>
<td>$D_e$</td>
<td>effective diffusivity for gas phase [cm$^2$ s$^{-1}$]</td>
</tr>
<tr>
<td>$D_{ea}$</td>
<td>axial effective diffusivity [m$_f^2$m$_r^2$ s$^{-1}$]</td>
</tr>
<tr>
<td>$D_{eff}$</td>
<td>effective diffusivity of solid [cm$^2$ s$^{-1}$]</td>
</tr>
<tr>
<td>$D_{12, eff}$</td>
<td>effective diffusion coefficient for bulk diffusion [cm$^2$ s$^{-1}$]</td>
</tr>
<tr>
<td>$D_{er}$</td>
<td>radial effective diffusivity [m$_f^2$m$_r^2$ s$^{-1}$]</td>
</tr>
<tr>
<td>$D_{k, eff}$</td>
<td>effective diffusion coefficient for Knudsen diffusion [cm$^2$ s$^{-1}$]</td>
</tr>
<tr>
<td>$e$</td>
<td>allowable error</td>
</tr>
<tr>
<td>$E$</td>
<td>exit age distribution</td>
</tr>
<tr>
<td>$E_a$</td>
<td>activation energy [kJ kmol$^{-1}$]</td>
</tr>
<tr>
<td>$f_{u1}$</td>
<td>calculated value of $C/C_0$ for measurement device response at $t_u$</td>
</tr>
<tr>
<td>$f_{u2}$</td>
<td>calculated value of $C/C_0$ for combined response at $t_u$</td>
</tr>
<tr>
<td>$F$</td>
<td>molar flow rate [mol s$^{-1}$]</td>
</tr>
<tr>
<td>SYMBOL</td>
<td>DEFINITION</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
</tbody>
</table>
| FR     | feed gas flowrate  
\[ \text{cm}^3 \text{min}^{-1} \] | |
| G      | superficial mass velocity  
\[ \text{kg m}^{-2} \text{ s}^{-1} \] | |
| \( h_f \) | heat transfer coefficient in film  
\[ \text{kJ m}^{-2} \text{ s}^{-1} \text{ K}^{-1} \] | |
| \( h_r \) | radiant heat transfer coefficient  
\[ \text{kJ m}^{-2} \text{ s}^{-1} \text{ K}^{-1} \] | |
| \( H_r \) | heat of chemical reaction  
\[ \text{kJ kmol}^{-1} \] | |
| I      | internal age distribution | |
| \( j_D \) | Chilton-Colburn factor | |
| \( j_H \) | Chilton-Colburn factor | |
| \( k_g \) | mass transfer coefficient  
\[ \text{m}^3 \text{ m}^{-2} \text{ s}^{-1} \] | |
| k      | reaction rate constant (1st order reaction)  
\[ \text{s}^{-1} \] | |
| \( k_r \) | first order rate constant  
\[ \text{s}^{-1} \] | |
| \( K_0 \) | geometric parameter characteristic of porous solid  
\[ \text{m} \] | |
| \( \omega \) | fraction of total reactor volume that is behaving as a series plug flow region | |
| L      | characteristic dimension of solid particle  
\[ \text{m} \] | |

xvi
<table>
<thead>
<tr>
<th>SYMBOL</th>
<th>DEFINITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>L'</td>
<td>reactor length [m]</td>
</tr>
<tr>
<td>m</td>
<td>fraction of total reactor volume that is behaving as a parallel plug flow region</td>
</tr>
<tr>
<td>M⁻¹</td>
<td>variance-covariance matrix for parameters (inverse of matrix M)</td>
</tr>
<tr>
<td>M_A</td>
<td>molecular weight [kg kmol⁻¹]</td>
</tr>
<tr>
<td>n</td>
<td>reaction order</td>
</tr>
<tr>
<td>n</td>
<td>fraction of total reactor volume that is being backmixed</td>
</tr>
<tr>
<td>n</td>
<td>total number of data points</td>
</tr>
<tr>
<td>N</td>
<td>number of tanks in series</td>
</tr>
<tr>
<td>N_A</td>
<td>molar flux [kmol m⁻² s⁻¹]</td>
</tr>
<tr>
<td>N_Nu</td>
<td>Nusselt Number = h_f dp/μ</td>
</tr>
<tr>
<td>N_Pr</td>
<td>Prandtl Number = C_p μ / k_f</td>
</tr>
<tr>
<td>N_Re</td>
<td>Reynolds Number = U L Q / μ</td>
</tr>
<tr>
<td>N_sc</td>
<td>Schmidt Number = μ / ρ D_12</td>
</tr>
<tr>
<td>N_sh</td>
<td>Sherwood Number = k_g L / D_12</td>
</tr>
<tr>
<td>PS</td>
<td>coded particle size</td>
</tr>
<tr>
<td>q</td>
<td>heat flux [kJ m⁻² s⁻¹]</td>
</tr>
<tr>
<td>Q</td>
<td>heat transfer rate from solid to fluid per unit mass [kJ kg⁻¹]</td>
</tr>
<tr>
<td>SYMBOL</td>
<td>DEFINITION</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$Q_R$</td>
<td>radiant heat transfer rate $[kJ\ s^{-1}]$</td>
</tr>
<tr>
<td>$r_p$</td>
<td>particle radius $[m]$</td>
</tr>
<tr>
<td>$r_{v, obs}$</td>
<td>observed or measured reaction rate $[kmol\ m^{-3}\ s^{-1}]$</td>
</tr>
<tr>
<td>$R$</td>
<td>fraction of the total flow that is being completely mixed</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant $[kJ\ kmol^{-1}\ K^{-1}]$</td>
</tr>
<tr>
<td>$R_0$</td>
<td>reactor radius $[m]$</td>
</tr>
<tr>
<td>RPM</td>
<td>impeller speed in revolutions per minute</td>
</tr>
<tr>
<td>$SS_1$</td>
<td>residual sum of squares for response 1</td>
</tr>
<tr>
<td>$SS_2$</td>
<td>residual sum of squares for response 2</td>
</tr>
<tr>
<td>$t_1$</td>
<td>mean residence time in one tank $[s]$</td>
</tr>
<tr>
<td>$t_R$</td>
<td>nominal holding time $[s]$</td>
</tr>
<tr>
<td>$T$</td>
<td>absolute temperature $[K]$</td>
</tr>
<tr>
<td>$T_b$</td>
<td>bulk fluid absolute temperature $[K]$</td>
</tr>
<tr>
<td>$T_s$</td>
<td>Temperature inside solid $[K]$</td>
</tr>
<tr>
<td>$T_s^*$</td>
<td>Temperature at solid surface $[K]$</td>
</tr>
<tr>
<td>SYMBOL</td>
<td>DEFINITION</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$T_{BR}$</td>
<td>residence time in backmix section [s]</td>
</tr>
<tr>
<td>$T_{PP/(1-R)}$</td>
<td>residence time in parallel plug flow section [s]</td>
</tr>
<tr>
<td>$T_w$</td>
<td>temperature of walls of cavity [K]</td>
</tr>
<tr>
<td>$u$</td>
<td>run number</td>
</tr>
<tr>
<td>$u_c$</td>
<td>unit step function</td>
</tr>
<tr>
<td>$U$</td>
<td>superficial fluid velocity $[m_f^3 m_r^{-2} s^{-1}]$</td>
</tr>
<tr>
<td>$v$</td>
<td>superficial linear velocity $[m s^{-1}]$</td>
</tr>
<tr>
<td>$V_o$</td>
<td>volumetric flowrate $[cm^3 s^{-1}]$</td>
</tr>
<tr>
<td>$V_F$</td>
<td>feed volumetric flowrate $[m_f^3 s^{-1}]$</td>
</tr>
<tr>
<td>$V_P$</td>
<td>pump recycle rate $[m_f^3 s^{-1}]$</td>
</tr>
<tr>
<td>$V_B$</td>
<td>volume of backmix region [mL]</td>
</tr>
<tr>
<td>$V_D$</td>
<td>volume of stagnant region [mL]</td>
</tr>
<tr>
<td>$V_{PP}$</td>
<td>volume of parallel plug flow region [mL]</td>
</tr>
<tr>
<td>$V_{PS}$</td>
<td>volume of series plug flow region [mL]</td>
</tr>
<tr>
<td>SYMBOL</td>
<td>DEFINITION</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$V_T$</td>
<td>total volume of reactor vessel [mL]</td>
</tr>
<tr>
<td>$W$</td>
<td>weight of solid bed [kg]</td>
</tr>
<tr>
<td>$x_0$</td>
<td>feed stream conversion</td>
</tr>
<tr>
<td>$X_1$</td>
<td>matrix of partial derivatives of response 1 with respect to the parameters</td>
</tr>
<tr>
<td>$X_2$</td>
<td>matrix of partial derivatives of response 2 with respect to the parameters</td>
</tr>
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<td>$X_T$</td>
<td>transformed variable for $\tau$ in minimization routine</td>
</tr>
<tr>
<td>$X_B$</td>
<td>transformed variable for $T_{pp}$ in minimization routine</td>
</tr>
<tr>
<td>$X_F$</td>
<td>exit stream conversion</td>
</tr>
<tr>
<td>$X_{pp}$</td>
<td>transformed variable for $T_{pp}$ in minimization routine</td>
</tr>
<tr>
<td>$X_{ps}$</td>
<td>transformed variable for $T_{ps}$ in minimization routine</td>
</tr>
<tr>
<td>$X_R$</td>
<td>transformed variable for $R$ in minimization routine</td>
</tr>
<tr>
<td>$Y$</td>
<td>co-ordinate</td>
</tr>
<tr>
<td>$y_{u1}$</td>
<td>measured value of $C/C_0$ for measurement device</td>
</tr>
<tr>
<td>$y_{u2}$</td>
<td>measured value of $C/C_0$ for combined response at $tu$</td>
</tr>
<tr>
<td>$Z$</td>
<td>co-ordinate</td>
</tr>
<tr>
<td>SYMBOL</td>
<td>DEFINITION</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$\beta$</td>
<td>heat of reaction parameter defined by Equation 3-24</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Arrhenius number defined in Equation 3-22</td>
</tr>
<tr>
<td>$\gamma^3$</td>
<td>skewness</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>relative experimental error in conversion</td>
</tr>
<tr>
<td>$\delta$</td>
<td>pore radius</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>packed bed voidage $[m^3m^{-3}]$</td>
</tr>
<tr>
<td>$\varepsilon_s$</td>
<td>porosity of solid, internal void fraction of solid $[m^3m^{-3}]$</td>
</tr>
<tr>
<td>$\bar{\varepsilon}$</td>
<td>emissivity of solid surface</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>ratio defined by Equation 3-21</td>
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<td>$\xi$</td>
<td>radial coordinate inside particle $[m_p]$</td>
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<tr>
<td>$n$</td>
<td>effectiveness factor</td>
</tr>
<tr>
<td>SYMBOL</td>
<td>DEFINITION</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>reduced time = $t/\bar{t}_R$</td>
</tr>
<tr>
<td>$\theta_s$</td>
<td>real value of parameter s</td>
</tr>
<tr>
<td>$\hat{\theta}_s$</td>
<td>estimate of parameter s</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>function defined in Equation 5-34</td>
</tr>
<tr>
<td>$\lambda_e$</td>
<td>effective thermal conductivity of packed bed with no fluid motion $[kJ \ m^{-1} \ s^{-1} \ K^{-1}]$</td>
</tr>
<tr>
<td>$\lambda_{ea}$</td>
<td>axial effective thermal conductivity in packed bed $[kJ \ m^{-1} \ s^{-1} \ K^{-1}]$</td>
</tr>
<tr>
<td>$\lambda_{ea}^f$</td>
<td>effective thermal conductivity of gas in axial direction in packed bed $[kJ \ m^{-1} \ s^{-1} \ K^{-1}]$</td>
</tr>
<tr>
<td>$\lambda_{ea}^s$</td>
<td>effective thermal conductivity of solid in axial direction in packed bed $[kJ \ m^{-1} \ s^{-1} \ K^{-1}]$</td>
</tr>
<tr>
<td>$\lambda_{eff}$</td>
<td>effective thermal conductivity of solid $[kJ \ m^{-1} \ s^{-1} \ K^{-1}]$</td>
</tr>
<tr>
<td>SYMBOL</td>
<td>DEFINITION</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$\lambda_{er}$</td>
<td>radial effective thermal conductivity in packed bed [ [kJ m^{-1} s^{-1} K^{-1}] ]</td>
</tr>
<tr>
<td>$\lambda_{er}^c$</td>
<td>effective thermal conductivity of fluid phase in packed bed [ [kJ m^{-1} s^{-1} K^{-1}] ]</td>
</tr>
<tr>
<td>$\lambda_{er}^s$</td>
<td>effective thermal conductivity of solid phase in packed bed [ [kJ m^{-1} s^{-1} K^{-1}] ]</td>
</tr>
<tr>
<td>$\lambda_f$</td>
<td>thermal conductivity of fluid [ [kJ m_f^{-1} s^{-1} K^{-1}] ]</td>
</tr>
<tr>
<td>$\lambda_s$</td>
<td>thermal conductivity of solid at $s = 0$ [ [kJ m_s^{-1} s^{-1} K^{-1}] ]</td>
</tr>
<tr>
<td>$\mu$</td>
<td>mean (centre of gravity of distribution about origin)</td>
</tr>
<tr>
<td>$\mu$</td>
<td>fluid viscosity [ [kg m^{-1} s^{-1}] ]</td>
</tr>
<tr>
<td>$\pi$</td>
<td>pi</td>
</tr>
<tr>
<td>$\rho$</td>
<td>fluid density [ [kg m^{-3}] ]</td>
</tr>
<tr>
<td>SYMBOL</td>
<td>DEFINITION</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stephan Boltzmann constant $[5.67 \times 10^{-8} \text{kJ/M}^2\text{s}^{-1}\text{K}^{-4}]$</td>
</tr>
<tr>
<td>$\sigma^2$</td>
<td>variance (spread of distribution)</td>
</tr>
<tr>
<td>$\sigma^2_{u_1}$</td>
<td>variance of response 1 at $t_u$</td>
</tr>
<tr>
<td>$\sigma^2_{u_2}$</td>
<td>variance of response 2 at $t_u$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>residence time in a single tank of measurement device tanks-in-series model $[s]$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>tortuosity factor</td>
</tr>
<tr>
<td>$\chi$</td>
<td>ratio defined by Equation 3-27</td>
</tr>
<tr>
<td>$\omega$</td>
<td>ratio defined by Equation 3-26</td>
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</table>
INTRODUCTION

Recently, the gasification of coal and biomass (bark, peat, woodchips, coconut shell, etc.) has received considerable attention in view of the growing interest in alternate forms of energy. There are various complete gasification systems in operation (Synthane, Lurgi, Kellogg, etc.), each having been developed to meet certain factors which include the availability of feedstock, the utilization of the product gas and the capital cost of the installation\(^{(1)}\). Even though this gasification technology has already been developed and is readily available, the renewed and vital role it plays today has provided the impetus for researchers to improve gasification processes in order to make them economically viable in a very competitive fuel market\(^{(2)}\).

Coal/biomass gasification may be thought of as occurring in several steps\(^{(3)}\). First the carbonaceous material is heated at high rates where pyrolysis and devolatilization occur according to the following reaction:

\[
\text{Coal/Biomass + Heat} \rightarrow \text{Volatile (CH}_4, \text{ CO, CO}_2, \text{ H}_2, \text{ H}_2\text{O) (g)}
\]

\[\text{ + Tar \quad (1)}
\]

\[\text{ + Char \quad (s)} \quad \text{ Equation 1-1}
\]

The volatiles then react in the gas phase. The char or solid residue remaining after this step consists primarily of carbon together with
the major part of the ash components and some volatile matter. The subsequent heterogeneous reactions between the char and oxygen, steam, carbon dioxide and hydrogen account for the majority of the time required for particle burnout. Furthermore, as pointed out in a recent review, economic feasibility of producing SNG and efficiency of in situ gasification also hinge on this important char gasification step. In view of this, attempts for improvements in gasification technology might well be directed towards this aspect of the overall process.

Knowledge of the kinetics of the char gasification step is fundamental to the design and optimal operation of commercial gasifiers, to the development and testing of suitable catalysts (in terms of both activity and selectivity) and to the better understanding of the basic gasification mechanism involved. Many investigations into char gasification kinetics have been carried out on both a bench scale and pilot scale. Numerous types of experimental reactor systems have been used to study the kinetics in question. The experimental arrangements include gas flow and static systems in which the char may exist as a fixed or fluidized bed of granular particles, particles falling through a hot zone, or a single massive piece. The operating variables encompass a wide range in temperatures (500-2300°C), pressures (10^-5 kPa-10^3 kPa) and gas velocities (0-100 m/s). While some experiments involve the reaction of an appreciable portion of the char, others are confined to reactions at very low burnoff. In this myriad of experimental investigations, disagreements are evident. Table 1-1 and Figure 1-1
TABLE 1-1 *

ARRHENIUS FACTORS AND REACTION ORDERS FOR SOME GASIFICATION REACTIONS

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A [kgm⁻²s⁻¹k Pa⁻¹]</th>
<th>E/R [K]</th>
<th>n</th>
<th>Particle Type</th>
<th>Particle Size [μm]</th>
<th>Temperature Range [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂-C</td>
<td>1.32 x 10⁻¹</td>
<td>16400</td>
<td>0</td>
<td>Brown Coal Char</td>
<td>22-89</td>
<td>630-1812</td>
</tr>
<tr>
<td></td>
<td>9.18 x 10⁻¹</td>
<td>8200</td>
<td>0.5</td>
<td>Brown Coal Char</td>
<td>22-89</td>
<td>630-2200</td>
</tr>
<tr>
<td></td>
<td>2.01</td>
<td>-9600</td>
<td>1</td>
<td>Semianthracite</td>
<td>6-78</td>
<td>1400-2200</td>
</tr>
<tr>
<td></td>
<td>5.43</td>
<td>20100</td>
<td>1</td>
<td>Semianthracite</td>
<td>6-78</td>
<td>1400-2200</td>
</tr>
<tr>
<td>H₂O-C</td>
<td>3.19 x 10²</td>
<td>25020</td>
<td>1</td>
<td>Graphite</td>
<td>-</td>
<td>1133-1233</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8240</td>
<td>1</td>
<td>Graphite</td>
<td>-</td>
<td>873-1273</td>
</tr>
</tbody>
</table>

| CO₂-C    | 1.38 x 10³          | 24000  | 1.4 x 10⁻⁴ | -7500 | Coke | 1073-1363       |
|          | 2.1 x 10⁴           | 20200  | 2.0 x 10⁻¹¹ | -27000| Coke | 1199-1423       |

* Table adapted from Tables 1, 3 and 6 of Chapter 9 in Smoot, L.D. and D. T. Pratt, Pulverized Coal Combustion and Gasification. Plenum Press, NY, CT, 1979
Figure 1-1 Effect of temperature and reactor type on hydrogasification
(Adapted from Reference 86)
contain some examples of experimental findings of kinetic parameters which have been reported in the literature. In as much as values for reaction order n, preexponential factor A and activation energy E are dependent upon the nature of the feedstock, it is unclear why these kinetic parameters are found to vary considerably from investigation to investigation, even for very similar feedstocks. The discrepancies found in these instances, are generally attributed to differences in pretreatment and source of the char being investigated. Although activity and selectivity of the char gasification step have been shown to be influenced by these factors,[120] the environmental history of the char during reaction (i.e. the heat up rate, temperature, pressure, composition of the gas phase, etc.) is an important factor which has often been poorly characterized. Proper interpretation of kinetic data depends upon reliable characterization of reaction conditions (temperature, reactant/product concentration, degree of mixing). In order to obtain reliable rate data and to facilitate data analysis, sound bench scale reactor design is critical. Unfortunately, there is little evidence in the gasification literature which indicates that reactor systems have been thoroughly evaluated.

Therefore, the preliminary objectives of the present work were:

1. to discuss the required features of laboratory reactor design for char gasification kinetics
2. to summarize and demonstrate the theoretical and experimental tests that may be applied to test an existing reactor system for temperature gradients, concentration gradients and residence time distribution
3. to summarize the types of reactors which have been used to date in char gasification studies and to evaluate them with respect to the above requirements.

As a result of this evaluation of the status quo in reactor design for gasification kinetics, it was desirable to consider and discuss possible alternative reactor designs which showed promise in overcoming many of the shortcomings of the reactor systems in current use. One of the alternate designs, namely an internal recirculation flow reactor was constructed in order to investigate its potential in studying char gasification kinetics. The development, testing and use of the reactor are discussed in detail.
2 CHAR GASIFICATION

In char gasification the primary process is a heterogeneous reaction between carbon and hydrogen, oxygen, carbon dioxide and steam. Consequently, carbon (in the form of graphite) has been used by many experimenters as a first approximation to the carbonaceous material in their effort to study the gasification reactions listed in Table 2-1. The reader is referred to an excellent treatise on the gas reactions of carbon by Walker et al.\(^8\). The authors discuss quite thoroughly the rates and mechanisms of several gas-carbon reactions and the various factors that affect them. Considerable emphasis is placed on the role of mass transport. The dated review by von Fredersdorff and Elliott\(^9\) which treats separately the topics of thermodynamics, physics, kinetics and diffusion in gasification reactions is also recommended as a summary of the work (mostly with pure carbon) done prior to 1960. Although much of the research carried out with pure carbon has contributed significantly to our understanding of the complex gas-char reactions, it has not been possible to predict char gasification rates from their carbon counterparts primarily because of inherent chemical differences. Char differs from pure carbon in that it contains chemically bound hydrogen, oxygen, sulfur and nitrogen as well as varying amounts of ash and mineral matter\(^3\). The latter items have been shown to influence reaction rates substantially through direct catalytic activity\(^1\). For these reasons, rate studies using char have been prompted. The reader's attention is focussed on a very comprehensive
<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reaction Equation</th>
<th>Heat of Reaction [CAL/MOL]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boudouard Reaction</td>
<td>( \text{C}_\text{(s)} + \text{CO}<em>2\text{(g)} \rightarrow 2\text{CO}</em>\text{(g)} )</td>
<td>41,200</td>
</tr>
<tr>
<td>Hydrogasification</td>
<td>( \text{C}_\text{(s)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_4\text{(g)} )</td>
<td>-17,890</td>
</tr>
<tr>
<td>Carbon-Steam Reaction</td>
<td>( \text{C}<em>\text{(s)} + \text{H}<em>2\text{O}</em>\text{(g)} \rightarrow \text{CO}</em>\text{(g)} + \text{H}_2\text{(g)} )</td>
<td>41,000</td>
</tr>
<tr>
<td>Incomplete Combustion</td>
<td>( \text{C}_\text{(s)} + \frac{1}{2} \text{O}<em>2\text{(g)} \rightarrow \text{CO}</em>\text{(g)} )</td>
<td>-26,400</td>
</tr>
</tbody>
</table>
review by Laurendeau\textsuperscript{(4)} in which the kinetics of the char reactions with oxygen, hydrogen, steam and carbon dioxide are considered in great depth with the emphasis being placed on the use of intrinsic chemical reaction rates, i.e. the rate per unit surface area (internal plus external), in the study of these heterogeneous reactions. The basics of gas-solid reactions will now be examined briefly.

The char gasification reactions listed in Table 2-1 are non-catalytic heterogeneous reactions involving a solid (char) and a gas (oxygen, hydrogen, steam, carbon dioxide). Gas-solid reactions are considered to observe the following mechanism or sequence of steps:

1. external mass transport of gaseous reactant(s) from the bulk fluid to the outside surface of the porous solid
2. diffusion of the gaseous reactant(s) within the pores of the solid to the surface
3. chemical reaction with the solid including the adsorption of reactants and the desorption of products
4. diffusion of the gaseous products from interior sites to the outer surface of the solid
5. external mass transport of the gaseous products from the gas-solid interface to the bulk gas stream

It is very important to understand the relative significance of these steps in order to understand the overall rates of the reactions. Any single step 1 through 5 can be rate-determining and often a combination of steps ultimately determine the overall gasification
rates depending upon what reaction conditions (temperature, pressure, gas concentrations and velocities, particle sizes) are being studied. Operating conditions in which the surface reaction is controlling (i.e. step 3) must be used to determine the true kinetics of the char-gas reactions since at any other conditions, the external mass transport (steps 1 and 5) and the intraparticle diffusion (steps 2 and 4) may significantly affect the overall rate, the activation energy and the apparent order of reaction\(^{(11)}\).

Since kinetic parameters must be determined through measurements on a reacting system, it is critical that the reactor be carefully described through an adequate design equation and that the experimental procedure and operating conditions be clearly defined.

The mathematical formulation for char-gas reactions in multiparticle systems (such as fixed beds, fluidized beds, entrained bed, etc.) is complex and as Wen\(^{(12)}\) points out "a rigorous treatment seems unattainable even for the solid of the simplest geometry" because of a number of factors:

1. the changing size and shape of the char particles during the reaction
2. the changing intricate pore network within the porous char during reaction
3. the complicated velocity profile of the surrounding gas and
4. the complicated temperature distributions within the reactor due to high heats of reaction.
Szekely et al. (13) have outlined a general approach to formulating models of nonisothermal systems where there may be a significant change in the molar flow rate of the reacting gas. Their approach consists in statements of heat balances and component and overall mass balances on the gas and solid. Typical relationships that enter into these equations are correlations of heat and mass transfer coefficients, temperature dependence of property values and expressions for the solid rate of reaction.

As an example, a summary of the governing equations for a tubular packed bed flow reactor for the transient state and for a single reaction are given in Table 2-2. Models of chemical reactors, therefore, must be based on the physical phenomena of mass, heat and momentum transfer and on chemical reaction kinetics. Reactor design and operation which can simplify the formidable task of modelling is invaluable to obtaining and interpreting gasification rate data. In this light, the merits and demerits of various laboratory reactors in facilitating kinetic studies will be examined in Chapter 4.

It is clear that the mathematical model used to describe the reacting system should be representative of the actual conditions existing inside the reactor. No analytical solution to the complete set of partial differential equations listed in Table 2-2 exists. Numerical solutions of this set of equations, although feasible, require considerable computation and to my knowledge solutions of this type have not yet been attempted. In order to obtain the kinetics from a tubular fixed bed, simplifying assumptions must be made. The interpretation of kinetic data therefore depends upon the quality of these underlying assumptions. When assumptions are made about reactor
TABLE 2-2

GOVERNING EQUATIONS FOR TUBULAR FIXED BED REACTOR

MASS BALANCE ON KEY COMPONENT OF GAS

\[
\frac{\partial (\varepsilon C)}{\partial t} = -\frac{\partial (\varepsilon UC)}{\partial z} - \kappa \frac{g \partial C_s}{\partial z} + \varepsilon D_e \frac{\partial^2 C}{\partial z^2} + \frac{1}{\varepsilon} \frac{\partial C}{\partial r} + \varepsilon D \frac{\partial^2 C}{\partial z^2}
\]

rate of acc of reactant
net convective
net transfer of flow of reactant into the solid to gas.
rate of acc of reactant
in axial direction
rate of acc of reactant
radial & axial dispersion

MASS BALANCE ON REACTING COMPONENT OF SOLID

\[
\frac{\partial C_s}{\partial t} = D_e (\varepsilon \frac{\partial^2 C_s}{\partial z^2}) - \rho_s r A
\]

rate of acc of reactant
effective diffusion
within solid particle
rate of production or consumption
rate of acc of reactive component due to chemical reaction

HEAT BALANCE ON GAS

\[
\frac{\partial (\varepsilon \rho_g c_p T)}{\partial t} = -\frac{\partial (\varepsilon \rho_g c_p T)}{\partial z} + h_f a_v (T_s - T) + \lambda_e \left( \frac{\partial^2 T}{\partial z^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right) + \lambda_e \frac{\partial^2 T}{\partial z^2}
\]

rate of acc of heat in gas
net convective
axial heat flow into differential volume due to radial & axial dispersion in gas
rate of heat of heat transfer to solid
rate of heat of heat transfer to solid
rate of heat of heat transfer to solid

HEAT BALANCE ON SOLID

\[
\frac{\partial (\rho_s c_p \varepsilon T_s)}{\partial t} = \frac{\lambda_e}{\varepsilon} \left( \frac{\partial^2 T_s}{\partial z^2} \right) + \frac{\rho_s \Delta H r A}{\varepsilon} + \frac{\lambda_s}{\varepsilon} \left( \frac{\partial^2 T_s}{\partial z^2} + \frac{1}{r} \frac{\partial T_s}{\partial r} \right) + \frac{\lambda_s}{\varepsilon} \frac{\partial^2 T_s}{\partial z^2}
\]

rate of acc of rate of heat transfer heat in solid to gas
due to effective thermal cond. within solid
rate of heat consumed due to heterogeneous reaction
heat flow into differential volume due to conduction & radiation in axial and radial directions.
conditions, it is important that experimental as well as theoretical tests be applied whenever possible to verify them. In the next chapter, the essential and desirable features of bench scale reactors and these experimental and theoretical tests will be discussed in an effort to evaluate bench-scale reactors in the study of char gasification kinetics.
3 EXPERIMENTAL DESIGN

3.1 Essential and Desirable Features of System Design

Before embarking on an evaluation of reactor systems, it is worthwhile establishing those features of a reaction system which are desirable and in some cases essential for the accurate determination of char gasification kinetics from single particle or multiparticle systems. When only chemical kinetic information is of interest, one must ensure that temperature and concentration gradients within the reactor are controlled and accurately modelled. This can be classified as an essential feature of system design since chemical kinetics depend directly on the concentration of reacting species and on the reaction temperature. These gradients may exist at three levels in gas-solid systems: intraparticle*, interphase** and interparticle***. Each of these will be considered separately.

3.1.1 Intraparticle Gradients

* within individual particles
** between the external surface of the particle and the gas adjacent to it
*** between local gas regions and between char particles (sometimes referred to as intrareactor)
Concentration gradients inside a single reacting porous particle exist whenever the reactants cannot diffuse in to the pores of the solid from the solid-fluid interface sufficiently rapidly. A good description of pore diffusion can be found in References 14 and 15. Diffusion rates in porous solids cannot in general be predicted because of several complicating factors (15), namely:

1. The volume occupied by the solids is not available for diffusive transfer.
2. The actual diffusion path will not follow a straight line but will be quite tortuous and the extent of this tortuosity will necessarily depend on the pore structure of the solid.
3. The diffusion in the pore volume will be influenced by the pore walls when the pores are small enough and Knudsen diffusion will become important.
4. Under some conditions, significant total pressure gradients may be established within the solid. Under these conditions transfer due to a pressure gradient has to be considered.

The approach usually taken to model an actual solid is to assume that the laws of molecular diffusion are obeyed in the porous medium and then to define an effective diffusivity (which is smaller than the binary molecular diffusion coefficient) to incorporate the various factors mentioned
earlier as follows:

$$Na = -D_{\text{eff}} \frac{dCA}{dz}$$  \hspace{1cm} \text{Equation 3-1}$$

Pore diffusion in the solid may occur by either bulk or Knudsen diffusion or both. If the pores are large and the gas relatively dense, the process is that of bulk or ordinary diffusion*. The bulk diffusion coefficient per unit cross section of porous mass may be expressed in the following way:

$$D_{12,\text{eff}} = \frac{\varepsilon_s D_{12}}{\tau}$$  \hspace{1cm} \text{Equation 3-2}$$

where $\tau$ is the tortuosity factor, $\varepsilon_s$ the internal void fraction or porosity of the solid, and $D_{12}$ the ordinary molecular diffusivity. Typical values for porosity of coals are in the range 2-30%\(^{(16)}\). The porosity of chars is usually somewhat higher and depends upon the extent of gasification (30-70%).

Experimental values of gaseous diffusion coefficients are in most cases readily available but when this is not the case, gas phase diffusivities may be predicted quite accurately\(^{(17, 18)}\). Typical values are given in Table 3-1 for low temperatures. Extrapolation of these gas diffusivities to higher temperatures and pressures can be accomplished by using

* Pore size/mean free path of diffusing species $> 10^{(4)}$
TABLE 3-1

GAS PHASE MOLECULAR DIFFUSION COEFFICIENTS

1 Atmosphere

<table>
<thead>
<tr>
<th>Gas Pair</th>
<th>Temperature [K]</th>
<th>Diffusivity [cm²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO-CO₂</td>
<td>315</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>473</td>
<td>0.39</td>
</tr>
<tr>
<td>H₂-CH₄</td>
<td>316</td>
<td>0.81</td>
</tr>
<tr>
<td>H₂O-H₂</td>
<td>273</td>
<td>0.75</td>
</tr>
<tr>
<td>H₂O-CO₂</td>
<td>273</td>
<td>0.138</td>
</tr>
<tr>
<td>O₂-CO₂</td>
<td>273</td>
<td>0.139</td>
</tr>
</tbody>
</table>
any of a number of empirical correlations based on reduced temperatures and pressures (e.g. Slattery-Bird Equation, Chapman-Enskog Equation). $D_{12}$ varies with $T^n$ where $n$ lies between 1.5 and 2 depending upon the temperature level. At low to moderate pressures, the diffusion coefficient of gases is inversely proportional to pressure or density$^{(18)}$.

If the gas density is low or if the pores are quite small or both** the molecules collide with the pore wall much more frequently than with each other. This is known as the Knudsen diffusion regime. In coals over 90% of the internal surface area is contained within a micropore ($\delta<20\AA$ or 200 nm) system that represents 50 to 80 percent of the total void space$^{(16)}$. Knudsen diffusion is distinctly possible in this microporous network. A simplified approach to defining the Knudsen diffusivity $D_{k, \text{eff}}$ is given below$^{(13)}$:

$$D_{k, \text{eff}} = \frac{4}{3} \left( \frac{8 \sqrt{\pi T}}{\pi M_A} \right)^{\frac{1}{2}} K_0 \quad \text{Equation 3-3}$$

where the term in the parenthesis can be interpreted as the root mean square of the velocity of the gas molecules of $A$; $K_0$ is a parameter characteristic of the solid with the dimensions of length. Methods are available for estimating $K_0$ for idealized geometries and can be found in Reference 13. Little information is available however on experimentally

** Pore size/mean free path of diffusion species $<0.1^{(4)}$
measured tortuositites and Knudsen diffusion coefficients for noncatalytic gas-solid reaction systems. The combined effects of both Knudsen diffusion and molecular diffusion in the transition region (for equimolar counterdiffusion) can be modelled to a good approximation by using the overall pore diffusion coefficient:

$$D_{\text{eff}} = \left[ \frac{1}{D_{k,\text{eff}}} + \frac{1}{D_{12,\text{eff}}} \right]^{-1} \quad \text{Equation 3-4}$$

Walker et al. (8) have found that $D_{\text{eff}}$ is directly proportional to the square of the porosity for $\varepsilon_s < 0.40$ with the proportionality factor equal to 0.095 cm²/s at NTP (20°C, 1 atm) for spectroscopic carbon rods. Unfortunately the temperature and pressure dependence of $D_{\text{eff}}$ were not studied. Recently, Desai and Yang (113) showed that the relation

$$D_{\text{eff}} = \varepsilon_s^2 D_{12}$$

for the effective diffusivity of carbon was limited to temperatures below 700°C. In their modeling studies they found that at temperatures above 1300°C the above relation predicts diffusivities that are too high by a factor of 74 to 80 as shown in Table 3-2. Because of the scarcity of the experimental data on effective diffusivities of char, a constant value is nearly always assumed in char gasification studies.

Temperature gradients inside a single porous particle may also exist whenever the thermal conductivity of the solid is
TABLE 3-2

EFFECTIVE DIFFUSIVITY OF CARBON AT HIGH TEMPERATURES

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$D_{\text{eff}}$ * [cm²/s]</th>
<th>$\tau$</th>
<th>$\tau^2_{0,12}$ [cm²/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1300</td>
<td>$1.35 \times 10^{-3}$</td>
<td>64</td>
<td>0.1</td>
</tr>
<tr>
<td>1400</td>
<td>$1.39 \times 10^{-3}$</td>
<td>65</td>
<td>0.11</td>
</tr>
<tr>
<td>1500</td>
<td>$1.56 \times 10^{-3}$</td>
<td>61</td>
<td>0.12</td>
</tr>
<tr>
<td>1600</td>
<td>$1.63 \times 10^{-3}$</td>
<td>60</td>
<td>0.13</td>
</tr>
</tbody>
</table>

* Obtained from modeling studies by Desai & Yang [113]
sufficiently low to hinder the transport of energy (by conduction within the solid). The usual approach taken for the representation of porous solids is to consider them homogeneous on a macroscopic scale and, then to relate the heat flux to the temperature gradient by means of an effective thermal conductivity:

\[ q_y = -\lambda_{\text{eff}} \frac{dT}{dy} \]  

Equation 3-5

If one assumes, in estimating the effective thermal conductivity of real porous solids, that the material consists of a continuous solid phase containing many closed and isolated pores filled with a gas that has a thermal conductivity much lower than that of the solid phase, then the thermal conductivity can be estimated by the following expression

\[ \lambda_{\text{eff}} = \lambda_s (1 - \varepsilon_s) \]  

Equation 3-6

where \( \lambda_s \) is the thermal conductivity of the solid at zero porosity. If on the other hand one assumes that the material consists of a gaseous continuous phase (of relatively low thermal conductivity) containing individual solid particles that are in point contact only, then the effective thermal conductivity of the porous solid depends on the thermal conductivity of the gas but is independent of the solid conductivity. Clearly these are two limiting cases. An actual porous solid will have an intermediate thermal conductivity.
It has been shown that the high porosity of coal makes its thermal conductivity very much dependent on the nature of the gas that suffuses its internal free space as demonstrated in the experimental work by Schumann and Voss\(^{114}\) presented in Table 3-5. Other investigators have also found that heat conductivities are similarly affected by moisture content. Since chars have somewhat higher porosities, marginally lower effective thermal conductivities are expected. The effective thermal conductivities of chars are in the range 3-9cals\(^{-1}\) cm\(^{-1}\) C\(^{-1}\) (4). It should be noted however that porosity and pore structure change with reaction so that strictly speaking both effective thermal conductivity \(\lambda_{\text{eff}}\) and effective diffusivity \(D_{\text{eff}}\) are a function of the extent of reaction.

Reaction rates are significantly altered by the intrusion of these intraparticle temperature and concentration gradients. The classical approach adopted in studying gas-solid reactions has been to define the effectiveness factor \(\eta\) as the ratio of the actual reaction rate \(r_{v,\text{obs}}\) to that which would occur if all of the surface throughout the inside of the solid particle were exposed to reactant and product of the same concentration and temperature as that existing at the solid-gas interface.

\[
\eta = \frac{r_{v,\text{obs}}}{r_{v}(C_s^S, T_s^S)} \quad \text{Equation 5-7}
\]
TABLE 3-3

**EFFECTIVE THERMAL CONDUCTIVITY OF COAL**

Dry Coal

Sized - 10 + 12 m

$\varepsilon_s = 44\%$

<table>
<thead>
<tr>
<th></th>
<th>AIR</th>
<th>H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective Thermal Conductivity [cal s$^{-1}$ cm$^{-1}$ K$^{-1}$]</td>
<td>$3.27 \times 10^{-4}$</td>
<td>$7.03 \times 10^{-4}$</td>
</tr>
<tr>
<td>Gas Thermal Conductivity [cal s$^{-1}$ cm$^{-1}$ K$^{-1}$]</td>
<td>$0.63 \times 10^{-4}$</td>
<td>$4.6 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
For the case where there is no pore diffusion limitation \( \eta \) approaches unity. Under isothermal conditions (i.e. no temperature gradients) \( \eta \) decreases in value as diffusion limitations become significant, but with a highly exothermic reaction (significant temperature gradient) \( \eta \) may exceed unity\(^{(19)}\). The effectiveness factor \( \eta \) is a function of the Thiele modulus, \( \phi \), as shown below.

\[
\eta = \tanh \frac{\phi}{\phi} , \text{ where } \phi = L \lambda_{\text{eff}} \sqrt{D_{\text{eff}}} \quad \text{Equation 3-8}
\]

It can be shown that for large particles (L large), small diffusivities or very rapid reaction rates, appreciable diffusion resistance can occur and must be considered.

Turkdogan et. al\(^{(62, 63)}\) have conducted very extensive studies on the carbon-dioxide reaction with charcoal and coke using an electrobalance. The extent of pore diffusion in solid spherical carbon specimens was shown to depend on the size of the carbon sample, the concentration of the reactant gas and on the temperature. Pore diffusion offered less resistance with decreasing particle size, decreasing partial pressure of CO\(_2\) and decreasing temperature. For a carbon dioxide partial pressure of 0.24 atm and a total pressure of 1 atm, the maximum critical sphere diameter for negligible pore diffusion resistance is about 2 cm at 900 - 950\(^0\)C. At much lower pressures (0.025 atm) for 1 cm diameter cylinders negligible pore diffusion resistance extends to 1300\(^0\)C.
3.1.2 Interphase Gradients

Steps 1 and 5 in the generalized mechanism of gas-solid reactions relate to the external mass transfer of reactant/product to/from the bulk fluid to/from the gas-solid interface. This mass transfer step has been extensively studied since the rates at which these species are transferred to and from the solid surface may play an important role in determining the overall rate of reaction. Mass transfer rates can be described by the usual mass transfer coefficient, \( k_g \), in terms of an appropriate driving force as follows (15):

\[
N_A = k_g (C_{AB} - C_{AS}) \quad \text{Equation 3-9}
\]

where
\( C_{AB} \) concentration of reactant/product A in bulk stream
\( C_{AS} \) concentration of reactant/product A at fluid/solid interface
\( N_A \) molar flux with respect to the fixed solid surface

Mass transfer coefficients for a particular reactor system can in general be obtained from numerous experimentally determined correlations (14, 15). Frequently the mass transfer coefficient is expressed as a Chilton-Colburn \( j_D \) factor which is defined in terms of dimensionless groups as:

\[
j_D = \frac{N_{Sh}}{N_{Re}^{1/3} N_{Sc}} \quad \text{Equation 3-10}
\]
The Sherwood, Schmidt and Reynolds numbers are defined as:

\[
N_{Sh} = \frac{k_g L}{D_{12}} \quad N_{Sc} = \frac{\mu}{\rho D_{12}} \quad N_{Re} = \frac{U L_p}{\mu}
\]

where
- \( \mu \) fluid viscosity
- \( \rho \) fluid density
- \( U \) superficial velocity of fluid
- \( D_{12} \) molecular diffusion coefficient
- \( L \) characteristic dimension of particle
- \( k_g \) mass transfer coefficient from bulk fluid to solid

In laboratory work, the Reynolds number \((N_{Re})\) will typically range from about 20 to as low as 0.1 or less. The following empirical correlation is recommended for packed beds in which the \( N_{Re} \) is between 3 and 2000 and the particle diameters are between 1.8 and 9.4 mm:\(^{(19)}\)

\[
\varepsilon_j D = \frac{0.357}{N_{Re}^{0.359}} \quad \text{Equation 3-11}
\]

For lower flow rates and smaller particle sizes, mass-transfer coefficients may be very low and a rough estimate may be obtained from the following \((0.0016 < N_{Re} < 55)^{(112)}\)

\[
\varepsilon_j D = 1.09 (N_{Re})^{-2/3}
\]
It must be stated however that at low flowrates, these average mass transfer coefficients may not be representative of the entire bed when there is a large degree of particle size distribution and hence distribution of voidage (19).

The rate of reaction at the solid surface for a first order reaction based on the interfacial surface area can be expressed simply as the product of the reaction rate constant and the concentration of reactant at the interface.

\[ -r_A = k_r C_{AS} \]  
Equation 3-12

At steady-state there is no accumulation of reactant at the interface and the rates expressed by Equation 3-9 and by Equation 3-12 must be equal. Combining these to eliminate the unknown surface concentration yields:

\[ -r_{A,obs} = k_o C_{AB} = \left( \frac{1}{k_g} + \frac{1}{k_{f'}} \right)^{-1} C_{AB} \]  
Equation 3-13

The meaning of external mass transfer resistance is clearly illustrated by Equation 3-13. When the mass transfer step is much more rapid than the surface reaction step (i.e. \( k_g \gg k_r \)) then the observed reaction rate approximates the surface reaction rate because \( k_o \approx k_r \) and \( C_{AB} \approx C_{AS} \). However, the other limit is that of almost instantaneous reaction, (i.e. \( k_r \gg k_g \)), the observed rate then corresponds to the fluid phase mass transfer step and is termed 'diffusion
controlling. Appropriately Smith(14) points out that significant external mass transfer resistance leads to false activation energies and orders of reaction.

Fluid to particle heat transfer resistances must also be considered in gasification reactions. The heat transfer coefficient is defined in terms of the temperature difference between the bulk fluid \(T_B\) and surface \(T_S\) as

\[
Q = h_f a_m (T_S - T_B) \quad \text{Equation 3-14}
\]

where

- \(Q\) = heat transfer rate from solid to fluid per unit mass
- \(a_m\) = external surface/unit mass
- \(h_f\) = film heat transfer coefficient

As in the case of the mass transfer coefficients, one has to rely for the most part on empirical correlation for obtaining the heat transfer coefficient. These empirical correlations also make use of a \(j\)-factor expression:

\[
J_H = \frac{h_f}{c_p G} N_{Pr}^{2/3} \quad \text{Equation 3-15}
\]

where the dimensionless Prandtl number is defined as \(c_p \mu / k_f\).

- \(h_f\) = heat transfer coefficient
- \(c_p\) = fluid heat capacity
- \(G\) = superficial mass velocity
- \(k_f\) = thermal conductivity of fluid
Satterfield\(^{(19)}\) suggests the following correlation as a rough guide for estimating heat transfer coefficients at low flow rates \((0.1 < N_{Re} < 10)\) in packed beds:

\[
N_{Nu} = 0.07 N_{Re}, \quad \text{where} \quad N_{Nu} = \frac{h_f d_p}{\lambda_f}
\]

It must be noted however that heat transfer coefficients evaluated from the \(j\)-factor expression do not include a radiation contribution. Smith\(^{(14)}\) points out that in general, radiation effects are negligible below \(400^\circ\text{C}\) for fixed beds of pellets not greater than 6mm in diameter. Since gasification reactions occur at higher temperatures, the radiative heat transfer should be considered. A simple expression holds for describing the radiant flux received by a small pellet, located in a large cavity (e.g. thermogravimetric balance) the surface of which is isothermal, in the presence of a nonabsorbing gas\(^{(13)}\):

\[
Q_R = \varepsilon \sigma (T_W^4 - T_S^4) \quad \text{Equation 3-16}
\]

where

\[
\begin{align*}
\sigma &= \text{Boltzmann's const} = 1.37 \times 10^{-12} \text{ cal cm}^{-2} \text{s}^{-1} \text{K}^{-4} \\
Q_R &= \text{net radiative flux at the solid surface} \\
\varepsilon &= \text{emissivity of the surface} \\
T_W &= \text{temperature of the walls of the cavity} \\
T_S &= \text{temperature of the solid surface}
\end{align*}
\]
This is often a good approximation for radiative heat transfer to single pellets held in a tubular furnace (e.g., the thermogravimetric balance). A radiative heat transfer coefficient may be defined in the following manner

\[
h_r = \varepsilon \sigma (T_w^2 + T_s^2) (T_w + T_s)
\]

Equation 3-17

for purposes of comparison with convective heat transfer coefficients.

The reactant gas and the solid surface may differ in concentration and temperature substantially\(^{20}\). Froment and Bischoff\(^{15}\) point out that it is especially likely to find large temperature and concentration differences in laboratory reactors which have rather low flow rates through the reactor. When this is the case, heat and mass transfer processes must be considered simultaneously. For large interphase temperature gradients care has to be taken in selecting the mean or film temperatures at which property values such as diffusivity and gas density are evaluated. Thermal convection may also play a strong role in defining the flow conditions around the particle and should be taken into account in calculating both the heat- and mass-transfer coefficients\(^{13}\). External heat and mass transfer rates should therefore always be estimated in order to ascertain what role they play in the observed or measured rates.
3.1.3 Interparticle Gradients

In fixed beds, as in most bench scale reactors, the interaction of the solid particles and the nature of the gas flow through the reactor may lead to interparticle temperature and concentration gradients. These gradients occurring both radially and axially within the reactor as a whole are particularly difficult to evaluate and control. Heat conduction problems due to a low effective thermal conductivity of the entire bed can lead to severe radial gradients in cases where the reaction rate and heat release (or intake) are large and heating is being provided at the reactor wall. Since reaction rates for the most part vary exponentially with temperature, it is critical that the temperature profile inside the reactor be known explicitly. Models to predict the detailed temperature and conversion pattern in a reactor make use of the effective transport concept(14, 15). A radial effective conductivity parameter $\lambda_{er}$ and an axial effective conductivity parameter $\lambda_{ea}$ have been defined by analogy to the mass transfer case:

$$q_r = -\lambda_{er} \frac{\partial T}{\partial r}, \quad q_z = -\lambda_{ea} \frac{\partial T}{\partial z}$$  \hspace{1cm} \text{Equation 3-18}

Owing to the complex heterogeneous system, $\lambda_{ea}$ and $\lambda_{er}$, the effective thermal conductivities, are properties of the bed that depend on a large number of variables such as gas flow rate, particle diameter, porosity, true thermal conductivity of
the gas and of the solid phases and the temperature level. Smith (14) points out that the axial effective thermal conductivity \( \lambda_{ea} \) is negligible in most cases except for very shallow beds and low gas velocities. Smith (14) discusses the use of an expression for estimating \( \lambda_{er} \) in packed beds based on a series mechanism of conduction, convection and radiation for various conditions of pressure, temperature and particle size. However, the correlation suggested has been tested only up to 400°C. In packed beds at moderate temperatures, convection is the predominant mode of heat transfer, however, thermal radiation may become significant at elevated temperatures and low gas flows. For example, radiation becomes important for 1mm particles at temperatures above 400°C and for 0.1mm particles above 1500°C (115). Below 400°C radiation contributes between 10 and 15 percent of the bed conductivity (14). Downing (13) has proposed the following expression for the effective thermal conductivity of a packed bed at high temperatures in the absence of fluid motion (T<700°C).

\[
\lambda_e = \frac{(1-\varepsilon) \lambda_s k*T^3}{\lambda_s + k*T} + k*T^3 \varepsilon
\]

Equation 3-19

where

\[
k* = .69 \varepsilon d_p/10^8
\]

\[
\lambda_s = \text{thermal conductivity of solid}
\]

\[
\varepsilon = \text{emissivity}
\]

\[
\lambda_e = \text{effective thermal diffusivity of entire bed}
\]

\[
\varepsilon = \text{bed void fraction}
\]
Reaction conditions in gasification will usually be at atmospheric pressure or higher and at higher temperatures than those for which the above correlations apply. At temperatures above 700°C the radiation contribution accounts for about 80% of the total thermal conductivity of the bed\(^{115}\). The flow of gas in a reactor increases the effective bed conductivity\(^{19}\). The radial thermal conductivity is generally correlated by an empirical equation of the form

\[
\lambda_{er} = A + B N_{Re} \quad \text{Equation 3-20}
\]

where \(A\) is the bed conductivity under stagnant conditions.

According to Satterfield\(^{19}\), Reynolds numbers in the order of 200 would be required to double the bed conductivity over the value in the absence of fluid motion. Froment and Bischoff\(^{15}\) have further distinguished between the effective thermal conductivity for the fluid phase \(\lambda_{er}^{f}\) and that for the solid phase \(\lambda_{er}^{s}\) in their approach. Although attempts are made to minimize radial temperature gradients, in order to approach isothermal operation, their occurrence is usually inevitable when the heat of reaction is high. Isothermal operation (i.e. the implicit assumption that temperature gradients are minimal) of a bench scale reactor is highly desirable because of the greatly simplified governing mathematical model (no energy balances required for the gas and solid phase).
Concentration gradients in a reactor may be due to flow maldistributions, by-passing, axial dispersion and radial velocity gradients. Concentration differences greatly influence reaction rates and are difficult to predict. The effective transport concept has also been used to describe the nonisotropic effective diffusivity in packed beds. A radial effective diffusion parameter $D_{er}$ and an axial effective diffusion parameter $D_{ea}$ have been defined based on the void volume in the bed and are readily calculated from available correlations\(^{(13)}\). Experimental research has shown that when $L \gg d_p$ and $Pe > 1$ for reasonable fluid velocities ($Re \approx 10$), axial dispersion is unlikely to be significant\(^{(13, 14)}\). However, axial dispersion may be important where the bed is only a few particle diameters deep or when the linear gas velocity is small. Experimental results on radial dispersion are less extensive. Nevertheless for Reynolds numbers above 40, the radial Peclet number is independent of flow rates and approaches 10. The terms in the continuity equation that involve radial gradients are generally small for isothermal operation since the only way that concentration gradients can develop is through variation of the velocity with radial position\(^{(14)}\). Unfortunately, if radial temperature gradients exist then the reaction rate can vary significantly with radial position and large concentration gradients develop. It is in the control of these interparticle gradients that reactor design plays a key role.
An understanding of the relative importance of intraparticle, interphase and interparticle gradients is fundamental to a complete description of data obtained from measurements of the overall rates of reaction in chemical reactors and to the validity of the mathematical models used to describe the reacting system. Failure to account for these gradients when they are significant leads to erroneous and meaningless rate expressions for scale-up or optimization.

3.1.4 Residence Time Distribution

Most of the bench scale reactors used to study chemical kinetics in char gasification are continuous flow reactors through which a fluid stream or solid stream or both are steadily being passed. If the volumetric flow rate of the stream is \( q \) and volume of the reactor is \( V \), then the average or nominal holding time of the material \( (\bar{t}_R) \) in the vessel is given by \( V/q \). However, it is not true that all the elements of matter passing through the system stay in the system for the same length of time; i.e. some elements of the stream may spend a longer period of time than \( \bar{t}_R \) in the system (such as stagnant zones) whereas other elements are retained for a shorter time period (as in the case of bypassing). This distribution or spread of residence times is an important characteristic of the system and may have a profound effect on its performance as a reactor since, when chemical reaction takes place inside a flow reactor, the length of time each
element of reactants spends within the reactor affects the overall conversion (14). An understanding of the mixing processes and the resulting residence-time distribution (RTD) can thus be classified as another essential feature of system design.

Two simple limiting cases, so-called ideal flow patterns are worth mentioning. At one extreme; the flow pattern in the reactor may be regarded as plug flow with no longitudinal mixing but with complete radial mixing. This flow pattern is characterized by an identical velocity and residence time of all the elements of the fluid stream within the reactor. Under these conditions there is no spread of the residence times and the residence time of the stream is a uniquely defined quantity. The other extreme is a completely mixed flow characterized by a well-defined residence time distribution of exponential form and the identical composition of the exit stream and the fluid within the reactor. It follows therefore that for completely mixed systems there is a large spread in the residence time distribution; some elements of the stream spend very little time in the reactor while other elements may be retained for much longer time periods than $\overline{t_R}$. The maximum effect of the residence time distribution (RTD) on conversion is evident from a comparison of plug flow and completely mixed flow in a reactor as shown in Figure 3-1 for first order kinetics ($r=kC$). As an example, when $k\overline{t_R} = 4$, the conversion for the case of complete mixing is 80% while for
Figure 3-1 Effect of mixing (RTD) on conversion for 1st order kinetics
Reference 14, Figure 4-14, p. 178.
the plug flow case it is 98%. The differences would be larger for second order kinetics and smaller for half-order kinetics. For a reactor which followed neither ideal flow, but showed an intermediate RTD, the conversion would be between the two extremes.

While plug flow and completely mixed flow are idealizations, the design of reactors so that the flow pattern approaches either extreme is desirable because of the simplified governing mathematical equations. In general, however, a reactor will not have the characteristics of either of these two limiting cases, i.e., nonidealities or deviations from the ideal flows will exist. These nonidealities can be on two levels: macromixing and micromixing. Residence time distribution is affected by both types of deviations. This implies that measurements of residence time alone cannot determine if the mixing process is on the microscopic or macroscopic scale. RTD concerns only the total period of time the elements have spent in the system rather than with the way the elements distributed their time in the various parts of the reactor. Since systems with differing flow pattern give rise to the same RTD, the RTD analysis should be looked upon only as supporting evidence on the validity of a reactor flow model.

3.1.5 Additional Features

In the previous two sections, the essential features of reactor design were discussed. In addition to these, practical
requirements dictate several desirable characteristics for bench-scale reactors. In any study of gas-solids reaction kinetics it is desirable to have a reactor system for which product sampling and analysis is simple and quick. Where small changes in gas composition must be observed (as for differential conversions) accurate analytical techniques are a necessity. A wide range of reactor operating conditions (e.g. gas flow rates, reactant composition, amount of solids, temperature, pressure) should be possible since the rate-determining step must be determined from the effects of changes in these conditions. Gas-solid reactors should also be designed with the object of facilitating the data analysis (i.e., by reviewing the design equations for the system). Finally, it is also preferable to keep the cost and difficulty of construction of these laboratory reactors low. These additional desirable features can greatly facilitate the investigator's work.

3.1.6 Summary

The desirable and essential features of reaction system design are summarized in Table 3-4. Although these features are generally common to any system for determining chemical reaction kinetics the inherent characteristics of char gasification reactions (i.e. high heats of reaction 50kcal/mol, severe operating temperatures ~ 1000°C, unsteady state nature of system) makes the realization of these features
TABLE 3-4

ESSENTIAL AND DESIRABLE FEATURES OF SYSTEM DESIGN

ESSENTIAL FEATURES

- Controlled intraparticle, interphase, interparticle
temperature and concentration gradients
- Well defined reaction temperature
- Well defined residence time distribution

DESIRABLE FEATURES

- Easy and quick product sampling and analysis
- Flexible operation
- Simple data analysis
- Low cost and simple construction and operation
particularly challenging. In the next three sections of this chapter analytical and experimental tests which can be applied to examine whether the essential design features have been achieved will be reviewed.

3.2 Analytical Criteria for System Design

Chemical reactor design must be based on four processes: chemical reaction kinetics and the transfer of mass, heat and momentum. These effects however should be studied independently in order to minimize the dependence of the data on the type and size of bench or pilot scale equipment. Physical effects in chemical reactors whether laboratory or pilot scale are often difficult to separate from the chemical rate processes. Therefore, prior to or in the early phases of a detailed kinetic study of a gas-solid reaction, certain preliminary tests should be carried out to establish whether the transfer processes are affecting the reaction to an appreciable extent. There are two ways of determining whether intraparticle, interphase or interparticle gradients are causing significant effects, first by experimentation and second by calculation. In this section, analytical criteria (developed mostly in the study of catalytic gas-solid reactions) to estimate the magnitude of these effects will be discussed. These criteria have been well reviewed by others\(^\text{21, 22, 19}\) and so only a few of the most common and useful tests will be described herein. It should be stressed
that care should be exercised in using the criteria in gasification since many of the physical properties of the char undergoing reaction are changing with time (extent of reaction) and the criteria were developed for the steady state case (unchanging catalyst surface and properties).

3.2.1 Testing for Intraparticle Gradients

The classical test for determining whether concentration gradients exist within an isothermal solid particle consists in evaluating the ratio of the observed reaction rate to the rate if pore resistance controls.

\[ \zeta = \frac{r_{v,\text{obs}} L^2}{D_{\text{eff}} C_s^S} \]  \hspace{1cm} \text{Equation 3-21}

where \( r_{v,\text{obs}} \) = observed reaction rate per unit particle volume

\( C_s^S \) = concentration of reactant at outer surface of solid particle

\( D_{\text{eff}} \) = effective diffusivity in a porous particle

\( L \) = ratio of particle volume to external particle surface area

The smaller the value of \( \zeta \), the smaller the concentration gradient throughout the solid particle. For an irreversible reaction of a single reactant whose kinetics can be represented by a power-law relationship \( -r_{v,\text{obs}} = k (C_s^S)^\eta \), the effectiveness factor approaches unity \( (\eta = 1 \pm 0.05) \) if
\[ \zeta < 6 \quad n=0 \\
\zeta < 1 \quad n=1 \\
\zeta < 0.3 \quad n=2 \\
\zeta < 1/n \]

and \( n \) is the reaction order. If the inequalities are satisfied then there are no pore diffusion limitations.

A diagnostic test for determining whether thermal gradients exist inside a solid particle has been derived by Mears\(^{(21)}\) based on heat transfer by conduction inside the solid particle. This test is presented below:

\[
\frac{|\Delta H_r| (r_{V, \text{obs}})^2}{\lambda_{\text{eff}} T_s^S} < \left( \frac{T_s^S}{E_a} \right) = \frac{1}{Y} \quad \text{Equation 3-22}
\]

where \( \Delta H_r \) = heat of chemical reaction

\( \lambda_{\text{eff}} \) = effective thermal conductivity of porous particle

\( T_s^S \) = absolute temperature at surface of particle

\( E_a \) = intrinsic activation energy for chemical reaction

\( R \) = universal gas constant

When the inequality is satisfied the observed reaction rate does not differ by more than 5\% of the isothermal reaction rate (reaction rate that would be observed if the particle had a uniform temperature profile) regardless of possible diffusion limitations.
The magnitude of the temperature difference inside a particle (without further complications of external mass and heat transfer resistances) was originally derived by Damköhler. The derivation based on simultaneous solution of heat and mass balances for a particle of any geometry can be found in References 14 and 15. The temperature difference is given by:

\[ T_s - T_s^S = \frac{D_{\text{eff}} (C_s^S - C_s^r) (\Delta H_r)}{\lambda_{\text{eff}}} \]  

Equation 5-23

where \( T_s \) = absolute temperature at centre of porous particle

\( C_s^r \) = concentration of reactant at centre of porous particle

It can be seen that the maximum gradient, \( \Delta T_{\text{MAX}} \), occurs for complete reaction, \( C_s^r = 0 \), so that

\[ \frac{T_s^S - T_s}{T_s^S} = \frac{(-\Delta H_r)D_{\text{eff}} C_s^S}{\lambda_{\text{eff}} T_s} = \beta \]  

Equation 5-24

This result holds for a particle of any geometry under steady-state conditions. The temperature gradient is therefore dependent on the heat of reaction, the transport properties of the particle, and the surface concentration of reactant. The so-called heat of reaction parameter \( \beta \) gives a simple method for estimating whether intrapellet temperature differences are significant.
For the absence of the combined effect of temperature and concentration gradients within the particle (i.e. $n \pm 1 \pm 0.05$) and power law kinetics, Mears has proposed the following criteria which applies for both endothermic and exothermic reactions:

$$\zeta < \frac{1}{|n-\gamma\beta|} \quad (n \neq 0)$$  

Equation 3-25

In this criteria, the range of the Arrhenius number $\gamma$ is from 10 to 40 while the range of the heat of reaction parameter $\beta$ is -0.1 to 0.1 [for catalysts].

The intraparticle effects are not influenced by reactor type but rather by the kinetics and the physical structure of the solid. Hence, this check should be carried out regardless of the experimental set-up.

3.2.2 Testing for Interphase Gradients

Since the external surface gas concentration is not necessarily equal to the bulk fluid phase concentration surrounding the solid particle, the effects of a concentration gradient in the film must also be assessed. To determine whether interphase concentration gradients are significant under isothermal conditions, Levenspiel\(^{23}\) has suggested looking at the ratio of the observed reaction rate (for reactions other than first order) to the rate if film resistance were controlling:
\[ \omega = \frac{(r_{v,obs}) \ L}{k_g \ C_b} \leq \frac{0.05}{n} \ \ \text{Equation 3-26} \]

where \( k_g \) = mass transfer coefficient between fluid and particle
\( C_b \) = concentration of reactant in bulk fluid

When the inequality is satisfied there are no film resistance limitations.

A criterion for detecting the onset of interphase temperature gradients has been proposed by Mears. If the observed rate is to deviate less than five percent from the true chemical rate (negligible diffusion resistance) the criterion requires that:

\[ \chi = \frac{(r_{v,obs}) \ |\Delta H| \ L}{h \ \ T_b} < \frac{0.05 \ R \ T_b}{E_a} \ \ \text{Equation 3-27} \]

where \( h \) = heat transfer coefficient between fluid and particle
\( T_b \) = bulk fluid absolute temperature

The inequality shows that interphase heat transport limitations can be expected when reaction heats and rates are high and flow rates low (corresponding to low convective heat transfer coefficients).
A simple estimate of the magnitude of the temperature difference in terms of the concentration gradient has been derived by Smith (14) by performing an energy balance on the solid particle at steady state:

\[
T_s^S - T_S = k_g |\Delta H_p| (C_S - C_S^S) \frac{1}{h} \quad \text{Equation 3-28}
\]

It must be mentioned that the heat transfer coefficient, \( h \), must include a convective term as well as a radiative term (radiation from the reactor wall, from other particles, between neighboring voids, etc.) when operating at temperatures above say 400°C. Mears (21) points out that temperature gradients become the source of deviation from ideality \((n - 1)\) long before concentration gradients do so. Also, when the Biot number (defined as \( h d_p/\lambda_{\text{eff}} \)), which expresses the ratio of thermal resistance of the particle to that of the film, is less than 10 (a condition usually met in bench scale reactors because of low flow rates) interphase resistance becomes limiting before intraparticle resistance.

Mears (21) has also derived a criterion using the perturbation approach for determining whether the combined intraparticle-interphase effects significantly affect the chemical rate. The criterion makes use of the Arrhenius number \( \gamma \), the heat of reaction parameter \( \beta \), the ratios \( \chi \), \( \omega \) and the reaction order in power law kinetics:

\[
\frac{(r_{v, \text{obs}}) L^2}{D_{\text{eff}} C_b} < \frac{1 + 0.33 \gamma \chi}{|1 - \gamma \beta_{\gamma} (1 + 0.33 \omega)|} \quad \text{Equation 3-29}
\]
where $\gamma_b$ and $\beta_b$ are both evaluated at bulk fluid rather than at the surface conditions. Satterfield\textsuperscript{(19)} has however indicated that criteria which treat two- or more gradients simultaneously usually require that the values of several parameters be known with a degree of precision that is seldom available thereby limiting their scope. A prior calculation of the possible effects of both interphase temperature and concentration gradients should be carried out whenever possible.

3.2.5 Testing for Interparticle Gradients

Interparticle heat and mass transfer effects are manifest by radial and axial temperature and concentration gradients in the reactor as a whole. Heat conduction problems due to low effective thermal conductivity of the solid bed can lead to severe radial temperature gradients especially where the reaction rate and heat of reaction are large. Other factors such as bypassing, axial dispersion and heat transfer resistance at the reactor wall also complicate the problem. It is in this domain more so than in the previous ones that reactor design is critical. Extensive studies have been conducted to determine diffusional and thermal effects in the tubular fixed bed reactor. For this reason, much of the discussion and tests which follow are based on the findings on integral packed bed reactors.
Analysis of integral tubular reactors is usually based on plug flow of the fluid through the reactor. Deviations from plug flow may be caused by several effects. The void fraction of a packed bed next to the wall is higher than at the centre\(^{(24)}\). Because of the lower resistance at the wall, the linear velocity next to the wall is greater. This contribution of wall flow to the total flow may be significant for low radial aspect ratios \(R_o/R_p\), reactor radius/particle radius) for example, 10 or less. At low Reynolds numbers molecular diffusion may cause significant axial dispersion. In general, it has been assumed that axial dispersion and axial heat conduction are negligible (ensuring plug flow) whenever the axial aspect ratio \((L'/d_p\), reactor length/particle diameter) is large, say above 30. Comparison of the actual and plug flow conversions for a first order reaction in a steady state flow reactor yields\(^{(15)}\):

\[
\frac{k\bar{E}_R}{(k\bar{E}_R)_{PF}} = 1 + \frac{k \bar{E}_R}{Pe_a} = 1 + Pe_a \frac{1}{\bar{E}_R} \ln \left( \frac{C_{AO}}{C_A} \right) \quad \text{Equation 4-30}
\]

This result shows that for a given plug flow conversion level, the reactor with axial dispersion will produce essentially the same results for large \(Pe_a\) \((Pe_a \rightarrow \infty)\). For a given type of reactor, the axial dispersion coefficient is usually correlated using a characteristic local length, \(\bar{E}_R\), (tube diameter, packing size, etc.) then
\[ Pe_a = \frac{\bar{V} L'}{D_a} = \frac{\bar{V} \varepsilon L'}{D_a} = Pe_{\varepsilon,a} \left( \frac{L'}{\varepsilon} \right) \] Equation 3-31

where \( Pe_{\varepsilon,a} \) is the local Peclet number for mass dispersion. Mears\(^2\) has combined these findings to provide a formal criterion to determine whether the reactor length is sufficient to minimize axial dispersion effects for \( n \)th order power law kinetics:

\[ \frac{L'}{\varepsilon} > \frac{1}{e} \frac{n}{Pe_{\varepsilon,a}} \ln \frac{C_i}{C_f} = \frac{1}{e} k_b \frac{t_R}{Pe_{\varepsilon,a}} \] Equation 3-32

where \( L' \) = reactor bed length
\( k_b \) = apparent rate constant per unit bulk particle volume \( (k_b = k (1-\varepsilon) n) \)
\( t_R \) = space time
\( C_i, C_f \) = initial and effluent concentration of reactant
\( \bar{V} \) = superficial linear velocity
\( n \) = integer exponent in power law expression
\( D_a \) = axial eddy diffusivity
\( e \) = allowable error

An allowable error of say five percent is usually the case for industrial reactors of the simple empty tube or packed bed types. This expression may not be true for laboratory studies especially in differential reactors or for reactors with more complicated flows leading to large characteristic dispersion lengths.\(^\text{15} \)
Radial heat transfer effects and to a lesser degree radial mass transfer effects are usually more serious than the axial conduction problem. In order to spread the heat release (in the case of an exothermic reaction) more uniformly and avoid 'hot spots', a technique by which the solid is diluted with inert material with dilution ratios decreasing with bed length has often been applied. Since dilution in large quantities introduces the hazard of bypassing, a check provided below should be performed to ascertain that this problem has been avoided:

\[
\frac{L'}{d_p} > 250 \frac{b}{\Delta}
\]

Equation 3-33

where \( b \) = dilution ratio
\( \Delta \) = relative experimental error in conversion

Another technique which has been used to reduce radial temperature gradients is to decrease the reactor diameter and thus the radial aspect ratio. However, as this ratio is decreased, the contribution of heat transfer at the inside reactor wall becomes increasingly more serious. Mears has developed the following criterion for the observed reaction rate not to deviate more than 5% from the isothermal case, assuming plug flow and assuming that there are no concentration or temperature gradients inside particles or between particles and bulk fluid, and based on a lumped parameter model for the effective thermal conductivity of the entire bed.
\[
\frac{\Delta H_r}{\lambda_e T_w} \frac{r_b R_o^2}{R_o} < 0.4 \frac{RT_w}{\Lambda E_a}
\]

Equation 3-34

where \( \Lambda = 1 \) for \( R_o/R_p > 100 \)

\( \Lambda = 1 + 16 \frac{R_p Bi_h}{R_o} \) for \( R_o/R_p < 100 \)

\[ Bi_h = \frac{h_w R_p}{\lambda_e} \]

\( \varepsilon \) = bed void fraction
\( \lambda_e \) = effective thermal conductivity of entire solid bed
\( T_w \) = absolute temperature of reactor wall
\( R_o \) = reactor radius
\( R_p \) = solid particle radius
\( r_b \) = average reaction rate per unit bed volume
\[ r_b = \frac{(1 - \varepsilon)}{(1 + b)} r_v,obs \]

The lower limit in the radial aspect ratio appears to be about 4 with a further reduction in reactor diameter leading to channelling near the reactor wall.

These interparticle gradients present severe problems. When varying the operating conditions does not succeed in minimizing the concentration and temperature gradients, the use of a distinct reactor type known to alleviate certain problems is advisable.
3.2.4 Summary

The analytical criteria presented are based on estimated values of pore diffusivity, thermal conductivity, axial dispersion, heat- and mass-transfer coefficients, nature of the kinetics and other coefficients. The accuracy with which such criteria can be applied varies widely and is limited by the certainty with which the properties can be obtained. The simple calculation procedures presented provide a method of reaching conclusions when experimentation is impractical. However, because of the possible inaccuracies it is often desirable to evaluate intraparticle, intraphase and interparticle effects experimentally whenever possible for the system under study.

3.3 Experimental Transport Checks

Although the analytical criteria presented in the previous section should be applied whenever possible, proper correlations for heat and mass transfer coefficients, thermal diffusivities and conductivities may not be readily available and the investigator must then resort to experimentation. Key experimental tests will be described in this section to determine whether the temperature and concentration gradients within the particle, in the film surrounding the particle and in the reactor as a whole are significant.
3.3.1 Intraparticle Transport

The classic experimental test for detection of intraparticle effects is to run the reaction using progressively smaller diameter particles. The lack of any dependence of rate of reaction per unit particle volume over an appreciable size range would indicate that intraparticle effects are minimal. However, by varying the particle size over too great a range, distortions in the flow field may be introduced thereby clouding the experimental results. Koros and Novak (25) have devised an alternate test which avoids complications due to distortions in the flow pattern. Their test is valid for first order reactions and is based on the fact that while in the kinetic regime (chemical reaction controlling) the rate of reaction is proportional to the number of sites per unit volume S, in the internal (pore) diffusion regime it is proportional to $S^{1/2}$. The test involves pelletizing mixtures of finely divided solid with an inert powder of comparable inert characteristics. If the fraction of the catalyst in the mixed pellet is $f$, the ratio of the rates must also be equal to $f$ in the kinetic regime.

3.3.2 Interphase Transport

The common experimental test to determine the existence of interphase effects is to check the effect of gas flow rate on the conversion while maintaining constant space velocity ($W/F$). Conversions should be independent of flow rate in the
kinetic regime while conversions should increase with flow rate if film diffusion is controlling. Chambers and Boudart\(^{26}\) have warned however that this test may be insensitive at the low Reynolds numbers (Re < 10) usually encountered in the laboratory. In order for the test to be meaningful a wide range of flow rates must be used and conversions must be measured very precisely. The critical mass velocity (velocity no longer affects the rate) must be determined at the maximum temperature if diffusion resistance is to be negligible at all other temperatures\(^{14}\). It must be noted here that this test is particularly difficult in gasification studies because of the unsteady state nature of the reaction. Both film and pore diffusion are also characterized by low values for pre-exponential factors and activation energies in Arrhenius-type expressions for temperature dependence of rate constants. Such results should motivate a thorough check of the significance of these effects.

3.3.3 Interparticle Transport

There are no simple experimental tests for detection of interparticle or intrareactor gradients. Axial and radial temperature profiles can be detected with a network of thermocouples carefully placed throughout the reactor. However, one must be aware that the measurements obtained are average gas-solid temperatures and not true measurements of the actual temperature of the gas and of the solid. The gas flow
pattern in a reactor must be determined through residence time distribution studies. This will be the subject of the next section.

3.4 Determination of Residence Time Distribution

It is the purpose of this section to briefly outline the techniques of residence-time distribution measurements and modelling. Excellent extensive treatments on this topic can be found by Wei and Fan (27), Levenspiel and Bischoff (28) and Levenspiel (23).

3.4.1 Age Distribution Functions

Age distribution information, originally discussed by Danckwerts, gives a description of the flow pattern inside a vessel and information about the fraction of material that resides a certain time in the vessel. The most widely used age distribution functions are the internal and exit-age distributions. The internal age distribution, \( I \), is a measure of the distribution of ages of elements in the vessel. The exit age distribution \( E \), on the other hand, is a measure of the distribution of ages of all elements of the stream leaving the vessel where age is measured from the time the elements enter the vessel. It has been shown that \( E(t) = -dI/dt \) (26). Age distribution information is useful in several ways. Reactor performance can be predicted with knowledge of the rate
equation and exit age distribution (also referred to as residence time distribution, abbreviated RTD) as stated below:

\[ \overline{C}_A = \int_0^\infty C_A(\Theta) E(\Theta) \, d\Theta \]

where \( \overline{C}_A \) is the mean concentration of reactant leaving the reactor unreacted and the concentration in an element \( C_A(\Theta) \) depends on the residence time of the element according to

\[ -\frac{dC_A}{d\Theta} = r_A(C_A(\Theta)) \]

with \( C_A|_{\Theta=0} = C_{A0} \), the feed concentration.

For linear systems the RTD leads to reactor design equations. For non-linear systems, age distribution information helps in selecting a suitable model which can give upper or lower limits on reactor performance. Age distribution also helps in detecting severe reactor shortcomings and problems such as short-circuiting, deadspace and non-uniform regions. The internal and exit age distributions for the idealizations of plug flow and complete mixing are given in Figures 3-2 and 3-3. Deviations of actual RTD from one of these two idealized flow patterns can often be detected by visual inspection of these curves as shown in Figure 3-4 in the case of dead space and in Figure 3-5 in the case of bypassing. Dead space or stagnant regions in the vessel can easily be seen from the \( E \) curve since for an ideal flow pattern the mean of \( E \) is at \( \Theta = 1 \).
Figure 3-2  Internal (---a---) and Exit (----b----) Age Distribution for Plug Flow Reactor
Figure 3-3 Internal and exit age distributions for backmix reactor

\[ I(\theta) \]

\[ \theta = t/\tau_R \]

\[ E(\theta) \]

\[ \theta = t/\tau_R \]
Figure 3-4  Diagnosing dead space from an exit age distribution
Figure 3-5 Diagnosing fluid by-passing from an internal age distribution
while stagnant zones move the mean to the left because of long tails in the distribution (corresponding to fluid held in the dead space which is extremely slow moving). Similarly fluid bypassing can be detected easily by the steps in an I-curve.

Both the internal and exit age distribution functions can be deduced experimentally from stimulus response techniques. These techniques have been used widely to derive age distribution functions. As illustrated below the tracer input signal (stimulus) may take on many forms. The advantages and disadvantages of several input tracer signals are listed in Table 3-5. The two most extensively studied are the pulse and step signals.

![Diagram of Tracer Input and Output Signals]

Exponentially the F curve can be obtained from the response at the exit of the system to a step change in tracerable quantity such as the concentrations of radioactive tracer or salt. Any tracer used in these experiments should be completely inert towards the system and should not alter the hydrodynamic flow characteristics being studied. When solids are present in the reactor, absorption or desorption of the tracer compound must
## Table 3-5

### Evaluation of Tracer Input Signals

<table>
<thead>
<tr>
<th>Tracer Signal</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impulse</td>
<td>- Output directly impulse response</td>
<td>- Difficult to experimentally generate</td>
</tr>
<tr>
<td></td>
<td>- Simplest model response</td>
<td>- 'Perfect impulse input'</td>
</tr>
<tr>
<td></td>
<td>- Brief disturbance in process</td>
<td></td>
</tr>
<tr>
<td>Step</td>
<td>- Simple to generate</td>
<td>- Long time of input stimulation required</td>
</tr>
<tr>
<td></td>
<td>- Output simply related to impulse response</td>
<td>- to achieve final 'lined out' response</td>
</tr>
<tr>
<td>Sinusoidal</td>
<td>- Only measurements of amplitude ratio and phase lag of output are required</td>
<td>- Relatively complex to experimentally generate a sine wave</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Long process disturbance since initial transients must die out to achieve stationary response</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Frequencies must be chosen in an optimum way</td>
</tr>
<tr>
<td>Random</td>
<td>- Lack of a need to generate any perfect specific input signal</td>
<td>- Two signals must be measured</td>
</tr>
<tr>
<td></td>
<td>- Results related to general convolution properties of system</td>
<td>- Deconvolution not always easy to perform numerically</td>
</tr>
</tbody>
</table>
not occur. An alternative approach used in gas phase studies is, if at a certain specified time \( t \), the feed to the system is switched from one supply to another which has the same physical properties (e.g. density and viscosity) and the same flow rate before and after the switch, the concentration of the second fluid in the exit stream \( C \) may be observed as a function of time. A true tracer should give the same internal age distribution regardless of whether a + or - step input is made. The dimensionless concentration response \( C/C_0 \), which results is termed the F curve leads directly to the internal age distribution as follows:

\[
I(\theta) = 1 - F(\theta)
\]

The response at the exit of the system to an instantaneous pulse tracer input yields the so called C-curve. This curve directly translates to the Exit Age distribution or RTD.

\[
E(\theta) = C(\theta) = \frac{d F(\theta)}{d \theta}
\]

The response to both a step tracer input (F-curve) and an impulse tracer input (C-curve) for a vessel whose flow pattern is described by one of the ideal flow models is illustrated in Figure 3-6 and Figure 3-7.

The Internal and Exit age distribution functions may be used as supporting evidence to check the validity of the
Figure 3-6  Step responses for a) plug flow and b) complete mixing
Figure 3-7 Pulse responses for a) plug flow and b) complete mixing.
proposed flow model for a vessel. However, simulating the age
distribution of the proposed model over the spread of the
entire distribution using experimental data is difficult. The
approach taken has in general been to compare the moments of
the distributions. In order to completely characterize an
arbitrary distribution function all moments are required,
however, for practical purposes it has been deemed sufficient
to use the first three moments in the tracer analysis. These
moments are described in Table 3-6.

The basic probability distribution curves which have been
used to represent the experimental age distribution function
are the normal, the Poisson, the Gamma, and the binomial
distribution functions. When the experimental data cannot be
approximated by one of the above distribution functions, the
age distribution curves are not directly useful since a
correlation of age distribution curves for various types of
equipment is not available and cannot readily be achieved. For
this reason, mathematical models such as the dispersion models,
combined models, and compartment models have been devised which
contain parameters that can be correlated for various flow
conditions and equipment geometries. These mathematical models
are discussed in the next section.

3.4.2 Mathematical Models for Homogeneous & Pseudo-Homogeneous Systems

Mathematical models have been formulated with varying
degrees of complexity in order to describe non-ideal flows.
### TABLE 3-6

Moments of Probability Distribution Functions

<table>
<thead>
<tr>
<th>Moment</th>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>μ</td>
<td>Mean (centre of gravity of distribution about origin)</td>
</tr>
<tr>
<td>2</td>
<td>σ²</td>
<td>Variance (spread of distribution curve)</td>
</tr>
<tr>
<td>3</td>
<td>γ³</td>
<td>Skewness</td>
</tr>
</tbody>
</table>
There are several types of models that have found useful applications. Velocity profile or convective models are applicable to reactors of simple geometry in which the laminar flows of reacting mixtures are predominant. The information necessary to describe velocity profiles in a reactor is usually not available for complex reactors. For description of flow behavior in a real reactor one must rely on a model which contains empirical parameters and approximates the actual behavior closely. These parameters are then correlated as functions of fluid and flow properties, reactor configuration and other important features.

For relatively small deviations from ideality, one and two parameter models such as the axial dispersion model and the tanks-in-series or mixing-cell model are often used in describing the flow. This is often the case for tubular reactors and single phase flow in packed beds. The dispersion model in which the diffusion is superimposed on plug flow has been used for both homogeneous and heterogeneous systems in which axial symmetry can be assumed and in which the flow behavior is not far from that of plug flow. The mass balance for the one dimensional axial dispersion model is

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial z} = \frac{\partial}{\partial z} \left[ D_a \frac{\partial C}{\partial z} \right] + r(C) \quad \text{Equation 3-35}$$

where $U$ = mean plug flow velocity through vessel,

$D_a$ = mixing dispersion coefficient
and the parameter $D_a$ is found from experiments. One common approach to determining the parameter $D_a$ is to perform a residence time distribution test on the reactor and choose the value of $D_a$ so that the model solution and experimental output curve agree. The axial dispersion model can represent plug flow behavior when $D_a \to 0$.

Besides the dispersion model, the tanks-in-series model is the other model widely used to represent non-ideal flow. Here one assumes the fluid flows through a series of equal size ideal stirred tanks, and the parameters of the model are the number of tanks in the chain and the residence time in a single tank. For $N$-tanks in series the exit age distribution can be described by

$$E(\theta) = \frac{N^N}{(N-1)!} \theta^{N-1} \exp(-N\theta) \quad \text{Equation 3-36}$$

$$\theta = \frac{t}{-N\bar{t}_1}$$

$$\bar{t}_1 = \text{mean residence time in 1 tank}$$

The model parameter $N$, need not strictly be an integer for curve-fitting purposes. Plug flow is approached as $N \to \infty$. In many ways the dispersion model and the tanks in series model are similar and the two models are often used interchangeably.
Where there is no symmetry of flow pattern and relatively large mixing problems exist (such as channelling, dead space, bypassing) as encountered in real stirred tank reactors and fluidized beds whose flow patterns are closer to the complete mixing case, many different models with as many as six parameters have been proposed to describe the macromixing. Combined models were first suggested by Cholette and Cloutier (110) as early as 1953 to handle a real stirred tank flow. These models view the reactor as consisting of interconnected flow regions (plug, backmix, dispersed and stagnant flow) with various modes of flow (by-pass, recycle and cross flow) between and around the flow regions. The pattern generated by the various combinations of these elements can be used to fit a large variety of flow through different vessel geometries. Using these components, the problem then reduces to finding the volumes of the various regions and the rate of each type of flow occurring such that the response curves of the model match as closely as possible the response curves for the real vessel. The number of parameters used in a model is an indication of its flexibility in fitting a wide variety of situations and in addition suggests the complexity of the accompanying mathematics. In fitting a real reactor, one should aim for the simplest model which fits the response curves and whose various regions are suggested by the actual flow patterns and reactor geometries.

Cholette and Cloutier (110) concluded by matching experimental data (F-curve) for their stirred tank with a
number of alternative models that a model consisting of complete backmixing with short circuiting and dead space represented the real vessel adequately. Their two-parameter model \( (n, m) \) is shown below:

![Diagram](image)

Several internal and exit age distribution curves of non-reacting systems for specific combined models are presented by Levenspiel and Bischoff\(^{(28)}\). Wen and Fan\(^{(27)}\) present several combined models for an irreversible first order reacting system and their dynamic responses to a host of input tracer signals (ramp, pulse, step).

In addition to the combined models discussed, circulation models have been used to describe complex systems. Circulation models have been proposed mostly to describe fluid mixing in homogeneous stirred tanks. The basis is a region of intense shear and mixing around the impeller followed by recirculating flows around the rest of the tank. Weber et. al\(^*\) proposed a circulation model which consists of a portion of the fluid recirculating the vessel; this portion of the fluid comprises \( m \) passes of plug flow. Van de Vusse\(^*\) proposed another type

\(^*\) as discussed in Wen and Fan\(^{(27)}\)
of circulation model in which there are three main loops circulating in a tank: one receives feed stream, another delivers to the outflow stream, and all other loops combined together to form the third loop as shown in Figure 3-8. This results in a highly complicated model form. These models are unfortunately almost always complex and have a large number of parameters to be estimated.

All of the models presented thus far are essentially homogeneous models. Although many of these mixing models have frequently been applied to heterogeneous reactors such as packed beds and fluidized beds with some success, a gross approximation must be made to do so. It is assumed that the mass exchange between different phases is negligible and a homogeneous model can be applied to each phase separately. Alternatively it is assumed that the whole reactor consists of a homogeneous mixture. When these approximations cannot be made reasonably (often true of fluidized beds) heterogeneous models must be applied to the system.

3.4.3 Mathematical Models for Heterogeneous Systems

Ever since the fluidized bed technique was first applied to the making of synthesis gas from coal by the Winkler generator, fluidized beds have remained popular. However owing to the complex gas flow and solid particle movement within the fluidized bed, and other reactor types (e.g. spouted beds),
Figure 3-8 Physical Diagram (a) and Block Diagram (b) for a Circulation Model (adapted from Reference 27)
quite complex heterogeneous flow models have been applied to describe the system. Two phase models, residence time distribution models, bubbling bed models have all been used to some extent to describe flow behavior. It is beyond the scope of this short discussion to elaborate on these models. The reader is referred instead to the excellent summary by Wen and Fan(27) on heterogeneous models.

3.4.4 Mathematical Model Parameter Estimation

With multiparameter flow models, the accurate estimation of the parameters is not a simple task. There are various techniques that have been used for the actual parameter estimation, among which are direct non-linear regression in the time domain, comparison of time moments of the data and of the model, and fitting of data in the Laplace transform space. Some good reference material has been suggested by Bishoff and Froment(15).

Direct non-linear regression in the time domain is the most straightforward in principle since one is comparing the actual data with the model response. Also, the least squares, maximum likelihood, or other criterion is minimizing errors directly with the data. The primary disadvantage of this method is that the time-domain solution of the model must be available. The alternative of repetitive numerical solutions during an extensive parameter search routine can involve very
large amounts of computer time. Also, it has been shown\(^{30}\) that the objective functions often have local in addition to global minima and/or long ridges because of correlation between the parameters---both of these cause difficulties.

The second technique is that of using time moments of the data to be compared with those of the model. The advantages are that they can be easily computed by numerical integration of the data and the integrations tend to somewhat smooth the data. Also, the moments can be readily found from the Laplace transform of the model without the necessity of a time domain solution. The main disadvantage is that the moments tend to emphasize the data for large values of time, and this data in the tail of the curve is usually not very accurate (because of low tracer concentrations). To decrease the importance of the tail, the moments can be defined with a weighting factor \(e^{-st}\). With or without this modification, it is often difficult to decide just where to truncate the tail of the data curve. Finally, the results must be checked in a time-domain solution to ascertain that the model with moment evaluated parameters fits the actual data.

The last technique uses fitting (e.g. least squares) in the Laplace transform space since the Laplace Transform space solution for the model is easily obtained. This method necessitates numerical transformation of the time domain data.
which is a serious drawback. The transformation can be carried out in the S domain or the frequency domain, \( \omega \). As for the previous method, the final results should be checked in the time domain since the fit obtained in the S-domain does not guarantee the best in the least squares sense in the time domain. This is not a necessary step in the \( \omega \)-domain but the complicated expressions for the model in the frequency domain are quite discouraging\(^{50, 51}\).

Numerical comparisons of the various methods have shown that the use of moments is the least accurate and sometimes leads to invalid parameter values. Direct fitting in the transform domain usually leads to valid parameter values but they are not always the same as would be found by time domain fitting. The final check is therefore always a comparison of the fit in the time domain. It appears, however, that the information contained in RTD experiments can sometimes only be used to determine a certain (small) number of parameters\(^{30}\). Unique discrimination will then require different types of experiments such as downstream injection of a tracer with measurements of backmixing. Then a crossplot can indicate which parameters are most sensitive to which type of experiments and how these combinations can be used to define the appropriate parameter combinations.
3.4.5 Summary

This section has demonstrated how the tracer experiment, the age distribution functions and mathematical models with appropriate parameter estimation techniques can be used to determine the flow pattern in a reactor. This task is of no less importance in laboratory reactors used for kinetic investigations. The major principles of experimental reactor design discussed heretofore, will be used to evaluate the bench scale reactors presently being used in gasification kinetic studies.
4 EVALUATION OF REACTOR SYSTEMS

4.1 Systems Reported in the Literature

The purpose of this section is to critically review laboratory reactors and experimental techniques used in the study of gasification kinetics. Major emphasis will be placed on evaluating the merits and limitations of these reactor schemes in view of the design features discussed in Chapter 3. Almost every conceivable gas-solid contacting pattern has been used in char gasification studies. The major types of bench-scale reactors used in studying char gasification kinetics are: the differential tubular fixed bed, the integral tubular fixed bed, the thermogravimetric balance, the fluidized bed and the transport reactor. In addition to these reactors, a number of miscellaneous contact devices (e.g. spouted beds) have been used and deserve brief mention. The reader is referred to Appendix A for a descriptive compilation of many gasification kinetics studies classified according to reactor type employed. This list is by no means exhaustive but it does provide a good sampling of the literature. Each of the major reactor types will be discussed in detail in the subsequent sub-sections of this chapter. Several excellent general reviews on the subject of laboratory reactors can be found in the papers by Weekman(32) and Doraismwamy and Tabji(33) and in the books by Shah(54) and Anderson(35).
4.1.1 The Tubular Fixed Bed Flow Reactor

The bench-scale tubular flow reactor shown schematically in Figure 4-1 has been used extensively in gasification studies because it is simple and relatively cheap to construct. This reactor is also desirable because in some cases it represents a scaled-down version of a large commercial gasifier. In the fixed bed reactor, the solid char is confined in the tubé and the reactant gas flows either upward or downward through the bed. The fixed bed reactor can be operated in a differential or integral mode. The basic difference between the differential and integral reactor is that the reactant conversion in the former is limited to a few percent (usually less than 10 percent). Since this difference significantly alters the interpretation of data the reactors will be discussed individually.

The integral reactor has the inherent advantage that large (finite) conversions are involved so that routine techniques are adequate for gas composition analysis. Determination of the kinetics of a reaction from the data in an integral fixed bed is usually based upon three main assumptions. First, the flow pattern of the gas inside the reactor is assumed to be plug flow (i.e. over any cross-section normal to the gas flow, the mass flow rate and the fluid properties such as pressure, temperature and composition are uniform). Secondly, the reactor is usually assumed to operate isothermally. Finally,
Figure 4-1 Schematic of fixed bed tubular flow reactor
the rates of film and pore diffusion are assumed to be much faster than the rate of chemical reaction. When these assumptions are made, the governing equations for the fixed bed tubular reactor given in Table 2-2 are greatly simplified and are given below:

\[
\begin{align*}
\text{Gas Phase Mass Balance} \\
\frac{\partial c A}{\partial t} &= -U \frac{\partial c A}{\partial z} - \rho_b r_A \\
\text{Solid Phase Mass Balance} \\
\frac{\partial c_s}{\partial t} &= -b' \rho_s r_A
\end{align*}
\]

where

\[
\begin{align*}
r_A &= \text{rate of reaction of component A per unit mass [kmol/kg s hr]} \\
\rho_b &= \text{solid bulk density [kg s /m}_f^3] \\
\rho_s &= \text{density of solid [kg s /m}_f^3] \\
c_s &= \text{molar concentration of reacting component A of gas [kmol/m}_f^3] \\
\epsilon &= \text{void fraction of bed} \\
U &= \text{superficial velocity [m}_f^3/m}_f^2 \text{ hr]} \\
b' &= \text{molar stoichiometric coefficient}
\end{align*}
\]

However, as mentioned in the previous chapter, deviations from any one or all of the three assumptions occur in laboratory studies and the experimental and theoretical checks described earlier should be carried out.
Deviations from plug flow in integral fixed beds can arise in a number of ways from radial temperature gradients (due to heat of reaction and poor heat transfer through the bed) and from various dispersion effects (e.g. local density changes, packing turbulence, etc)(45). In the report by the Institute of Gas Technology(46) on the gas reactions of carbon in an integral fixed bed, it is clearly stated that

"local variations in the fuel bed density and therefore in the distribution of the gas flow resulting in varying degrees of backmixing between reactant and products, varying radial concentration gradients and possible channeling and bypassing of portions of the fuel bed"

may have occurred especially at the high temperatures (1100°C). Nevertheless, no effort was made to ascertain to what extent these effects may have altered the kinetic results. As discussed earlier, the extent of nonideality in gas flow pattern can be identified by carrying out residence time distribution studies. These studies can be carried out in integral beds because the gas-solid contact times are relatively long in order to achieve high conversions. Channeling, often caused by non-uniform solid packing, is a problem which must be contended with in integral beds especially when the solid particles are introduced to the
reactor already at reaction temperature as in the work by Hunt et. al(47).

The major difficulty with the integral fixed bed is the problem of achieving isothermal operation during severely endothermic/exothermic reactions(14). The isothermal assumption for integral beds must be checked carefully. There are numerous examples of large axial temperature differences in bench-scale integral beds. Some examples are given below:

"Three thermocouples were located in a six inch reactor zone, 1/2", 3" and 5 1/2" from the top of the zone. The maximum temperature occurred at the middle thermocouple and was considered the nominal temperature of the reaction. The top and bottom bed temperatures were generally within ±5°C of the maximum temperature." (Haynes et. al(44) 750-950°C)

"Temperature control is less sensitive with this arrangement, nevertheless temperature variations of not more than ±0-50°F could be maintained in the carbon bed." (Hunt et. al(47), 1700-2000°F)

"At temperatures of 1800°F and above, we could not observe any consistent effect of temperature on the rate of gasification. Moreover during these tests at 1800°F and above, stainless steel screens which had been used to support the coal char charges were found to have MELTED, indicating
that very large temperature rises had occurred...sample temperatures could easily rise over 2500°F from a starting value of 2000°F, even with the high gas flow rates and small sample sizes used. (Feldkirchner & Huebler(48)).

The effect of these possible temperature gradients on the reaction rate constant for various temperature deviations and activation energies are shown in Table 4-1 following the analysis presented in Denbigh(45). The magnitude of the ratio of the rate constants emphasizes the biggest concern in fixed bed reactors, achieving isothermality. Besides the obvious examples of this problem quoted above there are many examples in the literature where large differences in both interphase and intraparticle temperature and concentration appear. For instance when a simple calculation using the criterion (Equation 3-27) presented in Section 3.2.2 is carried out for the kinetic results described by Feldkirchner and Huebler(48) for steam gasification of bituminous char at a temperature of 1200K and 50 SCF/hr steam flow rate in an integral packed bed, one finds that as much as a 30°C temperature difference may exist between the gas film and the solid char surface (see Appendix B for details). Dilution of reacting solids with inert solids has been used to minimize the problem of hot spots in hydrogasification studies in integral beds. Feldkirchner and Huebler(48) used a ratio of 12 to 1 inert alumina particles to char throughout the bed to act as a heat sink with very limited success. Unfortunately, no tests
TABLE 4-1

The Effect of Temperature Deviations on Reaction Rate Constants

<table>
<thead>
<tr>
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<tbody>
<tr>
<td></td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>800</td>
<td>1.2*</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>1.60</td>
<td>2.5</td>
</tr>
<tr>
<td>900</td>
<td>1.16</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>1.44</td>
<td>2.1</td>
</tr>
<tr>
<td>1000</td>
<td>1.13</td>
<td>1.27</td>
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<tr>
<td></td>
<td>1.35</td>
<td>1.80</td>
</tr>
<tr>
<td>1500</td>
<td>1.05</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>1.14</td>
<td>1.30</td>
</tr>
</tbody>
</table>

* $\frac{k_{T_1}}{k_{T_2}} = \frac{\exp(-E_a/RT_1)}{\exp(-E_a/RT_2)} = \exp\left[\frac{E_a \Delta T}{R T_1 T_2}\right]$
were carried out to determine whether flow problems such as bypassing and channeling occurred as a result of the high dilution ratio. Although radial temperature gradients may also exist in integral fixed beds\(^{(14)}\) (although to a lesser extent), they have rarely been looked at by workers studying gasification kinetics.

The third assumption in integral reactor data analysis, that of insignificant pore and film diffusion resistance, is not usually as troublesome as the nonisothermal behavior of the bed. The reason is that gas velocities and particle sizes can be varied substantially. However, increases in the gas velocity (e.g. to increase external mass transfer rates) and decreases in the particle size (e.g. to increase pore diffusion rates) can lead to substantial bed pressure drops. To account for the variation in pressure along the length of the reactor, a momentum balance must be introduced to describe the system. There is some evidence in the literature that mass transfer and pore diffusion effects\(^{(51)}\) which are significant have been neglected when interpreting rate data. Wicke\(^{(51)}\) has made a significant contribution in his approach\(^{(57)}\) to isolate transfer effects from chemical reaction data. He describes experiments in which the experimental conditions can be arranged easily to measure on the one hand the true activation energy (i.e. with no diffusional resistance) and on the other hand with the full effect of diffusion. His results for the study of the Boudouard reaction are given in Table 4-2. It may be seen that
### Table 4-2

**Observed Activation Energies for Boudouard Reaction**

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>Nicke(^{(51)}) (full diffusion) ((no\ resistance))</td>
<td>43 ± 1.5</td>
<td>850 - 1000</td>
<td>electrode carbon and charcoal</td>
</tr>
<tr>
<td>Blakeley(^{(53)})</td>
<td>84 ± 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mayers(^{(42)})</td>
<td>50 - 70</td>
<td>950 - 1100</td>
<td>coke</td>
</tr>
<tr>
<td>Taylor and Bowman(^{(54)})</td>
<td>52</td>
<td>850 - 1150</td>
<td>graphite</td>
</tr>
<tr>
<td>Smith and Tyler(^{(5)})</td>
<td>48.5</td>
<td>750 - 900</td>
<td>coke</td>
</tr>
<tr>
<td></td>
<td>57</td>
<td>750 - 900</td>
<td>test electrode</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>750 - 900</td>
<td>graphite</td>
</tr>
</tbody>
</table>
the activation energy for the diffusion limited case is half of the true activation energy as expected. Activation energies reported by other experimenters at similar temperature levels are included for comparison. Values of $E_a$ for very similar materials are found to vary greatly although they all lie within the extremes reported by Wicke. These intermediate values indicate that possible diffusion limitations exist.

To summarize briefly, the integral tubular fixed bed flow reactor offers the following advantages:
- simple construction and operation
- flexible operating ranges
- long residence times for RTD determination

However, these advantages are often outweighed by the following limitations:
- difficulty in achieving isothermality
- complexity of the model form when nonidealities in flow prevail
- large pressure drops complicate data analysis

4.1.2 The Differential Tubular Fixed Bed Flow Reactor

The differential tubular reactor, unlike its counterpart, requires a small quantity of solid and operating conditions are such that the gas conversion is kept low ($<10\%$).
Interpretation of kinetic data from differential reactors is based on three main assumptions. First, because of the low gas conversions, the gas composition in the bed is assumed to be the average composition of the gas at the inlet and exit of the reactor. The change in composition between the inlet and exit streams must be large enough for precise measurement, otherwise the rate of conversion in the reactor cannot be accurately established. This restriction imposes a limitation on the applicability of the method. A material balance for the reactant gas over the differential bed yields a point reaction rate directly (equivalent to the rate in an integral bed at a position where the partial pressures of the reaction components are equal to those of the differential reactor) which is highly advantageous. If precise analytical methods of determining small composition changes are not available however, for the particular reaction, a close approach to a point value of the rate cannot be ascertained. In gasification studies, the analysis of gases such as $O_2$, $H_2$, $CH_4$, $CO_2$ and $CO$ in low concentrations is required. Of these, accurate quantitative analysis of $H_2$ in the gas mixture is perhaps the most difficult to obtain (37).

The second assumption is that as a result of the high gas flow rates (short residence times) which are necessary to limit conversions, external mass transfer rates are fast enough to prevent significant interphase concentration gradients. In the study by Tyler and Smith (5) on the reactivity of coke to carbon dioxide, it was shown that operating conditions could be
attained to approach differential fixed bed behavior. These workers found through both experimentation and calculation that they could operate in a chemical reaction control region (i.e., rates of external mass transfer and pore diffusion were very fast). In view of the very short residence times inside the differential reactor, residence time distribution studies are difficult to carry out. With differential reactors however, nonideal flow does not present a serious problem because at low conversions, the effect of a distribution of residence times is small.*

The third assumption is that the reactor operates isothermally since low conversions lead to small overall heat effects. There are few examples in the gasification literature that show this assumption is being verified. Blackwood and McGrory (52) studied the carbon-steam reaction between 100 and 5000 kPa and 750-850°C using a differential fixed bed (17.6 cm³ volume). The clear silica tube reactor, the thermocouple arrangement and the bed characteristics are shown in Figure 4-2. By adopting a space velocity of 2s⁻¹ the authors were able to achieve steam decompositions of less than six percent so that the conditions approximate those of a differential reactor. In order to check for isothermality, nitrogen was allowed to flow through the bed at space velocities up to 4s⁻¹ at a nominal temperature of 830°C.

* The reader is referred to Figure 3-1 where it can be seen that the effect of mixing at low conversions for 1st order kinetics is negligible.
Figure 4-2  Differential reactor used by Blackwood and McGrory (52)
They observed no significant variations in temperature in the central sheath, in the annular bed and at the wall. However, when steam was passed through the bed and subsequently reaction occurred, the temperature at the centre of the annulus rose above that of the wall and the central sheath by about 5 to 7°C at a space velocity of 2 s⁻¹. Kayembe and Pulsifer(36) studied the steam-char reaction at similar temperature levels using a differential packed bed and found 5 to 7°C temperature variations in the length of the solid bed. It appears, that even with conversions in the order of ten percent, achieving isothermality presents a challenge under gasification conditions. Differential beds have nevertheless been found to operate isothermally for gas-solid catalytic reactions (with high heats of reaction) at lower temperatures(14). Smaller conversions (~ 5%) may be required to achieve isothermal operation in differential packed beds operating at very high temperatures.

Rate models found in a differential study have limited application since they may be valid only for the small range of conversions studied. This limitation can be overcome if synthetic feeds can be prepared to study reaction rates as a function of composition. Since the differential reactor gives the reaction rate directly, it is useful in analyzing complex reacting systems.
In summary, therefore, low conversions in differential beds can lead to small changes in temperature, pressure and composition in the reactor. As a result, a high degree of analytical precision is required to measure the low gas concentrations.

4.1.3 The Thermogravimetric Balance

In the laboratory study of char gasification, the progress of the reaction can be followed by the weight change in the char sample as it is gasified. This gravimetric technique is generally applicable to many gas-solid reactions including decompositions, absorptions or adsorptions. Figure 4-3 is a schematic diagram of a typical system for studying gas-solid reactions using a recording balance. The initial investment for thermobalances and accessory equipment is usually very high.\(^{(56)}\) Operating conditions for thermobalances range from vacuum to high pressure (\(\sim 1000\) psi) and from very low to very high temperatures (\(\sim 2000^\circ\)C). For above 300 psi, near conditions of industrial gasification, a number of high pressure balances are available including quartz spring, electronic and commercial units (e.g. Cahn, etc.\(^{(56)}\)). With regard to continuous weight measurement, these balances are capable of weighing specimen from the microgram range (microbalance) to as much as 100 grams. The solid specimen assume a variety of forms from granular particles contained in baskets to solid pellets formed under high pressure by extrusion.
Figure 4-3  Schematic of Thermogravimetric Balance (adapted from Reference 13)

A  Gas Cylinders  
B  Flowmeters  
C  Balance  
D  Recorder  
E  Thermocouple  
F  Furnace  
G  Power Supply  
H  Controller  
I  Control Thermocouple  
J  Packed Bed  
K  Sample  
L  Gases Out
The monitoring of the weight change of a very small sample of solid reactant offers a direct measure of the overall reaction rate without the need for analysis of all possible products. The microbalance is thus a differential reactor operating at point values of the partial pressure and the temperature. The usual assumptions made in interpreting the rate data from a microbalance are the same as those discussed in the previous section, i.e., because of the very low conversions (1-3%) operation is assumed to be isothermal and pore and film mass-transfer resistance are assumed to be very low. The thermobalance technique has led to defining an overall reactivity on a mass basis as follows:

$$R_m = - \frac{1}{w} \frac{dw}{dt}$$

where $R_m$ overall char reactivity

$w$ weight of unreacted char on a dry ash-free basis

Although this simple measure of conversion provides a measure of activity, a detailed analysis of the gas products is required to provide selectivity data. Product gas analysis for such small conversions requires expensive analytical equipment (e.g. mass spectrometer). The thermobalance has however emerged useful in quick determinations of the effects of various variables on the reactivity.

Gardner et al\(^{(40)}\) studied the catalyzed hydrogasification of chars using a thermobalance (0-1000°C,
Gas analysis was obtained by splitting a portion of the gas product stream to an infrared detector where methane content was continuously measured and a portion to a gas chromatograph where total gas composition was determined. They found that although the infrared measurement of methane production lead to qualitative agreement with the direct mass determination, quantitative agreement was not good. Two reasons for this poor agreement may be that precise regulation of the product stream flow rate is difficult and that axial dispersion and low concentrations in the gas product stream combine to make analysis difficult.

Ensuring isothermal operation in a thermobalance involves several factors. First, it is essential that the furnace (usually a tubular heater) have an adequate constant temperature zone where the reactant solid is placed. Second, the temperature of the furnace has to be maintained at the desired level within a specified accuracy through the use of a thermocouple which is placed close to the hottest part of the furnace heating element. This is preferable to placing the thermocouple near the sample since the delay between a change in the power level to the furnace and the resulting temperature change at the pellet is so great as to render the system uncontrollable by the second method. This implies that the flow rate of the reactant gas must be held constant during a run and the apparatus must be given sufficient time to reach steady state before the run begins. Finally, thermocouples
must be placed around the specimen to assist the experimenter in arriving at an isothermal region surrounding the sample and for recording the nominal temperature during reaction. In the case of highly exothermic or endothermic reactions as in gasification, it would be advisable to place thermocouples inside the solid sample itself. Although very fine thermocouples are available and the leads may be twined around the suspension wire\(^{(13)}\), it is still uncertain how this would interfere with the weighing or reaction of the sample.

Tien and Turkeoglu\(^{(6,13)}\) used an atmospheric pressure electrobalance to study the gasification of charcoal and coke with carbon dioxide. These workers checked the assumption that the carbon specimen were isothermal by making an approximate estimate of the intraparticle temperature gradient. The temperature gradient across a spherical pellet can be represented by the following:

\[
\frac{1}{r^2} \left[ \frac{d}{dr} \left( r^2 \frac{dT}{dr} \right) \right] = -\frac{R' |\Delta H_r|}{\lambda_{_{\text{eff}}}}
\]

where
\[
\begin{align*}
 r & = \text{particle radius} \\
 \Delta H_r & = \text{heat of reaction per unit mass carbon} \\
 R' & = \text{fractional mass loss per unit time} \\
 \rho & = \text{sample density} \\
 \lambda_{_{\text{eff}}} & = \text{solid thermal conductivity}.
\end{align*}
\]

Assuming a constant particle surface temperature \(T_s\), the
gasification rate is computed (at $T_s$) and using the above heat balance the temperature at the centre of the sphere, $T_c$, is estimated. A mean temperature $1/2 (T_c + T_s)$ and a corresponding average reaction rate is then computed. The results of these approximate calculations are given in Figures 4-4 and 4-5 for the reaction of a coke sphere (2 cm diameter) in 100 kPa CO$_2$. For the case considered the temperature difference ($T_s - T_c$) becomes appreciable only at temperatures above 1100°C. For this endothermic reaction, the nonisothermal reaction rate is lower than the corresponding isothermal rate. Intraparticle temperature gradients will probably not be significant for smaller particles and lower temperatures. When solid pellets are used in the thermobalance this check should nevertheless be carried out.

Dutta et. al (38) used an atmospheric pressure thermobalance to study the gasification of several chars in carbon dioxide. This group studied the effect of sample holder on reaction rates. The three sample holders are described in Table 4-5. Although no actual data is presented, Dutta et. al conclude that no significant difference was found among the observed reaction rates in the three cases at a gasification temperature of 1000°C and a gas velocity of 4 cm/s. Calculations, based on the interphase concentration and temperature criteria presented in Chapter 5, were carried out for the cylindrical holder in order to determine the extent of possible diffusion and temperature effects for IGT char HT155
Figure 4-4  Approximate Temperature Difference between surface and center of a coke sphere as affected by temperature of oxidation in CO₂ at 1 atm. (adapted from Reference 63).
Figure 4-5 Comparison of Computed Rates of Oxidation for isothermal and non-isothermal conditions within the coke sphere (adapted from Reference 63).
TABLE 4-3

Thermogravimetric Balance Sample Holders

<table>
<thead>
<tr>
<th>SAMPLE HOLDER</th>
<th>SHAPE</th>
<th>DIAMETER</th>
<th>HEIGHT</th>
<th>INITIAL WEIGHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Petridish</td>
<td>8.5 mm</td>
<td>2 mm</td>
<td>3.75 mg</td>
</tr>
<tr>
<td>B</td>
<td>Crucible</td>
<td>8.5 mm</td>
<td>7 mm</td>
<td>18.5 mg</td>
</tr>
<tr>
<td>C</td>
<td>Perforated Cylinder</td>
<td>6 mm</td>
<td>15 mm</td>
<td>36.02 mg</td>
</tr>
</tbody>
</table>
reported in their study. These calculations are given in detail in Appendix C. The criteria reveal that although pore and film diffusion do not limit the observed rates, the assumption of isothermality may not be valid. An interphase temperature difference of as much as 20 to 80°C was calculated.

Composition and temperature differences may be present in the bulk gas phase inside the balance unless sufficient agitation is present to fully mix the gas surrounding the sample. This is particularly important for very large porous solid pellets. Costa and Smith\(^{(41)}\) in their study of UO\(_2\) describe the use of a modified thermobalance in which a small agitator is inserted close to the reacting solid to ensure uniform gas composition. This method has not been used to my knowledge in any gasification studies. It was not been ascertained as yet how the gas circulation affects the balance mechanism.

There is a large amount of evidence that, although the gas reactions are usually carried out with a gas flow rate sufficiently high that the progress of the reaction is insensitive to flow rate, interphase mass transfer may still be affecting the measured reaction rates. In Section 3.3.2 it was pointed out that this experimental test for film diffusion may be invalid at low Reynolds numbers, which is often the case in thermogravimetric balances. To facilitate mass (and heat)
transfer between the bed of particles and its environment, the thickness of the solid bed should be kept below 3 particle diameters especially for bed weights above 1 gram.\(^{(57)}\). Verea and Bell\(^{(64)}\) studied the catalytic gasification of several chars in steam in an electrobalance. These workers observed diffusional limitations on cylindrical char pellets, 0.15 cm by 0.3 cm at temperatures above 700°C and steam flowrates of 150 cm\(^3\)/min. According to Verea and Bell, estimates were made of the gasification rates on the assumption that either internal or external mass transfer was rate limiting. No checks were carried out on possible temperature gradients within the pellet or in the film surrounding the pellet.

Otto and Shelef\(^{(65)}\) used an atmospheric pressure microbalance to study the catalytic gasification of several coals. This group tried to assess diffusional effects by performing experiments with cylindrical solid specimen supported from the hangwire and with these specimen sliced into several disks (equal weight and diameter of original sample). With some catalysts, e.g. Ru, they found the reaction to be partly diffusion controlled. Rates for gasification were reported on a per unit surface area basis. The SA of the samples was measured in situ before and after gasification.

Otto and Shelef\(^{(65)}\), Riede and Hanesian\(^{(66)}\) and Pilcher et. al\(^{(67)}\) all used very similar thermogravimetric
techniques and operating conditions to study steam gasification of graphite. The experimental details, operating conditions and activation energies reported by these workers are summarized in Table 4-4. The wide disparity in the activation energies reported supports the conclusion that true chemical kinetics are not being observed.

In summary the thermogravimetric method for all its simplicity in quick determination of char reactivity is fraught with limitations. Among these are the large investment required for the recording balance and for the analytical equipment and the uncertainty in weighing in highly sensitive balances when gas is recirculated and solid temperatures are measured. The need to carry out theoretical checks even for small samples in thermogravimetric balances has been demonstrated.

4.1.4 The Fluidized Bed

Bench-scale fluidized systems (Figure 4-6) represent potentially attractive alternatives to fixed bed operations for gas-solid contacting especially since many commercial scale processes for gasification utilize this technique (e.g. Synthane, Winkler, Hygas). The fluidized bed is quite popular in carrying out highly exothermic or endothermic chemical reactions since good solids mixing helps to minimize temperature variations\(^{14}\). The data analysis therefore is
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<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Otto and Shelef (65)</td>
<td>20</td>
<td>-</td>
<td>-</td>
<td>9mm x 4mm</td>
<td>0.35</td>
<td>0.026</td>
<td>0.15</td>
<td>850-1130</td>
<td>80</td>
</tr>
<tr>
<td>Riede and Hanesian (66)</td>
<td>25</td>
<td>3.175</td>
<td>0.3</td>
<td>12.7 x 25.4</td>
<td>5.5</td>
<td>0.09-0.16</td>
<td>1</td>
<td>500-900</td>
<td>16.4</td>
</tr>
<tr>
<td>Pilcher et. al (67)</td>
<td>20</td>
<td>2.858</td>
<td>0.25</td>
<td>12.7 x 50.8</td>
<td>8.8</td>
<td>0.04-0.47</td>
<td>1</td>
<td>1000-1100</td>
<td>40</td>
</tr>
<tr>
<td>Mayers (42)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>850-1000</td>
<td>49.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1000-1110</td>
<td>35.1</td>
</tr>
</tbody>
</table>
Figure 4-6 Schematic of a fluidized bed
usually based on the assumption that the entire reactor operates isothermally. The large power dissipation entailed in keeping the solids bed fluidized severely limits the particle size that can be handled ( > 200 mesh). However, because of the small particles, pore diffusion is usually assumed to be rapid enough not to affect the measured reaction rates. Furthermore, the high gas velocities required for fluidization usually correspond to conditions where external mass transfer is extremely rapid and thus is not thought to affect the chemical reaction rate. The principle drawback for the fluidized bed is that the gas-solids contacting and the degree of backmixing are very difficult to define and so characterization and control of residence times is also difficult. Because of this, data analysis is often based on the assumptions that the solids are completely mixed and the gas flow is either plug flow or completely mixed. Two commonly found departures from the ideal behavior of gas-solid fluidized systems are channeling and slugging. Channeling corresponds to the preferential flow of the gas through certain vertical sections of the bed, thus under these conditions a part of the bed may become fluidized while the remainder stays in a packed state. Slugging, on the other hand, corresponds to the presence of rather large gas bubbles occupying most of the cross-section of the bed, the periodic collapse of the bed as particles fall through these large bubbles would then cause fluctuations in the pressure drop across the bed. It has been shown that(13) in most gas-solid fluidized systems, a portion
of the gas equivalent to the amount required to maintain the bed in a fluidized state is more or less uniformly distributed in the bed (emulsion phase) whereas the remainder passes through in the form of gas bubbles. Gas bubbles have a major influence on the operation of the fluidized systems. Their presence is responsible for the good solids mixing which is a desirable feature but on the other hand, that portion of the gas passing through the system in the form of bubbles is not brought into intimate contact with the bed of particles as is the gas contained in the continuous or emulsion phase. Using the bubbling bed model for fluid beds and a first order catalytic reaction, Levenspiel (23) has shown that the performance of the bed varies considerably depending on the bubble size (Figure 4-7). Even for smooth fluidization (small bubbles) some mixing occurs in the gas. For this state, the dispersion model with a suitable value of axial diffusivity may represent the mixing very well (14). Large bubbles however do provide a means for the bypassing of the bed. The gas composition when slugging or channeling occurs is far from uniform and the gas enclosed in the bubbles contributes very little to the solid surface reaction thereby reducing the overall conversion. Many models have been proposed to account for the extent of mixing in fluid beds but reliable data for the mixing parameters are not yet available (14).

As noted earlier, another approximate way of accounting for mixing in the nonideal reactor is to measure the
Figure 4-7  Performance of a fluidized bed as a function of bubble size (adapted from Reference 23).
distribution of residence times (gas phase). Gilliland and Mason(70) used this technique in studying the fluidized bed and found ambiguous results because of material transfer between the gas bubbles and the emulsion phase. The experimental findings of gas flow patterns in fluidized beds indicate that most laboratory units operate somewhere intermediate between plug flow and complete mixing and that kinetic results probably cannot be adequately analyzed on either basis.

Heat and mass transfer in fluidized beds can be thought to occur in three categories:

1. heat and mass transfer between the gas in the emulsion phase and the solid
2. heat and mass transfer between the gas in the bubble phase and that in the emulsion
3. heat transfer between bed and reactor walls.

Gas to solid heat and mass transfer rates have been shown to be very high. The region of transfer is confined to a thin layer at the bottom of the bed and the remainder of the bed is in equilibrium with the gas. The thickness of this layer to which effective concentration or temperature gradients are confined is in the order of 6-10 particle diameters(13). Ayers(71) has experimentally determined gas temperature profiles in a fluidized bed with the solids and gas in crossflow
arrangement. He found that the gas temperature rapidly approached the temperature of the solids in less than 1 centimeter of the bed. Similar findings were reported in the area of mass transfer. Smith\textsuperscript{[14]} has shown in a rough comparison of fixed and fluidized beds that the mass transfer rate between particle and gas for a fluid bed is approximately 2 orders of magnitude greater than that for a fixed bed. With this large transport rate, it is evident that the interphase concentration difference will be negligible. Smith also points out that similar results apply for external temperature differences.

Heat and mass transfer rates between the gas in the bubble and that in the emulsion are not easily evaluated. Overall heat or mass transfer coefficients between the two gas regions must be estimated from correlations or approximated by some other means. The difficulty in predicting these rates arises from the fact that bed properties such as the average bubble size and the ratio of solids in the bubble to volume of the bubble are not readily measurable.

Heat transfer rates between the reactor wall (when heating is supplied at the wall) and the emulsion phase or between the heating elements immersed in the bed (heating coil) and the emulsion phase are very high. Typical heat transfer coefficients range from about 200-600 kcal m\textsuperscript{-2}h\textsuperscript{-1}C\textsuperscript{-1}. This represents a major advantage of the fluidized bed for
highly endothermic/exothermic reactions. Nevertheless, for very small diameter laboratory reactors (2.5 – 10 cm ID) the wall effects may be significant. At high temperatures, thermal radiation may also become an important mechanism for bed to wall heat transfer; however, thermal radiation in fluidized beds is unlikely to play a significant role at temperatures below about 1000°C (13). The foregoing discussion indicates that temperature can be kept essentially uniform in fluidized beds.

A few additional points must be mentioned about the fluidized bed. Because of the mode of operation, the range of operating variables is severely limited (small particle sizes, velocities between minimum fluidization velocity and elutriation velocity, etc). In gasification, the particles diminish in size and become less dense as chemical reaction progresses, these smaller or lighter particles may be elutriated as reaction proceeds. If the reactor is operated in a batch mode with respect to the solid particles, high burnoff may make particle carryover a problem. A preferred procedure would be continuous solids feed and removal. The distribution of the solids residence times will correspond to complete mixing when the fluidized bed height to diameter ratio does not exceed about 3:1 (13).

Ergun (72) carried out both steam and carbon dioxide gasification of activated carbon and of graphite in a fluidized
bed and looked at the influence of flow pattern and diffusion on gasification reactions. Ergun emphasizes the importance of evaluating flow conditions in the bed in order to carry out experiments over wide ranges of temperatures and yet prevent nearly complete conversion. He noted that the gasification experiments in his fluidized bed could only be carried out over a limited range of gas flow rates and thorough mixing in the gas phase was not achieved, making it difficult to interpret the kinetic data.

The kinetics of lignite char gasification by steam and steam-hydrogen mixtures was investigated by Curran et. al.\(^{(73)}\) at 1600°F. The experimental work was carried out in a fluidized bed operated batchwise with respect to the solid charge and continuously with respect to the fluidizing gas. Most of the runs were made with an initial char bed weight of 5 or 10 grams. The char was mixed with fused periclase in order to hold a nearly constant fluidized bed height of 2 1/2 inches regardless of the initial char weight or burnoff level. This group attempted to overcome one of the major limitations of the fluidized bed (i.e. determining the mechanics of the fluid flow) by using a graphical extrapolation procedure to yield differential rate data. These data were obtained from the two integral rates corresponding to initial char bed weights of 5 and 10 grams by linear extrapolation to zero bed weight (Figure 4-8). This procedure, however, also has its limitations since extrapolation far beyond the experimental range is unreliable.
Figure 4-8  Rate of reaction as a function of bed weight. Extrapolation plot to obtain differential methane formation rates. (Adapted from Reference 73)
Johnson (74) has developed specific kinetic correlations for char gasification. The gasification data obtained by Zielke and Gorin (75) and Goring et. al (76) and the bulk of the data obtained in studies at IG1 (46) with pilot scale fluid beds and with the thermobalance were used to evaluate parameters over a wide range of conditions in the quantitative model developed. These correlations for low rate gasification were used to predict carbon oxides and methane formation rates by May et. al (77) for batch gasification of Disco char with steam-H₂ mixtures in a fluid bed. In computing these values, it was assumed that the fluid bed was completely backmixed with respect to both gas and solids. It was found that carbon oxide yields were adequately predicted for the systems examined, however experimental methane yields obtained are generally higher than predicted. They give no clear explanation for the discrepancy. Incomplete mixing in the gas phase may have occurred thereby increasing the conversion to CH₄.

Feistel et. al (78) in their study of steam gasification of coal in a small scale pilot plant internally heated fluidized bed found that the reaction rate constants determined from experiments in the fluid bed were somewhat lower than those measured in a laboratory scale differential bed. The reason they suggest is that in the upper layers of the fluidized bed hydrogen (in significant percentages) is present and it reduces the reaction rates.
The fluidized bed has a distinct advantage in that isothermal operation can be maintained under conditions of high heats of reaction. Unfortunately the fluid flow behavior of the bed is not easily characterized and remains a major limitation in its use for gasification kinetic studies.

4.1.5 Transport Reactors

Transport reactors may be divided into two types, the entrained bed and the free fall reactor. In entrained bed gasifiers shown schematically in Figure 4-9a, pulverized coal and/or coal char and gasifying medium are fed cocurrently through a heated tube. The solid particles are thus suspended in the gas and are progressively carried over in the effluent stream. In the free fall reactors depicted in Figure 4-9b, the gas and solids do not have the same residence times and the contacting may be either co- or countercurrent. The objective in these transport reactors, as in the case of the fluidized bed, is usually to obtain data for the purpose of reactor scale-up (Koller-Totzck, Bi-gas). In the transport reactor, rapid heating is obtained with very short residence times but at the same time sufficient quantities of products are available for analysis (and sometimes for characterizing the flow). Solid particles leaving transport reactors consist of partially reacted particles which are either suspended in the carrier gas and product gas (in the case of entrained beds) or moving independently of the gas stream at some velocity v. The
Figure 4-9  Schematic of a) entrained bed  b) free fall reactor
solid particles must be removed from the gas stream by use of settling chambers, filters, condensers, etc. The experimental apparatus is usually quite elaborate.

Coates\(^{(81)}\) has studied the kinetics of coal/char gasification in a low-pressure, low residence time (0.012 - 0.343 s) entrained flow reactor. Finely ground coal was rapidly mixed with oxidizing combustion gases produced from a pre-mixed flame of pure oxygen and hydrogen. Reaction tubes of 4 5/8" in length with inside diameters varying between 3/4 - 2" were tested. The use of smaller diameter reaction tubes permitted testing at lower residence times. The coal was entrained into a stream of carrier gas (either \(N_2\) or \(H_2\)) flowing between 13-15 scfh. The reaction temperature was measured but not controlled. It ranged from 1200 - 1400K. The temperature in the reactor (i.e. a nominal gas-solid temperature) increased with the amount of combustion gas fed to the reactor per pound of coal. Figure 4-10 reproduced from Coates publication is a graph of conversion versus reactor residence time without regard for variations in other operating variables. Although Coates draws some conclusions from these graphs, it must be noted that any effect due to residence time would be masked by a moderate temperature change since the primary variable governing the composition of the reactor products is temperature.
Figure 4-10  Conversion data showing small effect of average reactor residence time.
- Reactor diameter 2 in, $H_2$ carrier
- Reactor diameter 2 in, $N_2$ carrier
- Reactor diameter 1.25 in, $H_2$ carrier
- Reactor diameter 0.75 in, $H_2$ carrier
Coal feed rate 1.2 lb/hr
In another study, Coates(82) obtained kinetic data from a high temperature entrained flow gasifier. The reaction chamber was 7.6 cm 10 by 28 cm in length. Pulverized coal was blown into the top of the reaction chamber with recycled product gas. The recirculation rate near the point where the feed streams were injected was estimated to be approximately 150% of the mass flow of the feed streams. The kinetic data were analyzed assuming the reactor to be completely mixed. Diffusion rates of steam and carbon dioxide to the surface of the char particles were considered by calculating the diffusion limited reaction rates. These were estimated to be of the order of 3000-6000 min⁻¹, several hundred times greater than the measured reaction rates. It is in general reasonable to assume very rapid intraparticle and interphase heat and mass transfer for conditions existing in entrained flow reactors. However, since most transport reactors are long narrow tubes with no external agitation other than that provided by the gas, the completely mixed assumption is questionable.

Johnson(83) discussed the use of a continuous dilute-phase entrained bed in studying the hydrogasification of lignite. The reactor had a unique feature of variable temperature control along the length of the reactor which permits the establishment of various desired gas-solid time-temperature histories. Results were reported for both isothermal conditions and for conditions of constant gas-solid heat-up rate (50°F/s) in the temperature range 900-1550°F.
and pressures from 18 to 52 atmospheres. The helical-coiled transport reactor measured 1/16" ID with a total length of 200 feet and a vertical height of 2 1/2 feet. The particle size was between 170-200 mesh. Such small particles flowed essentially at gas velocities and calculated temperature differences between the gas and solids and between the reactor tube wall and the flowing gas-solid stream were negligible. This assumption seems reasonable in view of the small particles and provided the apparatus has been given enough time to reach steady state before the run begins. Gas-solids residence times for the isothermal tests ranged from 5 to 14 s. Data analysis was based on the assumption that the gas and solids were in plug flow through the coil and slippage of the solids relative to the gas flow was negligible. Differential conversions were achieved in all experiments by using sufficiently small solid/gas feed ratios (0.02 by volume) in order to facilitate the quantitative kinetic analysis.

In free-fall reactors, the solid particles are usually introduced at the top of the reactor and are allowed to fall through the reactor. Uncertainties arise in the measurement(7) and/or calculation(85) of residence times based on terminal velocities. This is perhaps the most serious drawback of this type of reactor.

Feldmann and coworkers(86) found a simple rate model adequate to correlate hydrogasification data obtained from an
integral free-fall dilute phase reactor. The first-order rate constant \( k \) during their investigation depended quite heavily on the type of reactor used as was shown in Figure 1-1. When a differential bed was used to generate low temperature data they observed a wide disparity in reaction rate constants for methane formation. Although some tentative explanations were offered, the assumptions made about the transport reactor (i.e. total backmixing) were never verified.

Dotson et. al\(^{(7)}\) used a visual method for measuring solid residence times in their kinetic study of the steam carbon reaction in a free-fall reactor. In these experiments, residence time was the time required for carbon to travel from the feeder bowl at the top of the reactor to a collection plate and this time was measured with a stopwatch. When the residence time was estimated from Stokes law and the linear velocity of the steam in the reactor, the time calculated at 2000°F was 57% longer than the measured time. Furthermore, the longitudinal temperature profile for a 3 in. ID by 6 1/2 ft. long reactor was measured once at nominal temperatures between 1800 - 2500°F. These profiles were used to correct the data for deviation from the nominal furnace temperature. It was implicitly assumed that the particle temperatures were identical with these profiles which is not likely when there is a distribution of particle sizes.
One can see from the number and the type of assumptions that have to be made with these reactors that the reliability of the kinetic data is questionable.

4.1.6 Miscellaneous Reactors

While packed beds, thermogravimetric balances, fluidized beds and transport reactors account for the majority of gas-solid contacting schemes, it may be of interest to briefly mention some of the alternate contacting arrangements that have been used. Among these are the spouted bed, the electrofluid reactor, the batch reactor and the diffusion cell.

Spouting refers to a gas-solid contacting process somewhat similar to fluidization. A schematic diagram of a spouted bed is given in Figure 4-11. In spouted beds, the upward motion is very rapid and is restricted to a well defined central core (spout). In the remainder of the bed there is never any upward motion of particles, rather a packed bed moving steadily downward and to some extent inward. This steady motion eliminates backmixing of particles in the annulus. At the same time, the fairly fast bed turnover tends to reduce the temperature differences associated with packed beds. The spouting process does not require the small particles necessary for fluidization however the spouted bed does share some of the disadvantages of the fluid bed, namely, the gas flow pattern and the solid flow pattern are not clearly defined and require
Figure 4-11 Schematic of spouted bed
substantial modeling. Carbonization, pyrolysis and gasification have been carried out using spouted beds. A model which predicts the exit char volatile matter from low temperature carbonization of coal in a spouted bed has been forwarded by Ratcliffe and Rigby. Gas composition profiles, temperature profiles and the gas velocity distribution were all measured experimentally in their spouted bed (6" ID by 30" length). At the present time Foong et al. are investigating the possibility of using spouted beds on a commercial scale for steam gasification.

The electrofluid reactor is an electrically heated fluidized bed of conducting solids. It offers several important advantages over the other systems for carrying out reactions which are favored by high temperatures and require substantial energy inputs. These advantages are due to the direct conversion of electrical energy to heat within the reacting system. Pulsifer and Wheelock have investigated the use of such a reactor in steam gasification of chars. The electrical characteristics of the reactor have proven to be very complex and do not lend themselves to accurate analysis. The resistivity of the fluid bed is apparently affected by gas velocity, temperature, particle size and the electrical conductivity of individual particles.

A modified version of the batch reactor has been used by Butler and Snelson in their investigation of coal
gasification. All experiments were carried out using stainless steel tubing .375 inch OD with .035 inch wall thickness and length approximately 8 inches. Water and coal were weighed and inserted into the tube. The air was evacuated from the tube and replaced by argon. The two ends of the tube were welded shut. The tubes were then transferred to a heated oven and the temperature range studied was between 400-700°C. The length of time the sample remained in the oven varied between 15 and 60 minutes. The tubes were then removed from the oven after the allotted time and allowed to cool to room temperature. The reaction products were removed from the reactor and the volume, pressure and temperature of the collected gas were recorded for calculation of product yield and distribution. These experiments are very time-consuming and the exact reaction time is difficult to determine.

A diffusion-cell technique has been used for measuring the chemical reaction rates in the diffusion/chemical reaction combined controlled region in studies of the reaction between Cu₂ and both graphite and chars in the temperature range 1200-1600°C (92). In this method (see Figure 4-12), a solid sample is placed on the bottom of a cell (1-1.6 cm ID, 1-2.5 cm depth). The reactant gas is passed over the open end of the cell. The reaction system is maintained at a constant temperature and pressure. Weight of the cell is continuously measured and recorded on a thermobalance so that the overall rate of the gas-solid reaction can be calculated. The intrinsic surface reaction rate has to be extracted from the
Figure 4-12  Schematic of diffusion cell apparatus

A, to automatic recording balance
B, gas flow
C, thermocouple
D, alumina bell-jar
E, alumina bleeder
F, high temperature furnace
solution of the diffusion equations which govern the system. Estimation methods of determining diffusion coefficients in the high temperature range are inadequate and limit the usefulness of this approach in gasification studies.

4.1.7 Summary

A summary of the advantages and disadvantages associated with major bench-scale char gasification reactors used to date is given in Table 4-5. It appears from the reported investigations that the essential design features of bench scale reactors discussed in Chapter 3 are difficult to predict and control in the reactors presently in use. Either the maintenance of isothermality (absence of internal and external temperature gradients) or the assumption of an ideal flow pattern or both are often highly suspect. Bench-scale reactors which were specifically designed to address and facilitate these problems have been in use in catalytic engineering research for several years. The subsequent subsection is devoted to exploring the potential of these so-called 'gradientless' reactors in the study of noncatalytic gasification reactions.

4.2 Selected Alternative Reactor Systems

The term differential reactor refers to a reactor in which the gas conversion is limited to not more than a few percent. Furthermore, the gas and solid composition, pressure and
<table>
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<tr>
<th>REACTOR TYPE</th>
<th>ADVANTAGES</th>
<th>DISADVANTAGES</th>
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| 1. Differential Tubular Fixed Bed | simple to construct and inexpensive  
|                        | each run gives directly a value for the rate of reaction at the average concentration in the bed  
|                        | due to small conversions, heat effects will be small, isothermality is more easily maintained  
|                        | backmixing effects negligible due to low conversions                        | small conversions require high analytical precision for product analysis  
|                        |                                                                            | rate model has limited application to small range of conversion studied  
|                        |                                                                            | short residence times limit ability to ascertain flow pattern |
| 2. Integral Tubular Fixed Bed | simple to construct and inexpensive  
|                        | most closely resembles large industrial packed bed and useful for modelling their complex operation  
|                        | finite conversions facilitate analytical analysis  
|                        | RTD studies may be carried out                                              | difficult to maintain isothermality (significant temperature variations from point to point especially for gas-solids systems)  
|                        |                                                                            | channeling and other deviations from plug flow often encountered  
|                        |                                                                            | high reactor pressure drop  
|                        |                                                                            | analysis for complex kinetics is very difficult |
| 3. Thermogravimetric Balance | quick and direct measure of carbon consumption rate (reactivity)  
|                        | small sample size required  
|                        | can operate at high temperature and either high or low pressures             | expensive and fragile  
|                        |                                                                            | low gas conversion does not permit product gas analysis  
|                        |                                                                            | residence time distribution studies not easily carried out  
|                        |                                                                            | high balance sensitivity limits gas recirculation rate  
<p>|                        |                                                                            | different sample holders and sample pellets have shown concentration and temperature gradients |</p>
<table>
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<tr>
<th>REACTOR TYPE</th>
<th>ADVANTAGES</th>
<th>DISADVANTAGES</th>
</tr>
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</table>
| 4. Fluidized Bed | - direct bench-scale scale-up to industrial reactor (Synthane, Winkler, Hygas, etc.)  
- fluidization provides rapid heat transfer and thus isothermal conditions can be approached  
- product gas distribution can be obtained | - gas mixing not well defined even with mechanical agitators (complex dynamics)  
- limited operating range for gas flowrates  
- limited particle size for fluidization |
| 5. Transport Reactor | - direct bench-scale scale-up to industrial reactor (Kopper-Totzek, Bi-gas, etc.)  
- sufficient conversion can be attained for product gas analysis  
- residence time distribution studies may be carried out | - complicated auxiliary equipment for quick product separation  
- representative sampling may present a problem  
- isothermality difficult to maintain  
- relatively short residence times since high velocities are necessary to avoid slippage  
- flow patterns for gas and solid must be determined |
temperature must be uniform throughout the reactor for true
differential operation. A reactor operating in this way is
highly desirable for kinetic studies. As discussed earlier a
laboratory packed bed reactor may possibly be operated in a
differential mode but in practice it is difficult to do so over
a very wide range of operating conditions. This limitation as
well as the other major drawbacks of the differential reactor
( precise product gas analysis required, need for synthetic
feeds) can be overcome by the use of an external recycle
reactor. This reactor is able to achieve high overall
conversions through low conversions per pass. This basic
concept of the external recycle reactor has been used to design
other reactors for studying gas-solid catalytic reaction
kinetics, namely the continuous stirred tank and the internal
recirculation reactor. A good discussion of these so-called
'gradientless' reactors can be found in the publications by
Carberry(22), Bennett et. al(94) and Doraiswamy and
Tabj(33). Schematic drawings of these three reactor types
are provided in Figures 4-13, 4-14 and 4-15. In each case, a
small amount of catalyst is used and the relative velocity of
the gas with respect to the solid is increased over that
achieved in an ordinary laboratory fixed bed reactor. This
improves the heat- and mass-transfer characteristics external
to the solid particles. The possibility of using these
reactors to study gasification kinetics will now be explored.
Figure 4-13 Schematic of external recycle reactor
Figure 4-14 Schematic of continuous stirred tank reactor, two versions
Figure 4-15 Schematic of internal recycle reactor
4.2.1 The External Recycle Reactor

The schematic of an external recycle reactor in Figure 4.13 provides the notation for the following discussion. Feed $v_F$ at conversion $x_F$ is admitted steadily to the system and effluent at conversion $x_O$ is withdrawn at the same rate (assuming no volume change on reaction). Within the loop, a pump recirculates gas at a rate $v_P$. The conversion rate across the bed of volume $V$ per pass is

$$r_A = \frac{v_P + v_F}{V} (x_O - x_I) \quad \text{Equation 4-1}$$

The average overall rate based on feed and effluent is

$$\bar{r} = \frac{v_F}{V} (x_O - x_F) \quad \text{Equation 4-2}$$

By material balance,

$$x_I = \frac{v_P x_O + v_F x_F}{v_P + v_F} \quad \text{Equation 4-3}$$

In order for equation 4-1 to express differential rates, then $x_1 \rightarrow x_O$ or in terms of Equation 4-3, $v_P \gg v_F$. If the recycle flow is made much greater than the net feed, then the overall rate must equal the rate per pass:

$$r_{A,F} = \frac{(x_O - x_F) v_F}{V} = \frac{(x_O - x_I) (v_F + v_P)}{V} \quad \text{Equation 4-4}$$
Consequently, while the conversion per pass is differential, overall conversion is integral. One obtains, therefore, a direct measure of the rate of reaction from the measured difference between inlet and outlet concentrations.

With recirculation rates 10 to 15 times the feed rate, the reactor tends to operate nearly isothermally\(^{(22)}\). High velocities past the bed of particles may eliminate almost completely external mass-transfer influence on the reactor performance. This can be achieved simply by varying the recycle rates to establish the minimum rate beyond which mass transfer effects are negligible. The degree of mixing can be controlled and calculated from the recycle rate. It has been shown\(^{(22)}\) that at large values of \(v_p/v_f\) (> 25), the reaction proceeds at or very closely to discharge conditions found for the ideal continuous stirred tank reactor.

Finding the limits of the recycle flow rate is a critical point in the construction of a recycle reactor for kinetic studies. If a high recycle flow rate is chosen, which means the internal volumes of pump used and pipes are large compared to the reactor volume, the time needed to reach steady state will be long. If on the contrary, a low recirculation flow rate is chosen, it will be difficult to maintain constant gas concentrations throughout the solid bed. Nystrom\(^{(95)}\) discusses the derivation of a criterion for determining the highest recirculation flow rate required in a recycle reactor.
in order to be free from gradient effects. The criterion is
given below:

\[ q > 40 \frac{D_{\text{eff}} V (1-\epsilon)}{d_p^2} \]  \hspace{1cm} \text{Equation 4-5}

where \( D_{\text{eff}} \) = solid effective diffusivity
\( V \) = total bed volume
\( \epsilon \) = bed porosity
\( d_p \) = solid particle diameter
\( q \) = volume flow capacity of pump \( F/C_T \)
\( C_T \) = total concentration in bulk flow
\( F \) = molar flow rate

A critical hardware problem and expense associated with
the external recycle reactor is the recycle pump. The recycle
pump should have the following characteristics:
noncontaminating, leaktight, low hold-up and capable of
operating against a moderate back pressure. Some pumps have
been developed for specific applications which meet these
requirements (96, 97), but a pump which will satisfy the
diverse needs of a wide range of conditions characteristic of
gasification studies is not available.

An external recycle reactor, in which control of gas
concentration was achieved by adjustment of the feed rate, has
been used recently to study the kinetics of the
carbon-dioxide-carbon reaction (98). The influences of
reaction temperature, gas concentrations, degree of burnoff and methods of pretreatment upon the reactivity of carbon black were determined. The temperature range for the reaction (900-1200°C) made it necessary to separate the reactor bed from the recycle pump. Temperature control in this external recycle system was complicated by the necessity to thermostate several items, viz.: the reactor tube, the pump and the recycle loop. Perhaps most important, because of the large volume of the connecting loop necessary for heating and cooling the system components, the system had a relatively slow response to changes. Very little detail is provided in the publication on the experimental apparatus. It is also not known what recycle ratio was used and whether diffusional effects were hindering the progress of the reaction.

4.2.2 The Continuous Stirred Tank Reactor

The continuous stirred tank reactor illustrated in Figure 4-14 has many equivalent design versions. In the Carberry reactor(22) for example, the solid particles are placed in wire mesh containers forming the arms of the stirrer and the whole basket is rotated at high speeds. The agitation promotes good heat transfer and can lead to isothermal operation(22). The rotational speed (up to 5000 rpm) and the gas feed rate can be adjusted to achieve perfect mixing. The high linear velocities achieved tend to minimize external mass transfer effects. Bennett(94) has demonstrated that residence time
Distribution studies can be carried out easily. When the complete mixing assumption holds, a direct measure of the reaction rate can be found by measuring the inlet and outlet gas concentrations as stated below:

\[ r_{A,F} = \frac{x_{A,0} - x_{A,F}}{W/F_{A,0}} \quad \text{Equation 4-6} \]

Since these conversion levels are finite, gas composition can be accurately measured.

The catalyst baskets which have been used vary in form. Figure 4-16 illustrates a few. While the external recycle reactor often poses recycle pump difficulties, the CSTR may often exhibit agitator seal problems especially at high reaction temperatures. This type of reactor does not lend itself to temperature measurements of the solid bed because of the rotation and so the use of this type of reactor is not recommended for reactions involving high heats of reaction (due to the uncertainty in predicting the solid temperature (35)).

A common experimental difficulty of these reactors is how to determine whether all the solids see the gas uniformly. Also, in the Barberry reactor for instance, the bulk mass transfer characteristics may vary substantially between the particles close to the axis and those far from the centre (19). Since in these reactors, the true gas velocity relative to the catalyst is not known and varies radially as well, it is not
Figure 4-16 Catalyst baskets used in CSTR

a four rectangular paddle baskets for single layer of catalyst pellets
b four cylindrical baskets made of wire mesh for catalyst of any form
c wire mesh circular basket
possible to predict heat- and mass-transfer coefficients. In the revolving basket reactor, one must also ensure that bypassing of the feed gas to the exit does not occur. For a finely powdered solid (and in the case of a shrinking solid reactant) special containment methods must be devised. Although the CSTR has been used successfully in many catalytic gas-solids reaction studies, the disadvantages outlined above make it of limited potential in gasification studies.

4.2.3 The Internal Recirculation Reactor

In an internal recirculation reactor, gas phase mixing is achieved by recirculating the reaction mixture through a stationary solid bed using a specially designed impeller. Berty\(^{99}\) has demonstrated that the recirculation rate may be determined by the rotational speed of a centrifugal blower mounted on the top or bottom of the solid chamber. The flow rate of the reacting mixture and the degree of recirculation through the catalyst bed are well defined quantities for these reactors and the actual rate of internal recycle can be estimated by experiment\(^{99}\). Well-mixed isothermal conditions can be achieved with proper choice of impeller speed, gas flow rate and particle size. Internal recirculation reactors have proven to be versatile and have been employed in a number of gas-solid catalytic reactions successfully. The solid particles can be of any form or size since the solid bed
is stationary. Nominal bed temperatures can also be measured. Heat- and mass-transfer rate correlations obtained in a fixed bed reactor can be applied to this type of reactor to determine possible diffusional resistances. In comparison with the CSTR, an internally recycled reactor possesses two merits of some practical importance. First, the mounting and replacement of the solid is more simply carried out without any danger of unbalancing the stability of the rotating parts. Second, the effect of imperfect mixing in the internal recycle reactor can be estimated from a knowledge of flow rate through the solid bed\(^{(33)}\). Residence-time distribution studies can also be carried out with this reactor to determine flow pattern. As in the case of the CSTR, a direct measure of reaction rates result from the difference between inlet and outlet reactant gas concentration.

Two technological problems emerge in the design of an internal recycle reactor because of the insertion of an agitator shaft into the reaction chamber. The first problem is to protect the shaft bearing from overheating when high temperature reactions are studied. This problem may be solved by cooling the bearings or by using a long shaft with the bearings placed at one end safely removed from the high temperature zone. Both these methods of tackling the overheating problem have limitations and use of one method or the other depends upon the specific reaction conditions. The second problem is to seal effectively against leakage along the
shaft and along the reactor/shaft connections. The sealing problem for high pressure studies at moderate temperatures (500°C) has been solved using a magnetic drive(100). However, high temperature sealing still presents a challenge.

Mahoney(100) has employed a version of the internal recycle reactor modified for operation at high temperatures and pressures (1100°F maximum up to 1000 psig, 1000°F maximum up to 2000 psig) which are prevalent in petroleum processing. The studies were concerned with the reactions of n-heptane catalyzed by a commercial platinum-on-alumina catalyst. Process conditions were constant so that the catalyst deactivates at a constant temperature and pressure. Experiments were conducted using particles which ranged from 1/12 inch extrudates to small 40 mesh particles.

Berty(99) has recommended that a lower pressure limit of 45 psig be used "because at lower pressures and corresponding low gas densities it is difficult to maintain good mass velocities". High mass velocities are required to minimize the thickness of the stagnant boundary layer between the external catalyst surface and the bulk gas phase. Kuchcinski and Squires(116) however have shown that the internal recycle reactor can also be used at low pressure i.e., 1 atm, provided certain conditions are met. They found that the reactor could behave as a perfectly mixed vessel when the recycle ratio was greater than about 20.
4.2.4 Summary and Conclusions

The differential reactor with recirculation by means of an external pump, the stirred tank reactor and the internal recirculation reactor have been described and discussed in view of pointing out the major merits and demerits of these reactors for undertaking gasification kinetic studies. A summary of these findings is given in Table 4-6. The most important basic requirement of these reactors is that they should be operated under gradientless conditions. Physical measurements should therefore be carried out in order to evaluate the reactor behavior both with respect to the heat and mass transfer and mixing characteristics under different conditions of flow rate and stirring speed. Except for construction difficulties the internal recirculation reactor shows great potential in gasification studies. An internal recirculation reactor has been constructed in order to evaluate this potential for investigating gasification kinetics. The design, development and testing of the reactor are the subject of the following chapter.
<table>
<thead>
<tr>
<th>REACTOR TYPE</th>
<th>ADVANTAGES</th>
<th>DISADVANTAGES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. External Recycle Reactor</td>
<td>high degree of overall conversion can be obtained with essentially differential conversion per pass</td>
<td>critical hardware problem and expense to obtain a noncontaminating, leaktight, low hold-up pump that withstands moderate temperatures</td>
</tr>
<tr>
<td></td>
<td>isothermal operation possible</td>
<td>for low recirculation rates many of the disadvantages of the integral tubular bed exist</td>
</tr>
<tr>
<td></td>
<td>concentration gradients are easily minimized (with sufficiently high recirculation)</td>
<td></td>
</tr>
<tr>
<td>2. Continuous Stirred Tank</td>
<td>agitation promotes good heat transfer and leads to isothermal operation</td>
<td>surface temperature of solids difficult to measure</td>
</tr>
<tr>
<td></td>
<td>RTD studies easily carried out</td>
<td>solids may not &quot;see&quot; bulk gas uniformly</td>
</tr>
<tr>
<td></td>
<td>direct measure of reaction rate</td>
<td>containment of small particles difficult (especially at high conversions)</td>
</tr>
<tr>
<td></td>
<td>integral conversions simplify analysis of product composition</td>
<td>construction complicated by mechanical moving parts</td>
</tr>
<tr>
<td>3. Internal Recirculation</td>
<td>well-mixed isothermal conditions can be achieved</td>
<td>difficult construction, mechanical difficulties include protecting the shaft bearing from overheating and sealing effectively against leakage along the shaft</td>
</tr>
<tr>
<td></td>
<td>sampling and product analysis are simplified</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RTD can be accurately measured</td>
<td></td>
</tr>
<tr>
<td></td>
<td>solids temperature can be measured</td>
<td></td>
</tr>
<tr>
<td></td>
<td>fixed bed heat-and mass-transfer correlations can be used</td>
<td></td>
</tr>
</tbody>
</table>
5. TESTING AN INTERNAL RECYCLE REACTOR

5.1 Introduction

An internal recirculation flow reactor was constructed in order to investigate its potential in overcoming the shortcomings of the current bench-scale reactors used for studying char gasification kinetics. Descriptions of the reactor and its operation are given in the following sections. An evaluation of the reactor performance based on the results of tests carried out to determine mixing characteristics and possible temperature gradients within the reactor is presented. As a result of this evaluation no gasification runs were performed with the experimental set-up. A description of the ancillary equipment required to carry out steam gasification at atmospheric pressure and high temperatures as well as a product analysis system is nonetheless provided for future work with a modified version of this reactor or with alternate reactors.

5.2 Experimental Equipment and Materials

The experimental equipment set up in the present study is shown in Figure 5-1. It consists essentially of an internal recirculation reactor, a heating system, a system for generating steam and varying the steam partial pressure, equipment for removing unreacted steam and facilities for sampling, metering and analyzing the product gases. Each of these will be described in detail subsequently.
5.2.1 The Reactor

The bench-scale internal recirculation reactor used in the present study is shown in Figure 5-2. The two components of the reactor assembly are the stirrer drive unit with stirrer shaft and the reaction vessel. A detailed view of the reaction vessel internals is provided in Figure 5-3. The reactor shell was constructed of 316 stainless steel which can withstand temperatures up to 1100°C at moderate pressures. The cylindrical vessel measured 17.8 cm by 5.72 cm outer dimensions. The total free volume of the reaction vessel was 30 mL ± 1 mL and the volume available for the solids is 14.5 cm³. Up to 15 grams of char could be charged in the annular solid basket (7.6 cm height, 1.6 cm OD, .3 cm ID). The solid was supported by a fine mesh stainless steel screen. Four vertical baffles were placed at right angles to one another on the inner wall of the chamber. The feed gases entered the reaction chamber at constant rate through a 0.16 cm inlet port at the top of the vessel and the product gases left through a 0.16 cm outlet port at the side of the reactor. The gas in the chamber was recirculated by means of a flat-blade impeller mounted at the top of the chamber. A schematic of the impeller is shown in Figure 5-4. A thermowell was fixed inside the annular basket to permit temperature measurement with a chromel-alumel thermocouple embedded in a stainless steel tube sheath, throughout the height of the solids bed. A second chromel-alumel thermocouple inserted horizontally through a
Figure 5-2 Reactor Assembly
Figure 5-3 Reaction Chamber Internals

Scale 1 cm = 0.25 inch
hole in the side of the furnace with the hot junction placed against the outside wall of the reaction chamber was used for temperature control purposes.

A completely sealed, magnetically coupled drive was used to rotate the impeller at speeds up to 1900 RPM. Since the standard magndrive assembly supplied by Autoclave Engineers can withstand a maximum temperature of about 600°F, a modified version of this assembly was used, a schematic of which is given in Figure 5-5. There are two ways of protecting the shaft bearings (graphite or teflon) from overheating when high temperature reactions are studied. The first way is to cool the bearings with water jackets and the second is to use a long shaft with the bearings placed at one end safely removed from the high temperature zone. Both methods were combined in an effort to minimize the inherent weaknesses of the solutions when used separately. The magndrive is bolted to the reactor and a stainless steel ring, similar to a "Swagelok fitting", at the top of the neck of the reactor vessel prevents gas leakage along the joining flange even at high temperatures.

Heating for the reactor was supplied by 2 semi-cylindrical 0.1 m long Lindberg furnaces (model 5010-106S-00A) which could attain temperatures of 1200°C. Because of the length of time required for this short heater to reach temperatures of the order of 1000°C (4 hrs), a booster heater which consisted of a tightly wound coil of resistance elements was embedded in the insulation surrounding the furnace. Electrical leads from the
Figure 5-5  Modified Magnedrive Assembly
Lindberg heater were connected to an automatic on-off Honeywell controller actuated by a type K thermocouple. The current to the booster heater was controlled manually with voltage step-down through a rheostat.

Kaowool blanket and Kaowool bulk fibre were used to insulate the reactor/heater system. Kaowool, a trade name for ceramic fiber provided by Babcock and Wilcox, is non-combustible, has a low thermal conductivity and maintains its structural integrity up to 1300°C.

5.2.2 The Feed System

Distilled water, stored in three 20 milliliter gas tight syringes was supplied at constant flow rate by a syringe pump to an electrically heated vaporiser-superheater where steam was generated and superheated (\(\sim 300^\circ C\)). The Sage Model 355 syringe pump offered a continuously variable flow range. The pump was calibrated with the syringes to deliver the required water flow to the superheater (0.002 - 0.02 gm/s). The vaporiser-superheater was made from stainless steel tubing and measured 0.013 m-ID by 0.3 m in length. The syringe needles were welded to the superheater at one end and the other end of the heater was fitted with a quick opening valve. The entire vaporiser was packed with crushed quartz particles (0.004 m - 0.006 m diameter). The tube was wound with a heating coil connected to a variable transformer and insulated with 0.06 m of Kaowool.
Nitrogen could be circulated through the reactor during the heat-up time and could be used as the inert gas in the experiments. The inert gas supply train consisted of a tank of high purity nitrogen which discharged to a 0.15 m long drying tube (0.01 m ID) containing indicating drierite (CaSO₄) followed by a 0.3 m long purifying tube containing copper turnings (to remove traces of O₂) maintained at 300°C. The nitrogen flow was measured with a Matheson type 602 rotameter in the (0-5 L/s) range. The rotameter was calibrated against a standard wet test meter. The gas was passed to the vaporiser-superheater if H₂O/N₂ mixtures were to be used or directly to the reactor during the warm-up period. The process line connecting the vaporizer to the reactor inlet was wound with insulating tape to prevent condensation of the steam.

5.2.3 Product Analysis

The product gas, steam, and inert diluent gas at the reactor exit could be carried through 0.3 cm ID stainless steel tubing to a double-pipe heat exchanger for condensation of the unreacted steam. The condensate was collected in a 60 ml plastic receiver which could be emptied regularly. The product and diluent gases were separated from the water in the condensate collector. The main stream of effluent gases was subsequently passed through a 20 cm long 1.25 cm ID drying tube filled with anhydrous calcium sulfate (Drierite) and through a calibrated wet test meter. Experiments were carried out to
investigate whether reaction products such as CO and CO$_2$
would be adsorbed on the Drierite. These experiments described
in Appendix D determined the allowable size of the drying
tube. A small gas stream was continuously sent through a
sampling valve for analysis. Sampling of the gas at 12 minute
intervals was achieved through an air actuated 6 port automatic
Valco sampling valve with a loop volume of 0.5 mL and a digital
timing system provided by Chromatographic Specialties (Digital
Valve Sequence Programmer).

A system for product gas analysis was designed, calibrated
and tested although no gasification runs were performed. This
system will form the basis of product analysis systems for
future work and thus will be described briefly.

The gas samples were analyzed on a Fisher-Hamilton Model
29 dual column/dual detector gas partitioner. The detector was
kept at a nominal temperature of 70°C and the cell current
maintained at 225 ma. Helium supplied at 18 psig and a
flowrate of 40 cm$^3$/min was used as a carrier gas. The
chromatographic system consisted of 3 columns kept at ambient
temperature as shown in Figure 5-6. The first column consisted
of 2.4 meters of .64 cm ID aluminum tubing packed with 50% DEHS
on 60/80 mesh Chromosorb P. Its function was to separate CO$_2$
from the other gases in the mixture. The gas sample thus
separated was detected and recorded as two successive peaks,
one for the mixture of nitrogen, oxygen, carbon monoxide,
Figure 5-6 Chromatographic system for product gas analysis

A  Carrier gas inlet  E  Column 1
B  Reference  F  Columns 1 and 2
C  Sample Inlet  G  Exhaust
D  Drying Tube
FIGURE 5-3

REACTION VESSEL
hydrogen and methane and one for the carbon dioxide respectively. The columns in position number 2 were in series and consisted of 1.8 meters of .64 cm ID copper tubing packed with 60/80 m Chromosorb W followed by 1.22 meters of .64 cm ID copper tubing packed with 60/80 mesh Molecular Sieve 13X. The molecular sieve column separated H₂, O₂, N₂, CH₄ and CO in that order. However because of the short length of the molecular sieve column used, a spacer column was needed so that the time for hydrogen elutriation was far enough from the CO₂ peak to enable detection. Since the Chromosorb W packing is inert, Column 2 served as the delay column. This column therefore ensured that the first peak from column 3 (H₂ peak) did not overlap with the CO₂ peak on a chromatogram.

Since the DEHS and MS 13X columns readily adsorb water (103) a process which gradually causes deactivation of the column and results in the loss of separation of the gases, reactivation or conditioning is necessary. Column 1 was conditioned at 100°C overnight housed in a Varian Model 1400 Gas Chromatograph and Column 2 was conditioned at 325°C overnight in the same chromatograph. Helium gas was allowed to flow through the columns during conditioning at a rate of 10 cm³/min.

Complete gas mixture separation was accomplished in approximately 10 minutes. A typical chromatogram for a prepared gas sample is shown in Figure 5-7. Gas concentrations
Figure 5-7 Typical gas separation and analysis
could be determined from a chromatogram obtained on a
Hewlett-Packard Model 3380S integrator with the aid of
calibration curves. There are several procedures available for
gas calibration, namely direct calibration, internal
normalization and normalization of areas (correction factors).
The method adopted here is direct or absolute calibration.
Blends of the components \( \text{(H}_2, \text{CO, CO}_2, \text{CH}_4, \text{N}_2) \) were
prepared and chromatograms were made with these mixtures. The
value of the peak area was then plotted against the amount of
sample injected, thereby determining the calibration factors.
Once these factors were known the actual amount of component in
an unknown sample could be calculated from peak area and sample
size. This method is especially useful for gases since blends
of exactly known composition are not easily made. A method of
injecting a known fixed sample size (0.5 ml sample loop, 1 psig
pressure) was used as described in detail in Appendix E. The
main disadvantage of this procedure for calibration is that
calibration is time consuming. Also, frequent spot checks are
necessary since the sensitivity of the detector must remain
constant from run to run and day to day in order to compare
results with the calibration graph. After screening
experiments, when the composition range of the reaction product
gas is more or less known, the most exact analysis of the
mixture may be obtained by comparison of the chromatogram with
chromatograms obtained from synthetic mixtures of approximately
the same composition. Analyses of two synthetic mixtures
prepared by Matheson Gas Products are also given in Appendix E.
5.2.4 Materials

The char used in this investigation was prepared from Byron Creek coal by a devolatilization technique described in detail in Appendix F. The coal and coal char analyses are presented in Table 5-1 and 5-2 respectively. Char obtained from a sub-bituminous 'A' (Forestburg) coal was used in some of the preliminary experiments. It was obtained from Dr. B. Lu, University of Ottawa.

Indicating Ascarite II (8 mesh) was supplied by the Arthur H. Thomas Co., Philadelphia, USA and indicating Drierite (8 mesh) was supplied by Chromatographic Specialties, Brockville, Ontario.

Gases used for calibration purposes and for mixing studies were all high purity or ultra-high purity grade (99.8% min) supplied by Matheson Gas Co., Whitby, Ontario.

5.3 Gas Phase Mixing Tests

Residence time distribution studies were performed on the bench-scale internal recirculation flow reactor described in Section 5.2.1 in order to determine the operating conditions (agitator speed, gas flow rate, solid particle size) under which the completely mixed assumption prevailed. To investigate the degree of mixing in the gas phase of the
<table>
<thead>
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<th>Component</th>
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<td>Moisture</td>
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<tr>
<td>Ash</td>
<td>14.96</td>
</tr>
<tr>
<td>Volatile</td>
<td>25.69</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>57.36</td>
</tr>
<tr>
<td>Carbon</td>
<td>72.96</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.23</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.78</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.13</td>
</tr>
<tr>
<td>Ash</td>
<td>14.96</td>
</tr>
<tr>
<td>Oxygen (by diff)</td>
<td>3.95</td>
</tr>
</tbody>
</table>
TABLE 5-2

ANALYSIS OF BYRON CREEK CHAR

<table>
<thead>
<tr>
<th>Component</th>
<th>As Received</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>1.14%</td>
</tr>
<tr>
<td>Ash</td>
<td>21.5%</td>
</tr>
<tr>
<td>Volatile</td>
<td>3.50%</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>73.86%</td>
</tr>
<tr>
<td>Carbon</td>
<td>74.5%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.952%</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.32%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.28%</td>
</tr>
<tr>
<td>Ash</td>
<td>21.5%</td>
</tr>
<tr>
<td>Oxygen (by diff)</td>
<td>-</td>
</tr>
</tbody>
</table>
reactor, the classical stimulus-response experimental technique was used. For ease of experimentation and data analysis, the response of the non-reacting system to a step change in feed gas composition was monitored and modelled. Normally, for relatively large reactor volumes the dynamics of the measuring device (which usually have fast responses) can be ignored. However, for the small laboratory reactors the response time of the measurement device can be of the same order of magnitude as that of the reactor itself (1-2s). No evidence that this problem has been tackled by other workers could be found. It was necessary therefore, in this study to use a different approach with respect to the analysis of the step response data. The approach adopted here to handle the problem of deriving the RTU of the reactor when the measuring instrument dynamics are included is to model the two contributions to the experimentally measured response curve separately. Appropriate models were therefore found to simulate the behavior of both the instrument and the reactor. In this section, the experimental procedure, the basic approach, the instrument model, the reactor model, the data analysis and the mixing test results are discussed.

5.3.1 Experimental Apparatus

The experimental scheme adopted to impose the step change in inlet gas composition is given in Figure 5-8. To generate step changes, a 4-way manual switching valve was used. Known
Figure 5-8  Schematic flow diagram of experimental apparatus for mixing studies

A  needle valve
B  rotameter
C  He gas cylinder
D  N₂ gas cylinder
E  4-way switching valve
F  reactor
G  bypass line
H  thermal conductivity cell
I  power supply
J  wet test meter
compositions of feed gases were prepared from cylinder gases by adjustment of the rotameters. The needle valve on the vent stream was adjusted so that when a stream was switched from the reactor to the vent, there was no change in flow rate. The remaining needle valves were adjusted so that both gases flowed at the same rate. One stream from the 4-way valve could be directed either through the reactor or through a temporary bypass around the reactor. In this study, step changes from either pure He to pure N₂ or from pure He to He/N₂ mixtures were conducted by switching the 4-way valve from one position to another at a specified time. Negative step changes (e.g. N₂ to pure He) could similarly be applied. The physical properties of He and N₂ are similar and both gases are inert to the char.

The outlet stream from the reactor was fed continuously through a Gow Mac Model 40-001 thermal conductivity cell, consisting of 4 WX filaments. The heated cabinet was maintained at a constant temperature of 100°C. A current of 200 ma was maintained in the bridge circuit.

Analysis of the RTD data is greatly simplified if there is a linear relationship between thermal conductivity and gas composition. The results of tests carried out to ensure that such a linear relationship existed are shown in Figure 5-9. The linearity is clearly verified. Additional tests showed that the linearity of the response did not depend on flow rate
Figure 5-9  Instrument Calibration Curve

- ▲  1000 cm$^3/min^{-1}$ gas flowrate
- ●  100 cm$^3/min^{-1}$ gas flowrate
when varied from 100 cm$^3$/min to 1000 cm$^3$/min. The signal from the thermal conductivity cell was recorded on a WATANABE linear mark V high speed recorder.

5.3.2 Experimental Procedure

Before each run, approximately 5 grams of sized char was weighed and set aside. Quartz particles of the same size fraction were also prepared. The solids basket was then filled with the char and quartz as shown in Figure 5-10 with fine mesh stainless steel screens separating the layers. The manner of packing was identical to that planned for actual gasification experiments. In order to ensure consistency in the packing, the packing technique was not varied. The volume of each section (i.e.; A, B, C) was kept constant. The magne-drive assembly was then bolted to the reactor and the pressure in the vessel increased to 30 psi. If no pressure change was observed on a Bourdon pressure gauge on the upstream side of the reactor within one half hour, the reactor was considered leak-tight and the test continued. The appropriate gas flowrates were then established for the reference gas through the cell, the gas exiting the reactor and the gas being vented by adjusting the needle valves. The bridge current was then turned on. The thermal conductivity cell was always kept heated to the proper temperature. At this time the magne-drive was activated and the correct rotational speed was determined with the use of a stroboscope. Once a steady baseline was achieved on the
Figure 5-10  Schematic of bed packing
recorder with helium flowing through the reactor, the 4-way valve was manually switched to N₂ (or to N₂/He mixtures in case of calibration) and the output of the thermal conductivity cell recorded. At the same time the step change was introduced, a stopwatch was started and once the output on the recorder reached a new steady level (corresponding to 100% N₂) both the stopwatch and the recorder were turned off. In this way, the time at which the step input was applied was determined by the elapsed time and the chart speed. At the end of each run, the alternate char/quartz layers were carefully removed by first pulling out the screen and then pouring out the material.

The ranges of the operating variables explored are listed in Table 5-3. A 2³ factorial design described in Table 5-4 was used to examine the effects of these variables on mixing.

With the high gas flowrates used and the small reactor volume (30 mL³), the average residence time of the gas in the reactor was in the order of 2-3 seconds. In this time scale, it became important to measure the thermal conductivity cell's response to a step change as a function of flow rate. The instrument response was determined by imposing a step change in the feed gas from He to N₂, with the feed gas stream entering the temporary bypass line. The recorder time constant is in the order of milliseconds and can be ignored.
### TABLE 5-3

**Range of Operating Variables**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Flow Rate</td>
<td>500 - 1000 cm$^3$/min</td>
</tr>
<tr>
<td>Impeller Rotational Speed</td>
<td>0 - 1800 rpm</td>
</tr>
<tr>
<td>Particle Size</td>
<td>0.2 - 1.4 mm</td>
</tr>
<tr>
<td>Char/Quartz Particle Size [mm]</td>
<td>Gas Flowrate [cm³/min]</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>0.2 - 0.4</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>1000</td>
</tr>
<tr>
<td>0.4 - 1.0</td>
<td>500</td>
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<tr>
<td></td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>1000</td>
</tr>
<tr>
<td>&lt;1.0 - 1.4</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>750</td>
</tr>
</tbody>
</table>
All of these experiments were conducted at room temperature because this greatly reduced the time involved for the tests. Bennett et al.\(194\) have reported RTD studies by Brown (using an internal recycle reactor) carried out at room temperature and at reaction temperature \(300^\circ\text{C}\). It was noticed that as the temperature was increased to reaction temperature, natural convection improved mixing even with no agitation. This is thought to be true for the present study where temperatures are much higher \(600-1000^\circ\text{C}\).

5.3.3 Modelling Approach

As was mentioned in the introduction to this section, deriving the RTD of a bench scale reactor from response data in which the measurement device dynamics cannot be ignored is a problem which (to my knowledge) has not been tackled. It was necessary therefore to develop a means of handling it. The basic approach adopted here is to model the reactor and the instrument dynamics separately. A simple empirical model (the tanks in series model) has been shown to adequately describe the measurement device contribution. The recirculation reactor, on the other hand, was modelled using a mixed model which allows for possible deviations from complete mixing as represented by the parameters in the model.

The step-response curves for the measurement device and for the combined reactor/measurement device are continuous concentration-time curves. On the other hand, the estimation
of parameters in the models for the reactor and for the measurement device requires discrete data. Discretization by sampling the continuous data presents no problem in itself, however the question of the number and spacing of samples arises. The important factor here is that the discrete data points selected should allow accurate reconstruction of the continuous data.

A problem which does arise however is that the data taken from any one step response curve is autocorrelated. One of the basic assumptions involved in standard parameter estimation methods is that the response measurements are independent. Thus using data from only one step response curve would lead to unreliable parameter estimates. Several correlated error models and parameter estimation techniques for a simple system with cumulative errors are available in the literature\textsuperscript{(103-108)}. However, the search for an appropriate correlated error model is very time-consuming and requires considerable computation. To circumvent this problem it was decided to obtain uncorrelated data via experimentation. This was accomplished by repeating the step response experiments at each of the desired operating conditions a number of times and only one data point was taken from each of the continuous concentration curves generated. Since the duration of these experimental tests was relatively short ($\approx 30$ min) this represented a viable and favorable alternative. The response data used to fit both the measurement device model and the combined measurement device/reactor model were obtained in this manner.
5.3.4 Measurement Device Model

The thermal conductivity cell's response to a step change in feed gas at a gas flowrate of 500 cm$^3$/min is shown in Figure 5-11. The transient portion of the response takes place in approximately 1.2 seconds. This short response time would usually be negligible, however because the nominal reactor residence times are in the same order of magnitude, the dynamics of the cell had to be accounted for. The thermal conductivity cell's response curve has been modelled successfully with the tanks in series model ($N$ equal size backmix tanks in series). An advantage of this mathematical representation is that the parameter $N$ gives a measure of the approach to a perfect plug flow response (Figure 5-12). The exit age distribution for the model can be expressed as follows: \(^{(23)}\)

$$E(t) = \frac{1}{\tau} \left( \frac{t}{\tau} \right)^{N-1} \frac{1}{(N-1)!} \exp \left( -\frac{t}{\tau} \right)$$

where

$t = $ time  \\
$\tau = $ residence time in a single tank  \\
$N = $ number of tanks in series

Since the exit age distribution is the time derivative of the $F$-curve, the above expression can be integrated (details are found in Appendix G) to obtain the step response:

$$F(t) = \frac{C(t)}{C_0} = \left( \frac{1}{\tau} \right)^N \exp \left( -\frac{t}{\tau} \right) \sum_{r=0}^{N-1} \left( \frac{(-1)^r t^{N-1-r}}{(N-1-r)! \left(\frac{-1}{\tau}\right)^{r+1}} \right)$$

Equation 5-1
Figure 5-11

Actual measurement device step response, gas flowrate 8.3 cm³/s
Figure 5-12  F-curve for N tanks in series model.
A nonlinear least squares technique can be used to obtain the parameters $\tau$ and $N$ in the model provided the data satisfied the least squares assumptions. Uncorrelated data, obtained in the manner described in the previous section, were used in fitting the model. Figure 5-13 shows the results of modelling the measuring instrument using uncorrelated response values. For comparison, Figure 5-14 shows the results of fitting the model to the correlated response values obtained from one concentration-time curve. There is more scatter in the uncorrelated data which reflects the uncertainty in the data points obtained from different experiments. This scatter is not unrealistic when one notes the time scale of 1 second. The trend in the residuals (predicted concentration value at $t_\text{u}$ less the measured value at $t_\text{u}$) in Figure 5-14 is typical of autocorrelated data.

The two parameters $\tau$ and $N$ in the tanks in series model were obtained by using a non-linear parameter estimation technique in the Fortran package called NONLIN. The parameter $N$ presented a problem since values of $N$ were restricted to positive integer values. Therefore in order to estimate $N$, the value of $N$ in the model was fixed and the value of $\tau$ obtained by minimizing the residual sum of squares. The value of $N$ was then changed and the procedure repeated. Several values of $N$ then generated the graph shown in Figure 5-15. The ideal number of tanks to use to model the instrument response is that value of $N$ corresponding to the minimum in the parabolic
Figure 5-13  Instrument Response Curve Fit with Independent Data,
Gas Flowrate: 1000 cm$^3$/min, $N = 40$, $\tau = 0.014$ s
Figure 5-14  Instrument Response Curve Fit with Autocorrelated Data, Gas Flowrate 1000 cm$^3$/min, N = 12, $\tau = 0.039s$. 
Figure 5-15  Sum of squares surface as a function of N
Gas Flowrate 1000 cm$^3$/min
curve. Unfortunately for gas flow rates above 750 cm$^3$/min the number of tanks exceeded 40 which surpassed the computer calculation range. However, the shape of the curve in Figure 5-15 suggests a very shallow sum of squares surface so that very little improvement was taking place as $N$ increased beyond 20. The best-fit models in the least squares sense for the instrument response at three feed gas flowrates are presented in Figures 5-16, 5-17 and 5-18. These values of $\tau$ and $N$ were used as initial guesses for the multiresponse parameter estimation in the combined reactor/measurement device model.

5.3.5 Reactor Model

Many approaches exist to model the mixing characteristics of reactors. Some of these were discussed in Section 3.4. For the purpose of modelling the internal recirculation reactor used in this study, a mixed model was chosen because

1. complete mixing behavior could be described and

2. the extent and nature of any deviation from complete mixing behavior could be described.

A schematic of the reactor mixed model is given in Figure 5-19. The three different flow regions were suggested by the internal structure of the reactor. The series plug flow region ($T_{ps}$) represents a time delay encountered in the inlet and exit lines of the reactor. The parallel plug flow region ($T_{pp}$) represents that portion of the feed gas moving from the
Figure 5-16 Measurement device model fitted to uncorrelated data, gas flowrate 500 cm$^3$/min, $N = 26$, $\tau = 0.03$ (s)
Figure 5-17 Measurement device model fitted to uncorrelated data, gas flowrate 750 cm³/min, N = 40, τ = 0.016 s.
Data from two separate experiments.
Figure 5-18 Measurement device model fitted to uncorrelated data, gas flowrate 1000 cm$^3$/min, $N = 40$, $\tau = 0.0143s$
Figure 5-19 Schematic representation of reactor mixed model
reactor inlet to the reactor exit without being backmixed (e.g. gas flow up magnedrive shaft, gas flow short-circulating solid bed, etc.). The backmix region ($T_B$) represents that portion of the gas which is being completely mixed. If the free volume in the reactor assembly is denoted by $V_T$ (mL) and $1$, $m$ and $n$ correspond to those fractions of the total volume of the reactor that behave as the gas regions just described then one can define the following parameters:

$$T_{PS} = \frac{V_T}{V_0} = \frac{V_{PS}}{V_0}; \quad T_{PP} = \frac{mV_T}{V_0} = \frac{V_{PP}}{V_0}; \quad T_B = \frac{nV_T}{V_0} = \frac{V_B}{V_0}$$

where $V_0$ is the feed gas flow rate

$T_{PS}$ is the residence time of the gas in the series plug flow region

$T_{PP}$ is the residence time of the fluid in the backmix region

$R$ is the fraction of the feed gas flow being backmixed

$$\frac{T_{PP}}{(1-R)}$$ is the residence time of the fluid in the plug flow region in parallel with backmix region

$V_{PS}$ volume of series plug flow region

$V_{PP}$ volume of parallel plug flow region

$V_B$ volume of completely mixed region

$V_T$ total reactor volume

The step response of this reactor mixed model is derived in Appendix H and is summarized below in the time domain:
\[ F(t) = R[1 - \exp \left( \frac{R}{TB} \left( T_{ps} - t \right) \right) u(T_{ps}) + (1 - R) u(T_{pp} + T_{ps})] \]

Equation 5-2

This is a very flexible model and depending upon the values of the parameters \( R, T_{pp}, T_{ps} \) and \( TB \) several special cases can be described:

1. As \( R \to 1, T_{pp} \to 0, T_{ps} \to 0 \) complete mixing behavior is approached

2. As \( R \to 1, T_{pp} \to 0 \) complete mixing and plug flow sections exist in series (e.g. inlet and outlet lines of a completely mixed system are a significant portion of the total reactor volume)

3. \( 0 < R < 1, T_{pp} \to 0 \) some bypassing (short-circuiting) is occurring

4. \( 0 < R < 1, T_{pp} > 0 \) parallel plug flow region exists
5. As $R \to 0$, plug flow behavior is approached.

6. $V_T (V_B + V_{pp} + V_{PS} + V_D)$
   dead space or stagnant zone exists
   
   $< \text{known reactor volume}$

It is evident that the model chosen is general enough to cover a wide variety of flow situations that may exist within the reactor.

The reactor response to a step change in feed gas concentration cannot be determined independently of the measuring device. Therefore, the two models, the measurement device model discussed in the previous section and the reactor mixed model presented here must be combined to fit the step response data. A schematic representation of the combined reactor/measurement device model is depicted in Figure 5-20. The step response of this combined model can be derived most easily in the Laplace Domain as shown in Appendix I. The mathematical equation is given below:

$$F(s) = \frac{(1/\tau)^N}{1/(s + 1/\tau)^N} \left[ R \exp \left( -\frac{T_P}{s} \right) \left( \frac{R}{TB} \right) \left( \frac{s + R}{TB} \right) \right] + (1-R) \exp \left( -\frac{Ts}{T_P + T_{pp}/(1-R)} \right)$$  

Equation 5-3
Figure 5-20 Schematic representation of combined reactor/measurement device model
Analysis of the combined reactor/measurement device data alone using this model may yield misleading results since deviations from complete mixing behavior could be mistakenly accounted for by the instrument. The independent determination of the instrument response model as described in the previous section and the multiresponse parameter estimation technique discussed in the next section will help to avoid this pitfall.

5.5.6 Parameter Estimation

Conclusions about the mixing characteristics of the reactor are based upon the values of the parameters found in the mixed model. Reliable and precise estimates of these parameters are needed therefore to determine the significance of possible flow nonidealities. Multiresponse parameter estimation techniques offer some means of improving the precision of the parameter estimates for two or more responses. Since step response data was collected not only for the reactor/measurement device system but also for the measurement device alone, and since the mathematical expressions for the combined reactor/measuring device model and for the measuring device model share some common parameters, namely \( \tau \) and \( N \), multiresponse techniques can be used to fit the data simultaneously from the two responses.

A sample of the type of data collected with the mixing experiments is listed in Table 5-5. If it is assumed that there is no correlation for a single set of data between the
**TABLE 5-5**

Responses to a Step-Change in Feed Gas

<table>
<thead>
<tr>
<th>ELAPSED TIME (s) $t_u$</th>
<th>RESPONSE 1 $y_{1u}$</th>
<th>RESPONSE 2 $y_{2u}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.4</td>
<td>0.358</td>
<td>0</td>
</tr>
<tr>
<td>0.5</td>
<td>0.151</td>
<td>0</td>
</tr>
<tr>
<td>0.55</td>
<td>0.275</td>
<td>0</td>
</tr>
<tr>
<td>0.6</td>
<td>0.80</td>
<td>0</td>
</tr>
<tr>
<td>0.7</td>
<td>0.909</td>
<td>0</td>
</tr>
<tr>
<td>0.8</td>
<td>0.936</td>
<td>0.0980</td>
</tr>
<tr>
<td>0.9</td>
<td>0.977</td>
<td>0.0471</td>
</tr>
<tr>
<td>1.0</td>
<td>0.966</td>
<td>0.1568</td>
</tr>
<tr>
<td>1.3</td>
<td>1</td>
<td>0.2353</td>
</tr>
<tr>
<td>1.7</td>
<td>1</td>
<td>0.4471</td>
</tr>
<tr>
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</tr>
<tr>
<td>2.7</td>
<td>1</td>
<td>0.6941</td>
</tr>
<tr>
<td>3.2</td>
<td>1</td>
<td>0.8078</td>
</tr>
<tr>
<td>3.7</td>
<td>1</td>
<td>0.8627</td>
</tr>
<tr>
<td>4.2</td>
<td>1</td>
<td>0.9019</td>
</tr>
<tr>
<td>4.8</td>
<td>1</td>
<td>0.9451</td>
</tr>
<tr>
<td>5.3</td>
<td>1</td>
<td>0.9490</td>
</tr>
</tbody>
</table>

Response 1: Instrument Response for Gas Flow rate 1000 cm$^3$/min

Response 2: Combined Reactor/Measuring Device Response for Gas Flow Rate: 1000 cm$^3$/min, Particle Size: 1.0 - 1.4 mm, Impeller Speed: 1800 rpm
observed instrument response value at $t_u$ and the observed combined response value at $t_u$, then the appropriate criterion to use is to minimize the following weighted sum of squares (117).

$$SS = SS_1 + SS_2$$

$$SS_1 = \sum_{u=1}^{n} \frac{(y_{u1} - f_{u1}(t_u, \theta))}{\sigma_{u1}^2}$$

Equation 5-4

$$SS_2 = \sum_{u=1}^{n} \frac{(y_{u2} - f_{u2}(t_u, \theta))}{\sigma_{u2}^2}$$

where $t_u$ is the value of the independent variable, time, for the $u$'th observation.

$y_{u1}$ experimental value of $C/C_0$ for measurement device response at $t_u$.

$f_{u1}$ calculated value of $C/C_0$ for measurement device response at $t_u$ with parameters $\theta$.

$\theta$ vector of parameter values.

$y_{u2}$ experimental value of $C/C_0$ for combined reactor/measuring device response at $t_u$.

$f_{u2}$ calculated value of $C/C_0$ for combined response at $t_u$ with parameters $\theta$.

$\sigma_{u1}^2$ variance of instrument response at $t_u$.

$\sigma_{u2}^2$ variance of combined response at $t_u$.

This sum of squares is a generalization of the nonlinear least squares parameter estimation technique. The assumptions
involved are justified in the present context because the two responses were measured independently with very similar experimental arrangements.

The mathematical model form given in Equation 5-3 for the combined model \( f_{u2} \) is in the Laplace domain. In order to compare the actual experimental data with the model response in the time domain using the criterion just presented, it was necessary to obtain the time domain solution of the model. An IMS library algorithm (FLINV) was used to find the inverse Laplace of the model function at every required time value. The advantages of direct non-linear regression in the time domain over parameter estimation in the Laplace domain were discussed in Section 5.4.4. Briefly, regression in the time domain is preferred because one is comparing the actual data with the model response and so the criterion is minimizing errors directly with the data. Laplace domain techniques require transformations of the actual data to the S-domain. If the original data have constant variance, this may not be true of the transformed data. Also, a fit obtained in the S-domain does not guarantee the best in the least squares sense in the time domain.

Estimates of the parameters were obtained by using the criterion presented in Equation 5-4 and the IMS library minimization routine ZXMIN. ZXMIN is a general Fortran program which obtains the minimum of a function of n variables by a
Quasi-Newton method. Several parameter transformations were found useful in obtaining convergence. Since the parameters $T_B$, $T_{PS}$ and $T_{pp}$ must be positive real numbers, the simple transformations $T_B = x_B^2$, $T_{PS} = x_{PS}^2$, $T_{pp} = x_{pp}^2$, allowed the routine to search over all possible values of $x$. Similarly, the value of $R$, the fraction of the gas flow which is being backmixed must be in the range zero to unity. In order for the minimization routine to search over all possible values of $x_R$, the following transformation was found helpful, $R = \exp(-x_R^2)$. As the value of $x_R$ approaches zero, $R$ approaches unity. As the value of $x_R$ gets very large ($\pm \infty$), $R$ tends to zero. The minimization routine was highly sensitive to estimates of $\tau$, the tanks-in-series parameter. It was necessary to use the following transformation on the parameter $\tau$ in order to limit the range over which the search for $\tau$ could be carried out, $\tau = \sin^2(\pi x_\tau^2/2 \times 10^4)$. As $x_\tau$ varies between 0 and $\pm 100$, the value of $\tau$ ranges from 0 to 1. Initial estimates for $\tau$ which were obtained with the measuring device response as described earlier, proved useful. A procedure similar to that used for obtaining the initial estimate for $N$ was adopted in estimating the values of $N$ in the multiresponse case. Transformations of both the independent variable (time) and dependent variable (concentration ratios) by a simple multiplication by a constant was also necessary since the inversion algorithm (FLINV) encountered some difficulty when the time vector contained a wide range of values. Scaling the
time vector by a factor of 20 and the concentration ratios by a factor of 4 improved convergence to the accuracy required.

An approximate 100(1- α)% confidence interval for each of the parameters τ , T_B, T_pp, T_ps and R was calculated as shown below (148).

\[ \hat{\theta}_s - t_{\nu,\alpha} \sqrt{m^{ss}} \leq \theta_s \leq \hat{\theta}_s + t_{\nu,\alpha} \sqrt{m^{ss}} \]  

Equation 5-5

where \( \hat{\theta}_s \) is the estimated value of the parameter \( s \)

\( t_{\nu,\alpha} \) is the t-value from tables for \( \nu \) degrees of freedom at the (1- α) confidence level

\( m^{ss} \) are the elements of the inverse of the following matrix:

\[ M = X_1^T X_1 / \sigma_{11}^2 + X_2^T X_2 / \sigma_{22}^2 \]

The matrix \( X_i \) is the nxp matrix whose elements are \( \{ x_{us} \} \) shown below:

\[ (x_{us}) = \left\{ \frac{\partial f_i (t_u, \theta)}{\partial \theta_j} \right\} \bigg|_{\theta = \hat{\theta}} \]

where \( n \) = total number of time values or independent runs

\( p \) = total number of parameters

\( \theta \) = the vector of \( p \) parameters to be estimated

\( \hat{\theta} \) = the vector containing \( p \) estimates of the parameter
The variance $\sigma_{11}$ was estimated by $(SS_{11}/(n-p))$. The variance $\sigma_{22}$ was estimated by $S_{22}/(n-p)$. A copy of the fortran program and output is provided in Appendix J.

5.3.7 Results and Discussion

Parameter estimates obtained from using the multiresponse criterion and approximate 95% confidence limits are given in Table 5-6. It can be seen that in all cases, $T_{PP}$ and therefore $V_{pp}$ the parallel plug flow volume are negligible and $R$ the fraction of the total flow which is being backmixed is unity. The approximate confidence intervals for these two parameters encompass 0 and 1 respectively. These parameters were subsequently deleted from the combined model. It was not found necessary to search over different values of $N$ because of the closeness of the value of $\tau$ found in the multiresponse case to that value found in the single response case.

The completely mixed volume ($V_B$) and the series plug flow volume ($V_{PS}$) corresponding to $T_B$ and $T_{PS}$ respectively as well as the 95% confidence limits are given in Table 5-7. The fit of this four parameter model ($T_B$, $T_{PS}$, $\tau$, $N$) to a typical set of experimental data is shown in Figure 5-21. There are no significant trends in the residual plot shown in Figure 5-22, therefore the model appears to be adequate. Since the estimates from the single response fitting of the measurement device model yielded estimates of $N$ and $\tau$
<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th>Particle Size (mm)</th>
<th>Feed Gas Flowrate (cm$^3$/min)</th>
<th>Impeller Speed (rpm)</th>
<th>$T_B$ (s)</th>
<th>$T_{PS}$ (s)</th>
<th>$T_{PP}$ (s)</th>
<th>$R$</th>
<th>$S$ (s)</th>
<th>$N$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-</td>
<td>1000</td>
<td>1800</td>
<td>1.56 ± 0.19</td>
<td>0.675 ± 0.124</td>
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</tr>
<tr>
<td>0.2-0.4</td>
<td>500</td>
<td>-</td>
<td>1800</td>
<td>2.46 ± 0.30</td>
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<td>-</td>
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<td>26</td>
</tr>
<tr>
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<td>500</td>
<td>1800</td>
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<td>2.93 ± 0.37</td>
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</tr>
<tr>
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<td>1800</td>
<td>1.34 ± 0.21</td>
<td>0.155 ± 0.106</td>
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<td>-</td>
<td>0.014 ± 0.0007</td>
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<tr>
<td></td>
<td>1000</td>
<td>1800</td>
<td>1800</td>
<td>1.40 ± 0.28</td>
<td>0.493 ± 0.218</td>
<td>-</td>
<td>-</td>
<td>0.014 ± 0.0008</td>
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</tr>
<tr>
<td>0.4-1.0</td>
<td>750</td>
<td>900</td>
<td>-</td>
<td>2.10 ± 0.21</td>
<td>0.243 ± 0.129</td>
<td>-</td>
<td>-</td>
<td>0.016 ± 0.001</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>750</td>
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<td>900</td>
<td>2.23 ± 0.35</td>
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<td>-</td>
<td>-</td>
<td>0.016 ± 0.001</td>
<td>40</td>
</tr>
<tr>
<td>1.0-1.4</td>
<td>500</td>
<td>-</td>
<td>1800</td>
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<td>0.636 ± 0.128</td>
<td>-</td>
<td>-</td>
<td>0.030 ± 0.0012</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>1800</td>
<td>-</td>
<td>2.82 ± 0.20</td>
<td>0.871 ± 0.130</td>
<td>-</td>
<td>-</td>
<td>0.030 ± 0.0012</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>-</td>
<td>1800</td>
<td>1.50 ± 0.06</td>
<td>0.203 ± 0.056</td>
<td>-</td>
<td>-</td>
<td>0.014 ± 0.0007</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1800</td>
<td>1800</td>
<td>1.59 ± 0.07</td>
<td>0.203 ± 0.071</td>
<td>-</td>
<td>-</td>
<td>0.014 ± 0.0007</td>
<td>40</td>
</tr>
</tbody>
</table>


### TABLE 5-7

Specific Volumes of Components of Reactor Mixed Model

<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th>Particle Size [mm]</th>
<th>Gas Flowrate [cm³/min]</th>
<th>Impeller Speed [rpm]</th>
<th>V_B [mL]</th>
<th>V_PS [mL]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000</td>
<td>1800</td>
<td></td>
<td>25.9 ± 2.7</td>
<td>11.3 ± 3.6</td>
</tr>
<tr>
<td>0.2-0.4</td>
<td>500</td>
<td>0</td>
<td></td>
<td>20.5 ± 2.2</td>
<td>4.17 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>1800</td>
<td></td>
<td>24.4 ± 2.7</td>
<td>2.17 ± 1.9</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0</td>
<td></td>
<td>22.3 ± 3.1</td>
<td>2.58 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1800</td>
<td></td>
<td>23.3 ± 4.2</td>
<td>8.21 ± 3.2</td>
</tr>
<tr>
<td>0.4-1.0</td>
<td>750</td>
<td>900</td>
<td></td>
<td>26.2 ± 2.3</td>
<td>3.0 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>900</td>
<td></td>
<td>27.9 ± 3.9</td>
<td>3.88 ± 2.3</td>
</tr>
<tr>
<td>1.0-1.4</td>
<td>500</td>
<td>0</td>
<td></td>
<td>25.4 ± 1.7</td>
<td>5.33 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>1800</td>
<td></td>
<td>23.5 ± 1.5</td>
<td>7.25 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0</td>
<td></td>
<td>25.0 ± 1.8</td>
<td>3.33 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1800</td>
<td></td>
<td>26.4 ± 1.9</td>
<td>3.33 ± 1.0</td>
</tr>
</tbody>
</table>
Figure 5-21 Combined Reactor/Measurement Device Step Response
Particle Size 1.0 - 1.4 mm, Impeller Speed 1800 rpm,
Gas Flowrate 16.7 cm$^3$ s$^{-1}$
Figure 5-22 Residuals for combined reactor/measurement device model
Particle Size 1.0 - 1.4 mm, Impeller Speed 1800 rpm, Gas
Flowrate 16.7 cm$^3$ s$^{-1}$
which were not significantly different from those obtained from the multiresponse fitting, a graph showing the fit of measurement device model to the data is unnecessary.

The empty reactor volume found by water displacement experiments (i.e. by measuring the volume of water required to fill the reaction chamber) was found to be 30 mL ± 1 mL. The volume of the connecting lines to and from the reactor are estimated to be in the order of 1 mL. The total reactor volume found through the mixing experiments is 37.2 ± 6.1 mL. This is therefore consistent with the water displacement tests in the lower half of the interval.

Estimated theoretical voidage volumes in the char bed corresponding to the different particle sizes were found based on Leva's correlation, details of which may be found in Appendix K. A comparison of the total volume available for the gas found by the modelling and that estimated based on the voidages is presented in Table 5-8. The total gas volumes found with the two methods are consistent.

Analysis of the factorial design led to the following expression for the backmix volume:

\[ V_B = 24.50 + 0.55 \left( \frac{\text{RPM} - 900}{900} \right) + 0.41 \left( \frac{\text{FR} - 750}{750} \right) + 0.115 \text{PS} \quad \text{Equation 5-7} \]

where RPM = impeller speed
FR = feed gas flowrate
TABLE 5-8

Comparison of Free Gas Volume in the Reactor

<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th>Calculated</th>
<th>Estimated*</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Particle</td>
<td>Feed Gas</td>
</tr>
<tr>
<td></td>
<td>Size</td>
<td>Flowrate</td>
</tr>
<tr>
<td>[mm]</td>
<td>[cm$^3$/min]</td>
<td>[rpm]</td>
</tr>
<tr>
<td>0.2-0.4</td>
<td>500</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>1800</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1800</td>
</tr>
<tr>
<td>0.4-1.0</td>
<td>750</td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>900</td>
</tr>
<tr>
<td>1.0-1.4</td>
<td>500</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>1800</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>1800</td>
</tr>
</tbody>
</table>

* Based on an Empty Reactor Volume Between 32-42 mL
PS = particle size = 0 for particles 0.4 - 1.0 mm
-1 for particles -0.2 - 0.4 mm
+1 for particles 1.0 - 1.4 mm

The volume of the reactor which is being completely mixed can be increased therefore by increasing the impeller speed, increasing the feed gas flowrate, and decreasing the bed pressure drop by using larger particles. The small plug flow region, which under the operating conditions examined accounted for 8 to 12 percent of the reactor volume, may only be reduced by using feed gas flowrates above 1000 cm³/min since the impeller speed of 1800 rpm is at the maximum tolerance, and particles larger than 1.4 mm will present pore diffusion problems.

5.4 Other Tests

5.4.1 Gas Flow Pattern in Solids Bed

Tests were carried out in order to determine whether the gas flow through the solid char bed was uniform for those operating conditions which most closely approached the complete mixing assumption. For this purpose, the annular basket was charged with indicating drierite (CaSO₄) and indicating
ascarite II as shown in Figure 5-23. Helium with a small amount of CO$_2$ was fed to the reactor for 30 minutes. During use, the normally light greenish brown color of Ascarite II should gradually turn to white due to absorption of CO$_2$ and formation of sodium carbonate. At the end of the allotted time, the reactor was taken apart and the layers visually inspected. This experiment was repeated with various quantities of CO$_2$ added for varying lengths of time (up to 1 1/2 hrs). The results of all these experiments were the same. The layers of ascarite which should have turned white with the formation of Na$_2$CO$_3$ in the presence of CO$_2$ did not change color. Layer A was always very moist so that a small amount of reaction with carbon dioxide was taking place. However, very little if any color change was observed even in this layer. In the upper layers the ascarite was progressively less moist. This would indicate that some of the gas must be bypassing the solid bed since the quantities of CO$_2$ and the flowrates of the feed gas used should have made the ascarite turn white. Approximate calculations of the pressure head developed by the impeller (see Appendix L) show that the suction provided may not be sufficient to allow for recirculation through the ascarite/drierite bed.

5.4.2 Temperature Profile

The three Chromel Alumel Type K thermocouples used in measuring the reactor temperature were checked against a
Figure 5-23 Schematic of solid packing for gas flow determination
Figure 5-24  Thermocouple arrangement inside reactor bed
Figure 5-25  Axial temperature profile in char bed
mercury thermometer up to 650\(^\circ\)C and against a pyrometer over the range 400-1000\(^\circ\)C with a Leeds and Northrup model 8686 millivolt potentiometer. As expected, at temperatures above 600\(^\circ\)C there was very little difference in the millivolt readings from all three thermocouples (~ 0.3 mv equivalent to 8\(^\circ\)C). The positioning of the thermocouples inside the reactor is illustrated in Figure 5-24. The central TC could be moved throughout the height of the solid bed. With \(N_2\) flowing through the reactor, the reactor was heated to 800\(^\circ\)C. The magnedrive was activated and the temperature inside the central sheath was measured at the different positions. The axial temperature profile for the nonreacting system found in this manner is given in Figure 5-25. It can be seen from this profile that a large temperature gradient exists throughout the solid bed. This gradient may be due to a number of reasons. First, despite the heavy insulation, the influence of the water cooling (needed to keep the shaft bearings below 300\(^\circ\)C) on the temperature in the reaction chamber is significant, i.e. a large driving force exists for conduction of heat up the shaft. A longer shaft may improve this problem in the upper third of the bed however, increasing the length of shaft further is not possible because of problems encountered in vibrations of the impeller shaft. The reason for the large temperature drop in the bottom 1/3 of the solid bed is due to conduction of heat along the thermocouple well to the exterior of the reactor where water cooling is provided to keep the Teflon seal in operation. The seal allows the thermocouple to
be moved vertically in the bed. This problem could have been circumvented by using a multipoint thermocouple inside the well with the leads connected to a multipoint potentiometer. Finally, since there is some evidence of poor gas circulation in the char bed, this too may contribute to the existing temperature gradient.

The radial temperature profile inside the solid bed cannot be assessed with the present reactor. Nevertheless, there appears to be a large temperature difference between the temperature of the controlling thermocouple (800°C) and the central thermocouple. Some of this difference can be accounted for by conduction of heat across the steel surfaces. Isothermal operation even for the nonreacting system could not be achieved with this reactor without some major modifications. It was therefore decided to assess the potential of the reactor based on the testing carried out up to this point and to determine whether further testing was warranted.

5.5 Conclusion

Analysis of the reactor model parameters has revealed that the internal recirculation reactor designed and built in this study is not completely mixed under any of the operating conditions examined. A small plug flow region (in the order of 10% of the total available volume) exists in series with the
completely mixed section. This plug flow region is too large to be entirely accounted for by the inlet and exit lines to the reactor. This suggests that some minor changes in the reactor design or in the operating conditions are necessary to obtain complete mixing in the reaction chamber. Because of the nature of the reactor, modifications to it are both expensive and time-consuming.

Testing carried out to determine the reactor temperature profile has shown that even for the non-reacting system, isothermality has not been achieved. It remains quite a challenge in reactor assembly construction to minimize conduction up the shaft at elevated temperatures.

The problems enumerated above are serious since recirculation reactor data analysis is based on the assumptions of isothermality and complete mixing. In view of this, no gasification experiments were conducted with this reactor.
6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

1. A critical evaluation of bench-scale reactors in current use for studying gasification kinetics has led to the following conclusions:

a. Many investigators fail to completely characterize the reactor system and use unfounded assumptions about the system to derive gasification kinetic models from the measured rate data.

b. Two major weaknesses in the reactor systems in use have been identified. First, in all the reactors (with the exception of the fluidized bed, perhaps), the maintenance of isothermality is difficult. Second, the degree of gas phase mixing in the reactors does not usually approach the mixing state generated by either of the ideal flows.

2. Three alternative reactors which have some potential in overcoming the major limitations of the reactors presently being used in char gasification have been identified, namely, the internal and external recirculation reactors and the continuous stirred tank reactor.
3. Experimental testing has been carried out on an internal recirculation reactor designed and built in this study. Two distinct problems have not been overcome: severe conduction along the rotating shaft and reaction chamber design for complete mixing behavior to prevail.

4. The approach presented in this study for deriving the residence time distribution for small reactors where the measurement device dynamics are significant has been shown to be a useful tool for testing the gas phase mixing assumptions.

6.2 **Recommendations for Future Work**

It is recommended that further work with a modified version of the reactor discussed in this study be considered because of the potential of using an internal recycle reactor to study gasification kinetics. Modifications to the present reactor are needed in two major areas. First, the reaction chamber internals should be modified so that the fluid flow approaches complete mixing and second, the magnedrive assembly bearings and seals should be changed to allow operation at higher temperatures without the need for cooling. The latter may be accomplished by investigating the possibility of using ceramics instead of teflon and graphite as materials. Several suggestions for designing the reaction chamber so that complete mixing is approached are given below:
1. increase the capacity of the drive motor so as to increase the impeller RPM.
2. obtain the pressure drop versus flow relationship for the solid bed.
3. obtain the velocity head developed by the impeller as a function of its rpm by building a precursor to the reactor with special pressure taps.

The solid bed dimensions and the impeller design can be determined from 1, 2 and 3 accordingly.

If sufficient funds are available, commissioning this work to Autoclave Engineers is recommended.
REFERENCES


REFERENCES (cont'd)


REFERENCES (cont'd)


REFERENCES (cont'd)


REFERENCES (cont'd)


REFERENCES (cont'd)


REFERENCES (cont'd)


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REFERENCES (cont'd)


REFERENCES (cont'd)


REFERENCES (cont'd)


REFERENCES (cont'd)


REFERENCES (cont'd)


REFERENCES (cont'd)


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     (1966).
REFERENCES (cont'd)


REFERENCES (cont'd)


REFERENCES (cont'd)


REFERENCES (cont'd)


APPENDIX A

Compilation of Char Gasification
Bench-Scale Kinetic Studies
## APPENDIX A

Compilation of Char Gasification Bench Scale Kinetic Studies

<table>
<thead>
<tr>
<th>REFERENCES</th>
<th>REACTOR TYPE</th>
<th>CARBON/CHARACTERISTICS</th>
<th>SAMPLE PRETREATMENT</th>
<th>OPERATING CONDITIONS</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>118</td>
<td>Integral Fixed Bed L 10 cm D 3.1 cm</td>
<td>Charcoal 35 gm 8-10 B.S.S.</td>
<td>Active charcoal (from carbonization &amp; steam activation) of coconut shell &amp; briquetted coal</td>
<td>T: 700 - 800°C P: 10-760 mm Hg F: 1200 cc/min</td>
<td>Steam-carbon reaction kinetics</td>
</tr>
<tr>
<td>119</td>
<td>Differential Tubular Bed D 1.5 cm Integral</td>
<td>Porous graphite tubes length .75&quot; length 9&quot; 20 gm</td>
<td>Partial degassing in vacuum &amp; flushing with N₂</td>
<td>T: 862-930°C P: 1 atm F: 900 ml/min</td>
<td>Steam-carbon reaction kinetics</td>
</tr>
<tr>
<td>47</td>
<td>Integral Fixed Bed 3in1D</td>
<td>High temperature pitch coke .078-.053&quot;</td>
<td></td>
<td>T: 1800-2500°F P: 1 atm</td>
<td>Steam-carbon reaction kinetics at high temperature</td>
</tr>
<tr>
<td>120</td>
<td>Integral Fixed Bed L = 1.25 in D = 2-3 in</td>
<td>Coke .4 mm particles 30 gm</td>
<td>Coke was first flushed with nitrogen at required temperature.</td>
<td>T: 800-950°C P: 1 atm F: 35-75 1ph (NTP)</td>
<td>Reactivity of coke and steam vs Rank, Particle Size, Steam Flow, etc.</td>
</tr>
<tr>
<td>9</td>
<td>Integral Fixed Bed D = 3 in L = 5 in</td>
<td>Pitch coke -10 + 40 US sieve</td>
<td></td>
<td>T: 1700-2100°F P: 1 atm</td>
<td>Carbon reaction with steam &amp; CO₂ - Obtained &amp; interpreted reaction rate data</td>
</tr>
<tr>
<td>52</td>
<td>Differential Tube Reactor L 1.8 cm</td>
<td>Coconut charcoal 8.8 gm -7 + 14 mesh</td>
<td>Charcoal heated to 950°C in 2 hrs maintained for 1 hr and cooled to atmospheric temperature in 2 hrs in N₂ stream</td>
<td>T: 750-830°C P: 1-50 atm</td>
<td>Steam-carbon reaction. To examine effect of H₂ addition to steam gasification</td>
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<td>121</td>
<td>Differential Tube Reactor</td>
<td>Purified carbon 7.5 gm</td>
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<td>T: 790-870°C P: 5-40 atm</td>
<td>Carbon-carbon dioxide reaction at high pressure</td>
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## APPENDIX A

Compilation of Char Gasification Bench Scale Kinetic Studies (cont'd)

<table>
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<th>REFERENCES</th>
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<th>COMMENTS</th>
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<tbody>
<tr>
<td>122</td>
<td>Fixed Bed</td>
<td>Carbon wear dust</td>
<td>Sample heated to 850°C in vacuo for 3 hours</td>
<td>T: 500-600°C P: low 2.7-16 uHg</td>
<td>Carbon-carbon dioxide low-pressure gasification</td>
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<tr>
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<td></td>
<td>spectrographic graphite</td>
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<tr>
<td>123</td>
<td>Differential</td>
<td>Coconut-shell charcoal</td>
<td></td>
<td>T: 650-870°C P: 40 atm</td>
<td>Kinetics of system C-H₂-methane</td>
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<tr>
<td>tubular bed</td>
<td></td>
<td>8.8 gm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-7 + 14 mesh</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>124</td>
<td>Differential</td>
<td>Bituminous coal char</td>
<td></td>
<td>T: 1700°F P: 2500 psia</td>
<td>Kinetics of H₂/H₂O/C system at high pressure</td>
</tr>
<tr>
<td>D= 2 in</td>
<td></td>
<td>anthracite -16 +20 m</td>
<td></td>
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</tr>
<tr>
<td>L = 60 in</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>46</td>
<td>Differential</td>
<td>Coal char from</td>
<td></td>
<td>T: 1700-2100°F P: 1000 psig F: 50 scf/hr</td>
<td>Carbon-H₂/H₂O kinetics</td>
</tr>
<tr>
<td>reactor</td>
<td></td>
<td>Pittsburgh seam coal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D = 1 1/4 in</td>
<td></td>
<td>-16 +20 USS 2.5-5 gm</td>
<td></td>
<td></td>
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<tr>
<td>125</td>
<td>Differential</td>
<td>Variety of coals</td>
<td>Slow heating 10°C/min to required temperature pyrolysis &amp; gasification</td>
<td>T: 400-1100°C P: 1-70 atm</td>
<td>Non-isothermal kinetics of steam gasification</td>
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<tr>
<td>fixed bed</td>
<td></td>
<td></td>
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<tr>
<td>44</td>
<td>Fixed bed</td>
<td>Bituminous coal 20 - 60 mesh</td>
<td>Pretreated at 450°C with steam-air mixture to remove caking properties</td>
<td>T: 1500-1800°F P: 300 psi F: 2000 cm³N₂/hr</td>
<td>Catalytic study of steam gasification</td>
</tr>
<tr>
<td>L = 6 in</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D = 3/4 in</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>126</td>
<td>Fixed bed</td>
<td>Sub-bituminous coal</td>
<td></td>
<td>T: 650°C P: 2 atm</td>
<td>Catalytic study of steam gasification (N₂, alkali carbonate catalysis)</td>
</tr>
<tr>
<td>D = 1 in</td>
<td></td>
<td>60-100 mesh 100 gm coal 110 gm catalyst</td>
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# APPENDIX A

Compilation of Char Gasification Bench Scale Kinetic Studies (cont'd)

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<tr>
<th>REFERENCES</th>
<th>REACTOR TYPE</th>
<th>CARBON/CHARACTERISTICS</th>
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<th>OPERATING CONDITIONS</th>
<th>COMMENTS</th>
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<tr>
<td>127, 128</td>
<td>Fixed bed</td>
<td>Brown coal char 89-22 um</td>
<td>Partial combustion of pulverized brown coal</td>
<td>T: 3.57-4.87°C P: 1 atm</td>
<td>Reactivity of char to O₂ - intrinsic reactivity</td>
</tr>
<tr>
<td>5</td>
<td>Fixed bed</td>
<td>Petroleum coke -14 +25 mesh 3 gm</td>
<td>Coke sample brought to temperature in nitrogen atmosphere</td>
<td>T: 750-950°C, P: 1 atm F: 660-1330 cm³/min NTP</td>
<td>CO₂ gasification kinetic studies intrinsic rate measurement</td>
</tr>
<tr>
<td>36</td>
<td>Fixed bed</td>
<td>Western Kentucky &amp; Bear coal chars 149-177 mm 5 gm</td>
<td>Mixing of char with catalyst in slurry Evaporation of H₂O at low temperature</td>
<td>T: 600-850°C P: 1-2 atm F: 1 ml/min</td>
<td>Kinetic &amp; catalytic study of coal-steam gasification</td>
</tr>
<tr>
<td>54</td>
<td>Differential flow packed bed</td>
<td>Chars from Roland &amp; Felix seam subbituminous Wyoming coals 35 gm</td>
<td>Coal first pyrolysed in H₂, or CO₂. Char sample prepared by heating coal at 800°C in flowing argon</td>
<td>T: 475-675°C P: 1 atm F: 45-425 l/hr</td>
<td>C-H₂O, C-CO₂ reaction Analysed data in terms of average initial rates for 0-20% burnoff and average final rates for 70-100% burnoff</td>
</tr>
<tr>
<td>78</td>
<td>Differential packed bed</td>
<td>German bituminous coal</td>
<td></td>
<td>T: 600-1100°C P: 1-70 atm</td>
<td>Steam/H₂ gasification</td>
</tr>
<tr>
<td>49</td>
<td>Integral fixed bed</td>
<td>Illinois coal #6 20 gm</td>
<td>Purge catalyst impregnated char with helium &amp; raise temperature</td>
<td>T: 1200-1300°F P: 0-500 psig F: 3-100 gm/hr steam</td>
<td>Catalytic steam gasification conversions high</td>
</tr>
<tr>
<td>159</td>
<td>Thermo-gravimetric</td>
<td>AGKSP spectroscopic graphite 0.27 gm 9.91 1; 0.71 ID; 0.47 OD [cm]</td>
<td>Specimen were boiled in distilled H₂O desicated, washed in absolute methanol, and then heated to 1000°C in vacua for 1 hr</td>
<td>T: 500-900°C P: 7.6 cm Hg V</td>
<td>Reaction: CO₂-C Purpose: To determine the nature of the time dependence of the reaction rate for several temperatures, the nature &amp; the role of surface oxide in the reaction, and the role of traces of impurities on the rate of the reaction.</td>
</tr>
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<td>REFERENCES</td>
<td>REACTOR TYPE</td>
<td>CARBON/CHARACTERISTICS</td>
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<tr>
<td>130,8</td>
<td>Thermo-gravimetric</td>
<td>Spectroscopic carbon Extrusion into rod reactor tube: 1 1/2&quot; ID, carbon rods 2&quot; long x 1/2&quot; OD and 1/8&quot; hone in centre 8.8 gm</td>
<td>T: 925-1305°C P: 1 atm F: 2200 cc/min</td>
<td>Reaction: CO₂ - C Purpose: Investigate mass transfer and diffusional effects</td>
<td></td>
</tr>
<tr>
<td>131</td>
<td>Thermo-gravimetric</td>
<td>Speer moderator - 2 graphite &amp; ATJ graphite 19 gm 2.54 cm D sperical specimen Specimen was degassed for 4 days under vacuum at 1025°C prior to use</td>
<td>T: 775-925 &amp; 875-1025°C P: 1 atm F: 300 cc/min</td>
<td>Reaction: H₂O vapor/CO₂-C Purpose: To study oxidation rates of two different graphites and to compare the results</td>
<td></td>
</tr>
<tr>
<td>132</td>
<td>Thermo-gravimetric</td>
<td>TSC nuclear graphite 8 gm 1.08 cm ID 5.08 cm 1erature for 18-24 hours cylindrical solid specimen Specimen was exposed to helium at the set temp</td>
<td>T: 790-850°C P: -</td>
<td>Reaction: H₂O vapor/H₂-C Purpose: Mechanistic study of H₂O-H₂-C gasification</td>
<td></td>
</tr>
<tr>
<td>133</td>
<td>Thermo-gravimetric</td>
<td>Cokes &amp; calcined chars from subbituminous coals 200-500 mg -16 + 20 mesh U.S. granular</td>
<td>T: 900-1100°C P: 1 atm V: 10-15 cm/s F: 2879-47:30 cc/min</td>
<td>Reaction: CO₂-C Purpose: To develop a test that would compare reactivities of granular carbons and to gain some knowledge of the influence of rather mild thermal treatment on the reactivity of these cokes</td>
<td></td>
</tr>
<tr>
<td>134</td>
<td>Thermo-gravimetric</td>
<td>Spectroscopic graphite SP-1</td>
<td>T: 800-1000°C P: 1 atm</td>
<td>Reaction: CO₂-C Purpose: Catalytic study using Fe, Ni, Co as catalysts for gasification</td>
<td></td>
</tr>
<tr>
<td>135</td>
<td>Thermo-gravimetric</td>
<td>Electrode graphite spheres 7/8&quot;-7/8&quot;D blocks</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
## APPENDIX A

Compilation of Char Gasification Bench Scale Kinetic Studies (cont'd)

<table>
<thead>
<tr>
<th>REFERENCES</th>
<th>REACTOR TYPE</th>
<th>CARBON/CHARACTERISTICS</th>
<th>SAMPLE PRETREATMENT</th>
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<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>136</td>
<td>Thermo-gravimetric</td>
<td>Coconut charcoal, 1% ash, electrode graphite AUC &amp; (.03%) metallurgical coke (7.5% ash) 70-200 mg granules (.5 mm D) -10 ± 16 m</td>
<td></td>
<td>T: 700-1400°C  P: 10-3-40 atm  F: 1200 cc/min - 1500 (STP)</td>
<td>Reaction: CO₂-C  Purpose: A kinetic and mechanistic study of gasification using CO₂ and mixtures of CO &amp; CO₂</td>
</tr>
<tr>
<td>46</td>
<td>Thermo-gravimetric</td>
<td>Ireland-Mine, Pittsburgh, etc. Bituminous coal char 0.5-1.5 g granules: 20-40 USS (wire-mesh basket)</td>
<td>Several pretreatment modes: nitrogen, air  char pretreated</td>
<td>T: 815-1040°C  P: 1-40 atm</td>
<td>Reaction: H₂-C  Purpose: Kinetic study of hydrogasification using hydrogen and steam-hydrogen mixtures: Modeling</td>
</tr>
<tr>
<td>40</td>
<td>Thermo-gravimetric</td>
<td>Pittsburgh Seam Ireland Mine Bituminous Coal 1.5 - 2.5 g granules: 18x35 mesh</td>
<td>No pretreatment for char A, and preoxidation using air for char B</td>
<td>T: 1000°C  P: 136 atm  F: 4700-19000cc/min</td>
<td>Reaction: H₂-C  Purpose: To study the kinetics of catalysed hydrogasification at high temperatures and pressures</td>
</tr>
<tr>
<td>10</td>
<td>Thermo-gravimetric</td>
<td>Variety of coals (20) 5-30 mg AO x 100 US mesh granular</td>
<td>Sample heated in a stream of dry nitrogen to a max. temp. at a const. heating rate and held there for 2 hrs.</td>
<td>T: 500°C  P: 1 atm  F: 500 cc/min</td>
<td>Reaction: Air-C  Purpose: To develop a simple reactivity test to be used on a wide range of coal chars &amp; to obtain some measure of the variables which affect it</td>
</tr>
<tr>
<td>74</td>
<td>Thermo-gravimetric</td>
<td>Pittsburgh #8 chars &amp; Ireland coal mine char (Bituminous) -20 +40 USS granular-basket (2-3 diameter layer)</td>
<td>Air pretreatment</td>
<td>T: 840-1210°C  P: 0-80 atm</td>
<td>Reaction: H₂-C  Purpose: Study kinetics of char gasification using hydrogen and hydrogen-steam mixtures</td>
</tr>
</tbody>
</table>
## APPENDIX A

Compilation of Char Gasification Bench Scale Kinetic Studies (cont'd)

<table>
<thead>
<tr>
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<th>REACTOR TYPE</th>
<th>CARBON/CHAR CHARACTERISTICS</th>
<th>SAMPLE PRETREATMENT</th>
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</tr>
</thead>
<tbody>
<tr>
<td>137</td>
<td>Thermo-</td>
<td>Metallurgical coke coal char from FMC pulverized graphite</td>
<td>Preheat in N₂ atmosphere</td>
<td>T: 1800-2240°F P: 1 atm</td>
<td>Shrinking core model for gasification of graphite using SO₂ to get CO + elemental sulfur</td>
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<tr>
<td></td>
<td>gravimetric</td>
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<tr>
<td>38</td>
<td>Thermo-</td>
<td>Several coals: IGT, Varied Hydrane, Pittsburgh, etc. 15-50 mg -35 +60m granular-platinum pan</td>
<td></td>
<td>T: 840-1100°C P: 1 atm F: 200 cc/min</td>
<td>Reaction: CO₂-C Purpose: Find relationship between reactivities and physical characteristics of samples, i.e. porosity, surface area, etc.</td>
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<tr>
<td></td>
<td>gravimetric</td>
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<td></td>
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</tr>
<tr>
<td>138</td>
<td>Thermo-</td>
<td>4 coals of low rank 10 mg 35 x 80 mesh granular plan</td>
<td>Coal pyrolysed in N₂ at H.R. - 80³/min to 900³C &amp; held there for 2 hours</td>
<td>T: 750-900³C P: 1 atm</td>
<td>Reaction: Both H₂O-C and O₂-C Purpose: To determine the apparent activation energy for the separate reactions and to estimate the value of the relative rates at a common temperature</td>
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<tr>
<td></td>
<td>gravimetric</td>
<td></td>
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</tr>
<tr>
<td>66</td>
<td>Thermo-</td>
<td></td>
<td></td>
<td>T: 500-900³C P: 1 atm F: 5-15 cm/s</td>
<td>Reaction: H₂O-C Purpose: Kinetics</td>
</tr>
<tr>
<td></td>
<td>gravimetric</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>139</td>
<td>Thermo-</td>
<td>Variety of coals 5-10 mg 40 x 100 m granular, pan</td>
<td>Coal was heated at a rate of 10⁹/min to 1000³C in N₂ and held there until no further weight loss occurred. Demineralizing</td>
<td>T: 900³C P: 1 atm F: 300 cc/min</td>
<td>Reaction: CO₂-C Purpose: To study different factors which affect char reactivity and to compare with air-C reaction results</td>
</tr>
<tr>
<td></td>
<td>gravimetric</td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
### APPENDIX A

Compilation of Char Gasification Bench Scale Kinetic Studies (cont'd)

<table>
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<th>REACTOR TYPE</th>
<th>CARBON/CHARACTERISTICS</th>
<th>SAMPLE PRETREATMENT</th>
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</tr>
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<tbody>
<tr>
<td>140</td>
<td>Thermo-gravimetric</td>
<td>FMC char: Illinois #6 coal + some others. 2 gm 18-35 m granular, basket</td>
<td>Coal was pyrolysed at 1550°C -catalyst impregnation -preoxidation -varied pretreatment</td>
<td>T: 650-850°C  P: 34 atm</td>
<td>Reaction: H2O-C  Purpose: To look at the effect on reactivity of dual catalyst systems, varying catalyst concentrations, catalyst annailing &amp; catalyst preparation</td>
</tr>
<tr>
<td>141</td>
<td>Thermo-gravimetric</td>
<td>SP-1 pure natural graphite GRAPHON 1/16&quot; or 1/32&quot; thick plates 0.35-0.58 g</td>
<td>Heat-treated to 2500°C in Ar to remove impurities added on compaction. Then plates were burned off to 12% wt loss at 1100°C</td>
<td>T: 950-1150°C  P: low pressure  F: 11.61 liters reactor volume</td>
<td>Reaction: CO2-C  Purpose: To study the kinetics at low pressure and H2 inhibition</td>
</tr>
<tr>
<td>65</td>
<td>Thermo-gravimetric</td>
<td>6 coals of different rank single crystal SP-1 graphite 9 mm ID specimen -200 m pellet</td>
<td>-surface area measurement conditions for sample SA measurement -devolitized in N2 at 250/°min up to 1000°C</td>
<td>T: 700-1200°C  P: 1 atm</td>
<td>Reaction: H2O-C  Purpose: To study the effects of N2 and K catalysts on the gasification of several coals. Gasification rate expressed/ unit SA</td>
</tr>
<tr>
<td>142</td>
<td>Thermo-gravimetric</td>
<td>Graphimets &amp; SP-1 graphite 0.35 gm pellet 9mm D 4mm height cylindrical</td>
<td>Samples heated to 850°C in vacuo</td>
<td>T: 520-1150°C  P: 1 atm  F: Recirculation of balance volume - 6 1/5 min</td>
<td>Reaction: H2O-C  Purpose: To study the effects of different catalysts on steam gas rates. Product retardation looked at</td>
</tr>
<tr>
<td>143</td>
<td>Thermo-gravimetric</td>
<td>SP-1 spectroscopic graphite. Plates = 3/8&quot;x1&quot;x1/16 thick or 3/8&quot;x1&quot;x1/32 thick</td>
<td>Plates were gasified to 10% wt loss at 1150°C on a flowing 10% CO-90% CO2 atm prior to any measurements</td>
<td>T: 900-1007°C  P: .02 atm-.2 atm</td>
<td>Reaction: CO2-C  Purpose: To use a simple well-defined (spectroscopically) graphite to study Langmuir-Hinshelwood kinetics</td>
</tr>
</tbody>
</table>
## APPENDIX A

### Compilation of Char Gasification Bench Scale Kinetic Studies (cont'd)

<table>
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<tr>
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<th>SAMPLE PRETREATMENT</th>
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</tr>
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<tbody>
<tr>
<td>144</td>
<td>Thermo-gravimetric</td>
<td>Montour #4 mine of Pittsburgh #8 seam treated with CaO and NaOH (BTC) 1/16&quot; long 3/16&quot; D cylindrical + 20 gm pellets</td>
<td>BTC pretreatment using CaO + NaOH to avoid caking</td>
<td>T: 1200°C P: 102 atm</td>
<td>Reaction: H₂-C Purpose: Study a novel treatment process for catalyst incorporation and define a comparative reactivity index at a given conversion X for two samples as $R_X = \frac{t_{AX}}{t_{BX}}$</td>
</tr>
<tr>
<td>145</td>
<td>Thermo-gravimetric</td>
<td>Several US coals of different rank 5-10 mg 40x100 m pan, granular</td>
<td>Coal carbonized in N₂ at 1000°C for 2 hours (at a rate of 10°C/min)</td>
<td>T: 900°C P: 1 atm</td>
<td>Reaction: Air, H₂, CO₂-C Purpose: To study the reactivities of different chars and the effects of minerals in the coal on gasif. rates, char pretreatment, etc.</td>
</tr>
<tr>
<td>146</td>
<td>Thermo-gravimetric</td>
<td>Pitts. #8 Illinois #6 raw, coking bituminous coals 0.5-1 gm, -50 to +10 m granular, basket (.63 OD)</td>
<td>Initial hydrogasif. stage with different temperatures 700-900°C</td>
<td>T: 700-1000°C P: 68 atm F: 0.04-0.23 1/s 2500 cc/min</td>
<td>Reaction: H₂-C Purpose: To determine the kinetics of hydrogasification of char with H₂-CH₄ mixtures</td>
</tr>
<tr>
<td>64</td>
<td>Thermo-gravimetric</td>
<td>Western sub-bituminous coal 400 mg 1/2&quot; D 1/8&quot; thick pellets</td>
<td>The pellets were charred in H₂ at 900°C for 7 min.</td>
<td>T: 700-900°C P: F: 130 cc/min</td>
<td>Reaction: H₂O=C Purpose: A Study of the effects of alkali metal catalysts on steam gasification of char using H₂O-H₂ mixtures</td>
</tr>
<tr>
<td>111</td>
<td>Thermo-gravimetric</td>
<td>2 low rank coals (lignite) one high rank (Pittsburgh seam coal) 0.5 gm 9 mm ID cylindrical pellets</td>
<td>Coal pellets were devolatilized in flowing N₂ at a heating rate of 20°C/min and kept at 1000°C for 2 hrs.</td>
<td>T: 850°C P: .5 atm F:</td>
<td>Reaction: H₂O=C Purpose: To study catalysis of carbon-steam gasification by ash components from two lignites</td>
</tr>
</tbody>
</table>
## APPENDIX A

Compilation of Char Gasification Bench Scale Kinetic Studies (cont'd)

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<th>SAMPLE PRETREATMENT</th>
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<tr>
<td>147</td>
<td>Thermo-gravimetric</td>
<td>Metallurgical coke 3 mm particles</td>
<td>Coking time 22 hr at 1200°C</td>
<td>T: 1200°C P: 1 atm F: 21 min</td>
<td>Gasification with steam and CO₂ mixtures</td>
</tr>
<tr>
<td>73</td>
<td>Fluidized bed</td>
<td>Disco char from Pittsburgh seam coal 65-150 m 1 lb or 25&quot; height 1 1/2&quot; ID</td>
<td>Varied pretreatment times (0-24 hrs) using N₂ at 1600°F</td>
<td>T: 871°C P: 1 atm F: .59 ft/s CO₂ .55 ft/s H₂O</td>
<td>Reaction: H₂O-C, CO₂-C Purpose: To look at the effect of high temperature pretreatment on reactivity of low-temperature char to steam and CO₂</td>
</tr>
<tr>
<td>73</td>
<td>Fluidized bed</td>
<td>Disco char from Pittsburgh seam coal 65-150 m 1 lb or 25&quot; height 1 1/2&quot; ID</td>
<td>N₂ pretreatment for 1 hour at 1600°F</td>
<td>T: 871°C P: 1 atm-30 atm</td>
<td>Reaction: H₂O-C Purpose: To look at the effect of pressure and carbon burnoff on the rate of gasification of char in steam-hydrogen mixtures</td>
</tr>
<tr>
<td>72</td>
<td>Fluidized bed</td>
<td>Activated carbon, graphite &amp; ceylon graphite 1-12 gm 1.8 mm-.081 mm 2.22 cm ID tube</td>
<td>No pretreatment</td>
<td>T: 700-1400°C P: 1 atm</td>
<td>Reaction: CO₂-C Purpose: A study of the kinetics and the mechanization of the reaction</td>
</tr>
<tr>
<td>55</td>
<td>Fluidized bed</td>
<td>Graphite, activated carbons, metallurgical cokes 3 gm 0.08 - 1.8 mm 2.22 cm ID</td>
<td>No pretreatment</td>
<td>T: 700-1500°C P: 1 atm F: 180 cc/min STP</td>
<td>Reaction: CO₂-C, H₂O-C Purpose: To summarize the work of Ergun &amp; Mentser at B of Mines on gasification of C using H₂O and CO₂. They use a mechanistic approach to the kinetics of the reactions</td>
</tr>
<tr>
<td>75,76</td>
<td>Fluidized bed</td>
<td>Disco char 65-100 mesh 0.4 lb 1 1/2&quot; ID</td>
<td>Pretreated for 1 hr at the reaction temperature</td>
<td>T: 8,16-9270°C P: 1 atm in N₂ (.44 ft/s velocity)</td>
<td>Reaction: H₂-C, H₂O-H₂C Purpose: To study the rate of gasification of carbon in pure hydrogen &amp; hydrogen-steam mixtures in an effort to correlate results in a single empirical correlation</td>
</tr>
</tbody>
</table>
## APPENDIX A

Compilation of Char Gasification Bench Scale Kinetic Studies (cont'd)

<table>
<thead>
<tr>
<th>REFERENCES</th>
<th>REACTOR TYPE</th>
<th>CARBON/CHARACTERISTICS</th>
<th>SAMPLE PRETREATMENT</th>
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<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>Fluidized moving bed</td>
<td>Bituminous coal +40 - 325 m (.0029&quot; avg) +40 - 80 m (.0095&quot; avg) Bed Height: 2, 4.7, 7, 9 (ft)</td>
<td>Pretreated by low-temperature oxidation</td>
<td>T: 704-927°C P: 34-136 atm F: .01-.59 ft/s</td>
<td>Reaction: H$_2$-C Purpose: To study the kinetics of coal char hydrogasification on pilot plant scale</td>
</tr>
<tr>
<td>6</td>
<td>Fluidized bed</td>
<td>High sodium, lignite char from North Dakota 35x65m 5-10g, 2 1/2&quot; height of bed Reactor 7&quot; x 1&quot;</td>
<td>Coal was carbonized in N$_2$ at 565°C and devolutilized by heating in fluid bed in H$_2$ at 1400°F for 1 hr and 6 atm</td>
<td>T: 816°C-871.1°C P: 11-20 atm</td>
<td>Reaction: H$_2$O-C Purpose: To study the steam gasification kinetics of lignite char</td>
</tr>
<tr>
<td>58</td>
<td>Fluidized bed</td>
<td>Kentucky #9 coal minerals 30/35 m, 50/60 m, 200/270 m, 100 g, height 7&quot;</td>
<td>N$_2$ flow through apparatus</td>
<td>T: 1040-1430°C P: 1 atm</td>
<td>Reaction: H$_2$O-C Purpose: To study the kinetics of coal mineral carbon with steam. They use the shrinking core model to describe kinetics</td>
</tr>
<tr>
<td>59</td>
<td>Fluidized bed</td>
<td>Hydrane char 5 gm</td>
<td></td>
<td>T: 750-900°C P: 70 atm</td>
<td>Reaction: H$_2$O-C, CO$_2$-C Purpose: To obtain kinetic information concerning the water gas reaction (reaction with steam). The char used contains 50% of initial carbon of raw coal. To improve hydrane process</td>
</tr>
<tr>
<td>7</td>
<td><em>Falling Particle</em></td>
<td>Coke + graphite 200-230 m</td>
<td>Petroleum coke devolutilized and shrunk at 1350°C in absence of air then mixed with binder. Graphite baked in oven at 750°C for 20 hrs. Graphitization occurred during 7 hrs at app. 2850°C</td>
<td>T: 1800-2500°F P: 1 atm</td>
<td>Reaction: Steam-Carbon Purpose: To examine the effect of temperature on the reaction rate</td>
</tr>
<tr>
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</table>
| 60         | Entrained flow | Pulverized Coal | None | T: 746-1180°C  
|            |               |                        |                     | P: 15-97 atm  
|            |               |                        |                     | F:         | Reaction: H$_2$-H$_2$O-C  
|            |               |                        |                     | Purpose: To understand & improve Bi-gas process gasifier. Kinetic study of pertinent rate equations |
| 61         | Dilute phase reactor | Pittsburgh seam coal  
3" ID; 5 ft | Illinois #6 lignite  
50 x 100 m | T: 650-1000°C  
|            |               |                        |                     | P: 68-136 atm  
|            |               |                        |                     | Reaction: H$_2$-C  
|            |               |                        |                     | Purpose: To investigate the direct conversion of coal methane using entrained concurrent flow of coal in hydrogen |
| 81         | Entrained flow 3" ID | Pulverized coal  
11" long | Utah Bituminous coal  
70-80% - 200 m | T: 1066°C  
|            |               |                        |                     | P: 150 psi  
|            |               |                        |                     | Reaction: H$_2$O-O$_2$-C  
|            |               |                        |                     | Purpose: To examine a pressurized entrained flow gasifier with the intent of decreasing industrial reactor size |
| 82         | Entrained flow with recirculation | Highly volatile low sulfur bituminous | None | T: 1130-1730°C  
|            |               | coal 70-80% - 200 m |                     | P: 10 atm  
|            |               |                        |                     | F: steam to coal feed rates 0.5g/g  
|            |               |                        |                     | Reaction: O$_2$-Coal, Char-CO$_2$, H$_2$O  
|            |               |                        |                     | Purpose: To obtain kinetic data from high temperature entrained flow gasifier which is a scaled down version of the existing gasifier well-mixed |
| 61         | Entrained flow reactor 1 1/4", 3/4" tubes | Highly volatile bituminous coal  
- 200 mesh | Coal is dried, ball milled and screened  
Entrain coal in stream of carrier gas H$_2$, N$_2$ | T: 650-1370°C  
|            |               |                        |                     | P: 1 atm  
|            |               |                        |                     | F: 13-15 scfh  
|            |               |                        | avg. residence time | 0.12 - .343 s  
|            |               |                        |                     | Reaction: Oxidizing combustion gases  
|            |               |                        |                     | Purpose: To investigate the potential for increased volatility and also the production of unsaturated hydrocarbons as a result of rapid pyrolysis using partial combustion gases |
## APPENDIX A

Compilation of Char Gasification Bench Scale Kinetic Studies (cont'd)

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<th>CARBON/CHARACTERISTICS</th>
<th>SAMPLE PRETREATMENT</th>
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<tr>
<td>83</td>
<td>Dilute phase transport reactor, helical, coiled (integral)</td>
<td>Montana lignite, .0029&quot; to .0035&quot;</td>
<td>250-200 mesh</td>
<td>T: 480-840°C P: 18-52 atm F: 5-50 scf/hr</td>
<td>Reaction: H₂-H₂-Char Purpose: To study the rapid-rate methane formation reaction in both isothermal &amp; with constant gas-solid heat-up rate (50°F/s)</td>
</tr>
<tr>
<td>80</td>
<td>Electrofluid reactor charged (Fluidized bed)</td>
<td>Single crystals of graphite</td>
<td>Graphite annealed at 2300°F in vacuo by electron beam, heating</td>
<td>T: 850-1075°C P: 1 atm</td>
<td>Reaction: H₂O-graphite Purpose: To determine rates of reaction by measuring the rates of increase in diameters of etch pits produced from lattice vacancies</td>
</tr>
<tr>
<td>84</td>
<td>Electrofluid reactor charged (Fluidized bed)</td>
<td>Variety of coal chars, 20-200 mesh</td>
<td>Chars produced by pyrolysis at varying temperatures</td>
<td>T: 1500-1960°F P: 1 atm Batch F:</td>
<td>Reaction: Char-steam Purpose: To discover the electrical properties &amp; behavior of coal gasification in bench scale electrofluid reactor. Bench scale-continuous-large scale. To investigate the pertinent parameters for scale-up purposes</td>
</tr>
<tr>
<td>87,88</td>
<td>Spouted bed</td>
<td>Ranigahji coal, 1.2-2.05 mm</td>
<td></td>
<td>T: 600°C-1000°C P: 1 atm</td>
<td>Reaction: Air-steam-coal Purpose: To study 1. low-temperature carbonization, 2. kinetics of coal pyrolysis, 3. gasification of coal, air-steam-jet-coal</td>
</tr>
<tr>
<td>89,93</td>
<td>Spouted bed</td>
<td>Western Canadian Coals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>REFERENCES</td>
<td>REACTOR TYPE</td>
<td>CARBON/CHARACTERISTICS</td>
<td>SAMPLE PRETREATMENT</td>
<td>OPERATING CONDITIONS</td>
<td>COMMENTS</td>
</tr>
<tr>
<td>------------</td>
<td>--------------</td>
<td>------------------------</td>
<td>---------------------</td>
<td>---------------------</td>
<td>----------</td>
</tr>
<tr>
<td>97</td>
<td>Free-fall Dilute-phase reactor</td>
<td>Pittsburgh, Illinois #6</td>
<td>None</td>
<td>T: 725-900°C P: 10-205 atm</td>
<td>Reaction: Hydrogasification Purpose: To consolidate kinetic information yielded from hot-rod, free-fall dilute phase reactors</td>
</tr>
<tr>
<td>68</td>
<td>Vortex Tube <em>Adiabatic</em></td>
<td>Pulverized bituminous C coal -200 m (80%)</td>
<td>None</td>
<td>T: 1300-2700°F P: 1 atm</td>
<td>Reaction: Coal+O₂+steam Purpose: To assess potentialities of this type of reactor for producing synthesis gas and to obtain basic information on the critical variables affecting gasification under these conditions</td>
</tr>
<tr>
<td>69</td>
<td><em>Impinging</em> <em>Jet</em></td>
<td>AGKS spectroscopic graphite</td>
<td>Addition of catalyst via heating &amp; slurrying</td>
<td>T: 975-1100°C P: low</td>
<td>Reaction: Steam-Carbon Purpose: Examine catalytic effects of Cobalt, Iron, Nickel and Vanadium Oxide on reaction rate</td>
</tr>
<tr>
<td>79</td>
<td><em>Furnace Tube</em></td>
<td>Spectroscopic graphite electrode</td>
<td>None</td>
<td>T: 900-1300°C P: 1-40 m</td>
<td>Reaction: Steam-Carbon Purpose: Kinetic study at high temperatures</td>
</tr>
<tr>
<td>101</td>
<td>Explosion chamber</td>
<td>Pem-Rilton 'Sea coal' hvBA bituminous 200 mesh (70%)</td>
<td>None</td>
<td>T: 2000°C P: 1-11 atm</td>
<td>Reaction: Carbon-Steam Purpose: Rapid non-steady state coal gasification at very high temperatures is investigated</td>
</tr>
<tr>
<td>92</td>
<td>Diffusion cell</td>
<td>Char, graphite</td>
<td></td>
<td>T: 1000-1600°C P: 1 atm</td>
<td>Reaction: CO₂-C Purpose: Study intrinsic rates in chemical reaction diffusion regime</td>
</tr>
</tbody>
</table>
APPENDIX B

Testing for Film Temperature Gradients

Feldkirchner and Huebler (48) in their study of steam-hydrogen gasification using a thermobalance reported the following operating conditions and results:

- TGA BALANCE TUBE DIAMETER: 1 inch
- SUPERFICIAL GAS VELOCITY: 50 SCF/HR
- PARTICLE SIZE: -16+20 (0.0328 - 0.039 inch)
- TOTAL PRESSURE: 1000 psi
- BULK DENSITY OF SOLID: 50 lb/ft³
- SOLID THERMAL CONDUCTIVITY: 3.3 - 8.6 x 10⁻⁴ cal/scm°C
- EMISSIVITY: 0.55
- BED POROSITY: 0.40
- AVERAGE BED TEMPERATURE: 1700°F
- GASIFICATION RATE: (0.4 - 6 lb C)
  1 lb hr
- CROSS-SECTIONAL AREA OF TUBE: \( \frac{\pi D^2}{4} = \frac{\pi (1)^2}{4} = 2.54^2 = 5.067 \text{ cm}^2 \)

SUPERFICIAL MASS VELOCITY OF GAS:

\[ \frac{1.416 \times 10^6 \text{ cm}^3/\text{hr}}{22,400 \text{ cm}^3/\text{mol}} \times \frac{1}{5.062 \text{ cm}^2} \times \frac{1}{3600 \text{ s}} \times \frac{18 \text{ g}}{\text{mol}} = 0.062 \text{ g cm}^{-2}\text{s}^{-1} \]

PARTICLE SIZE: 0.091 cm diameter

VISCOSITY (steam 1700°F) = 425 x 10⁻⁴ cp = 425 x 10⁻⁶ poises

Reynolds Number: \( \text{Re}_\text{N} = \frac{dpG}{\mu} = \frac{(0.091)(0.062)}{425 \times 10^{-6}} = 13.28 \)

MASS TRANSFER number \( j_D = 0.84 \text{ N}_\text{Re}^{0.51} = 0.22 \)

HEAT TRANSFER \( j_H = 1.076 j_D = 0.242 \)
CONVECTIVE HEAT TRANSFER COEFFICIENT

\[ h_c = \frac{c_p g j_H}{(c_p j / k)^{2/3}} = \frac{(0.5)(0.062)(0.242)}{(0.7)^{2/3}} = 9.52 \times 10^3 \text{ cal cm}^{-2} \text{s}^{-1} \text{C}^{-1} \]

RADIATIVE HEAT TRANSFER COEFFICIENT

\[ h_r = 1.37 \times 10^{-12} (1200^3) \]

\[ h_r = 1.37 \times 10^{-12} (1200^3) \frac{4}{3} \]

\[ = 5.02 \times 10^{-5} \text{ cal cm}^{-1} \text{s}^{-1} \text{C}^{-1} \]

\[ h = h_c + h_r = 0.0145 \text{ cal cm}^{-2} \text{s}^{-1} \text{C}^{-1} \]

Using the appropriate criterion for determining whether interphase temperature gradients exist,

(Equation 3-27) \[ \Delta T_f = \frac{r_{v, obs} L \Delta H_r}{h} \]

For, \( r_{v, obs} = 0.4 \text{ gC/gC hr} \)

\[ \frac{r_{v, obs} L \Delta H_r}{h} = \frac{1 \text{ mol}}{12 \text{ gC}} \frac{1 \text{ hr}}{3600 \text{ s}} \frac{0.4 \text{ gC}}{\text{gC hr}} \frac{0.8 \text{ gC}}{\text{cm}^3} \frac{(0.091)(41000)}{\text{cal mol}} \]

\[ \Delta T_f = 1.91^\circ \text{C} \]

For \( r_{v, obs} = 6 \text{ gC/gC hr}, \Delta T_f = 29^\circ \text{C} \)
APPENDIX C

Testing for Transport Limitations

Dutta et al. (39) in their study of the reactivity of coal char with carbon dioxide at atmospheric pressure in a thermobalance report the following findings:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermobalance diameter</td>
<td>19 mm</td>
</tr>
<tr>
<td>Sample holder dimensions</td>
<td>cylinder 6 mm x 15 mm (35 mg)</td>
</tr>
<tr>
<td>CO₂ flowrate</td>
<td>150 ml/min (NTP)</td>
</tr>
<tr>
<td>Reaction temperature</td>
<td>10000°C</td>
</tr>
<tr>
<td>Char sample</td>
<td>IGT char #155</td>
</tr>
<tr>
<td>Density</td>
<td>1.54 g/cm³</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.767</td>
</tr>
<tr>
<td>Reactivity</td>
<td>0.067 min⁻¹</td>
</tr>
<tr>
<td>Activation Energy</td>
<td>59.26 kcal/mol</td>
</tr>
<tr>
<td>Heat of Reaction</td>
<td>41 kcal/mol</td>
</tr>
</tbody>
</table>

Since the resistance to gas flow is so much less outside of the wire mesh cylinder, it is not unlikely that the entire holder and contents behave as a single pellet. It will be treated as such in the following analysis.

Effective length: \[ L = \frac{\text{volume of holder}}{\text{external surface area}} \]

\[ L = \frac{\pi D^2 h}{4} \]

\[ \pi D^2 / 2 + \pi Dh \]

\[ L = 1.25 \text{ mm} = 1.25 \times 10^{-3} \text{ m} \]
Linear Velocity: \[ U = \frac{150 \text{ cm}^3/\text{min}}{\pi \frac{1273}{298}} \left( \frac{1}{4} \right) (1.9)^2 \text{ cm}^2 \]

\[ U = 226 \text{ cm/min} \]
\[ U = 136 \text{ m/hr} \]

Carbon Dioxide Physical Properties at 1000°C

Density: \[ \rho = \frac{P}{RT} = \frac{1 \text{ atm}}{(82.05)(1273)} = 9.6 \times 10^{-6} \text{ mol/cm}^3 = 9.6 \text{ mol/m}^3 \]

\[ \rho = 0.4224 \text{ kg/m}^3 \]

Viscosity: \[ 9.4 \times 10^{-7} \text{ lb}_f \text{ s x} \frac{1}{\text{ft}^2} \frac{1}{\text{N s/m}^2} = 4.5 \times 10^{-5} \text{ kg/m s} \]

\[ \mu = 4.5 \times 10^{-5} \text{ kg/m s} \]

Kinematic Viscosity: \[ \nu = \rho/\mu = 1.07 \times 10^{-4} \text{ m}^2/\text{s} \]

\[ \nu = 0.385 \text{ m}^2/\text{hr} \]

Thermal Conductivity: \[ 0.046 \text{ Btu/hr ft } ^\circ \text{F} = 0.0685 \text{ kcal/hr m K} \]

Effective Diffusivity: \[ * Walker et al. \]

\[ D_{eff} = 0.14 \Theta^2 \left( \frac{T}{298} \right)^{1.3} \]

Average porosity, \( \Theta \), 0.53
Temperature 1273 K

\[ D_{eff} = 0.113 \text{ m}^2/\text{hr} \]

Effective Thermal Conductivity of Char: 0.004 – 0.005 cal/cmsk

\[ = 1.8 \text{ kcal/hr mK} \]
PREDICTION OF MASS TRANSFER COEFFICIENT: (RANZ and MARSHALL CORRELATION)

Reynolds Number: \( N_{Re} = \frac{UL}{\nu} = \left(1.35 \text{ m/hr}\right)\left(1.25 \times 10^{-3} \text{ m}\right) \quad \frac{0.385 \text{ m}^2/\text{hr}}{0.438} \)

Schmidt Number: \( N_{Sc} = \frac{\nu}{\mu_{CO-CO_2}} = 0.385 = 0.489 \)

Molecular Diffusion coefficient calculated using Slattery-Bird Equation as follows:

\[
\begin{align*}
A & = \text{CO} \\
B & = \text{CO}_2 \\
T_c & = 132.9 \quad 304.2 \text{ K} \\
P_c & = 34.5 \quad 72.8 \text{ atm}
\end{align*}
\]

\[
\begin{align*}
(T_c A)^{1/2} & = 83.07 \\
(T_c B)^{1/2} & = 201.1 \\
(P_c A B)^{1/3} & = 13.59
\end{align*}
\]

\[
\left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2} = 0.242
\]

At 1273 K,

\[
\frac{T}{(T_c A B)^{1/2}} = \left[\frac{1273}{201.1}\right] = 1.823 = 28.9
\]

\[
D_{CO_2-co} = (2.745 \times 10^{-4})(28.9)(0.242)(83.07)(13.59)
\]

\[
= 2.16 \text{ cm}^2/\text{s}
\]

\[
= 0.79 \text{ m}^2/\text{hr}
\]

Sherwood Number: \( N_{sh} = 2 + 0.6 \left(\frac{N_{Re}}{N_{Sc}}\right)^{1/3} \)

\[
= 2 + 0.6 \left(\frac{0.438}{0.489}\right)^{1/3} (0.489)^{1/3}
\]

\[
= 2.313
\]

Mass Transfer Coefficient: \( k_g = D N_{sh} = (0.778)(2.313) \)

\[
L = 1.25 \times 10^{-3}
\]

\[
k_g = 1440 \text{ m/hr}
\]

Calculation of Rate of Reaction:

According to Dutta et al.,

\[
\frac{dx}{dt} = a k_v C_A (1-X)
\]

\[
a = 1 + 100 X \quad B_e - BX
\]

\[
k_v = k_v_0 e^{-E/RT}
\]

IGT char: \( k_v_0 = 0.113 \times 10^{15} \text{ cm}^3/\text{mol min} \)

\[
T = 1273
\]

\[
= 0.75
\]

\[
= 5.5
\]

\[
X = 0.20
\]

\[
a = 1 + 100 (0.2)(0.75)(5.5) e^{-5.5}(0.2) = 1.0435
\]
\[ k_v = 0.113 \times 10^{15} \exp(-59,000/(1.987 \times 1273)) = 8376.5 \text{ cm}^3 \text{ mol min} \]

\[ r_{obs} = \frac{dx}{dt} = (1.0436)(8376.5)(9.6 \times 10^{-6})(1 - 0.2) = 0.067 \text{ gC gC min} \]

\[ r_{v,obs} = \left[ 0.067 \text{ gC gC min}^{-1} \right] \left[ 1 \text{ g mol C} \text{ cm}^3 \right] \left[ \sigma_a \text{ gC cm}^3 \right] \]

where \( \sigma_a = \) the apparent density of the char = 1.3-1.5 (Laurendieau)

\[ r_{v,obs} = (4.3 \times 10^{-3} - 8.5 \times 10^{-3}) \text{ mol C min cm}^3 \]

\[ r_{v,obs} = (2.6 \times 10^5 - 5.2 \times 10^5) \text{ mol C hr m}^3 \]

**Convevtive Heat Transfer Coefficient**

Prandtl Number: \( \text{N}_p = 0.72 \)

Nusselt Number: \( \text{N}_N = 2 + 0.6 (0.438)^{1/2}(0.72)^{1/3} \)

= 2.356

Heat Transfer Coefficient: \( h = \frac{kqN_u}{L} \)

\[ h = \frac{0.685 \times 2.356}{1.25 \times 10^{-3}} = 129 \text{ kcal hr m}^2 \text{ K} \]

**Radiative Heat Transfer Coefficient**

\[ h_r = \varepsilon \sigma (T_e^4 + T_s^4)(T_e + T_s) \]

For \( T_e + T_s = T, \) \( h_r = 4 \varepsilon \sigma T^3 = 4(0.53)(1.37 \times 10^{-12})(1273)^3 \)

= 5.99 \times 10^{-3}

= 6 \times 10^{-3} \text{ cal cm}^2 \text{ s} \text{ K}^{-1}

\[ h_r = 216 \text{ kcal m}^{-2} \text{ h}^{-1} \text{ K}^{-1} \]
Transport Criteria

Pore Diffusion:

Equation 3-18,
\[
\frac{r_{v, obs}}{D_{eff} C_s^{ \frac{L^2}{C_s}}} < \zeta \quad \text{where} \quad \zeta \begin{cases} 6' \quad n=0 \\ 1 \quad n=1 \\ 0.3 \quad n=2 \end{cases}
\]

\[
\frac{(3.9 \times 10^5)(1.25 \times 10^{-3})^2}{(0.113)(9.6)} = 0.56
\]

This result is conclusive if the reaction rate is known, no pore diffusion limitation is expected.

Film Diffusion:

EQN. 3-26,
\[
\frac{r_{v, obs}}{k_g C_b} < 0.05^n
\]

\[
\frac{(3.9 \times 10^5)(1.25 \times 10^{-3})}{(1440)(9.6)} = 0.035
\]

No film diffusion is suspected. An approximate calculation of the mass transfer rate will help to confirm this conclusion:

\[
J_{CO_2} = -k_g \frac{P}{RT} \ln \left[ \frac{1 + N_{CO_2}}{1 + N^{*}_{CO_2}} \right]
\]

Avg Particle Size: 0.0333 cm

X-section of gap between cylinder and wall: 2.55 cm²

X-section of empty tube: 2.84 cm²

Avg. linear velocity at 1000°C: 4 cm/s

N_{CO_2} = 1 \quad \text{i.e. pure CO}_2\text{feed}

N_{CO_2}^* = 0
\[ J_{\text{CO}_2} = 2400 \text{ cm/min} \times 10^{-5} \times \ln 2 = 1.66 \times 10^{-2} \text{ mol min}^{-1} \text{cm}^{-2} \]

\[ J_{\text{CO}_2} = 1.66 \times 10^{-2} \text{ mol/min cm}^2 \left[ \frac{44 \text{ g CO}_2}{\text{gmol CO}_2} \right] \left[ \frac{12 \text{ gC}}{\text{gmol CO}_2} \right] = 0.2 \frac{g}{\text{min cm}^2} \]

Initial Weight of Char: 0.035 g
Char Density ( \( \sim 1.54 \text{ g/cm}^3 \) )

Number of particles = \( \frac{0.035}{1.54} \left( \frac{\pi (0.0333)^3}{3} \right) = 586 \)
(assuming spherical geometry)

Rate of Reaction: \( (0.067) \text{min}^{-1} \times 0.035 \text{ gC} \)
\[ \frac{586 (\pi(0.0333)^2) \text{ cm}^2}{0.035 \text{ g}} \]
\[ = 1.15 \times 10^{-3} \frac{g}{\text{min cm}^2} \]

Ratio of reaction rate to mass transfer rate
\[ \frac{1.12 \times 10^{-3} \text{ g/min cm}^2}{0.2 \text{ g/min cm}^2} = 0.006 \]

The mass transfer through the film does not appear to be rate limiting.

**Intraparticle Temperature Gradient**

Equation 3-19
\[ \frac{\Delta H_v \cdot r_{v, \text{obs}} L^2}{\lambda_{\text{eff}} T_s^5 R} < \frac{T_s^5 R}{E_a} \]
\[ \frac{(41)(5.2 \times 10^5)(1.25 \times 10^{-3})^2}{(1.8)(1273)} = 0.014; \quad \frac{1273(1.987)}{(1000)(59)} = 0.04 \]

No temperature gradient is suspected inside the particle.
Temperature Gradient Across the Film

\[ \frac{\Delta H_r r_{V,obs}^L}{h T_b} < 0.05 \frac{R T_b}{E} \]

\[ \frac{\Delta H_r r_{V,obs}^L}{h T_b} = \frac{(41)(5.16 \times 10^5)(1.25 \times 10^{-3})}{(129 + 216)} \times 1273 \]

\[ 0.05 \frac{R T_b}{E} = \frac{(0.05)(1.987 \times 10^{-3})}{59} \times 1273 \]

A temperature difference across the film appears to be likely. The magnitude of this temperature difference is calculated below.

\[ \frac{r_{V,obs}^L \Delta H_r}{h_c + h_r} = T_g - T_s \]

\[ \frac{r_{V,obs}^L \Delta H_r}{h_c + h_r} = \frac{(5.16 \times 10^5)(1.25 \times 10^{-3})(41)}{(129.1 + 216)} \times (T_g - T_s) = 80^\circ C \]

This represents a sizeable temperature difference.
APPENDIX D

Experimental Tests for Absorption of CO/CO₂ on Commercial Drying Agent

Experimental tests were carried out in order to determine whether Drierite, a tradename for anhydrous calcium sulfate, could be used as a drying agent for the moist effluent gas from the reactor. The reaction products present in the effluent gas include CO and CO₂. It was necessary to determine whether these gases would be significantly absorbed by the drierite (or by a thin H₂O layer which covers the drierite when it is spent). These tests would also help to determine the maximum size of the drying tube that could be used in gasification.

The experimental setup used to carry out these investigations is shown in Figure D-1. Basically, the gases were supplied from high pressure cylinders at or near atmospheric pressure. The flowrates of both gases were measured with calibrated rotameters. The composition of the gas mixture was checked by bleeding some gas to the gas partitioner. The main gas stream was sent through a 0.5" ID transparent plastic tube of varying length packed with drierite (64 mesh). Most of the gas mixture exiting the drying tube was subsequently vented while a small fraction of this gas was again sent to the partitioner for analysis. Moist air could be sent through the drying tube to deactivate parts of the packing.
The results from these tests are shown in Figures D-2 for CO₂ and D-3 for CO. The blanks are analysis of the gas mixture before it enters the drying tube. For carbon dioxide, Table D-1 shows no significant difference between the analysis before or after the drying tube regardless of how used the tube was. On the other hand, Table D-2 shows that there is some difference in the carbon monoxide analysis. The carbon monoxide content in the exit line from the drying tube is somewhat lower after the tube was approximately half spent. In order to avoid any loss of CO the maximum size of the product drying gas tube for the gasification runs was 20 cm.
TABLE D-1

Carbon Dioxide Analysis

<table>
<thead>
<tr>
<th>Blank Runs (A)</th>
<th>Drierite Runs (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_A = 14$</td>
<td>$n_B = 32$</td>
</tr>
<tr>
<td>$x_A = 730,540$</td>
<td>$x_B = 732,314$</td>
</tr>
<tr>
<td>$s_A = 6772$</td>
<td>$s_B = 10,133$</td>
</tr>
<tr>
<td>$s_A^2 = 45.9 \times 10^6$</td>
<td>$s_B^2 = 102.7 \times 10^6$</td>
</tr>
<tr>
<td>$\nu_A = 13$</td>
<td>$\nu_B = 31$</td>
</tr>
</tbody>
</table>

\[
\frac{s_B^2}{s_A^2} = \frac{102.7}{45.9} = 2.24
\]

\[
F(31, 13; 0.95) = 2.38
\]

\[
\frac{s_B^2}{s_A^2} < F
\]

The variances of A and B are the same

\[
s_p^2 = \frac{\nu_A s_A^2 + \nu_B s_B^2}{\nu_A + \nu_B} = 85.9 \times 10^6
\]

100 $(1 - \alpha)$% confidence interval for $(\mu_A - \mu_B)$ is

\[
(x_A - x_B) \pm t_{\nu} \frac{1}{\sqrt{n_A}} + \frac{1}{\sqrt{n_B}} s_p \left( \frac{1}{\nu_A} + \frac{1}{\nu_B} \right)^{\frac{1}{2}}
\]

\[
t_{44, 0.05} = 2, \quad s_p = 9269
\]

\[
1774 \pm 5932
\]

Interval contains zero, therefore $\mu_A = \mu_B$. 

TABLE D-2

Carbon Monoxide Analysis

Blank Runs (A)                                      Drierite Runs (B)

\( n_A = 14 \)
\( x_A = 1,098,796 \)
\( s_A = 6317.4 \)
\( s^2_A = 39.9 \times 10^6 \)
\( v_A = 13 \)

\( n_B = 32 \)
\( x_B = 1,091,491 \)
\( s_B = 11,312 \)
\( s^2_B = 127.9 \times 10^6 \)
\( v_B = 31 \)

\[ \frac{s^2_B}{s^2_A} = 3.0185 \]

\[ F(32, 13, 0.99) = 3.6 \]

\[ \frac{s^2}{s^2} < F \]

The two variances are the same

\[ s_p^2 = \frac{v_A s^2_A + v_B s^2_B}{v_A + v_B} = 101.9 \times 10^6 \]

100 \((1 - \alpha)\)% confidence interval for \((\mu_A - \mu_B)\) is

\[ (x_A - x_B) \pm t_{v_A/2, \alpha/2} s_p \left( \frac{1}{n_A} + \frac{1}{n_B} \right)^{\frac{1}{2}} \]

\[ t_{44, 0.05} = 2, \quad s_p = 10,095 \]

\[ 7305 \pm 6460 \]

Interval does not contain zero, therefore \(\mu_A \neq \mu_B\).
Figure D-1 Experimental arrangement used in testing absorption of CO, CO₂ mixtures on drying agent.

A CO₂ cylinder
B CO₂ cylinder
C Moist air
D Rotameter
E Drying Tube
F On-off valves
Figure D-2  Carbon Dioxide area response, total flow 400 cm$^3$/min. □ blank runs
FIGURE 5-19

Schematic Representation of Reactor Mixed Model
FIGURE 5-20

Schematic Representation of Combined Reactor/
Measurement Device Model
APPENDIX E

Calibration Procedure for Gas Partitioner

The experimental setup used to determine calibration factors for each of the product gas components on the gas partitioner is shown schematically in Figure E-1. Mixtures of ultra-high purity gases were metered through calibrated rotameters and a small bleed stream was continuously sent to the partitioner. A constant pressure of 1 psi was maintained upstream of the gas sampling valve so that the amount of gas in the 0.5 mL sample loop could be kept constant. Three to five samples were taken of every gas mixture prepared. The He gas flowrate through the partitioner was 40 cm$^3$/min at about 18 psig throughout the calibrations. The integrator slope sensitivity was kept at 0.03 mv/m.

The calibration curves for N$_2$, CO, CO$_2$, CH$_4$ and H$_2$ are given in Figures E-2 to E-6. Two commercially prepared gas mixtures were analysed on the partitioner and a comparison of the gas analysis is given in Table E-1. The analyses compare favorably with the exception of perhaps hydrogen. However, Matheson Gas Products Co. did not analyze for H$_2$ separately and report it as a difference which may be misleading.
Figure E-2 Calibration Curve for Nitrogen Gas
Figure E-3 Calibration Curve for Carbon Monoxide Gas

Volume Percent

Area Response

0 500,000
1,000,000
1,500,000
2,000,000

0 10 20 30 40 50 60 70 80 90 100

0 CO
Figure E-4 Calibration Curve for Carbon Dioxide Gas

CO₂

Area Response

1,000,000

500,000

0

100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 0

Volume Percent
Figure E-6: Calibration Curve for Hydrogen Gas
TABLE E-1

Comparison of Analysis of Commercial Gas Mixtures

<table>
<thead>
<tr>
<th>Species</th>
<th>Matheson Analysis (mole %)</th>
<th>from Calibration Curves (mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>30.2 ± 0.6</td>
<td>30.5</td>
</tr>
<tr>
<td>CO</td>
<td>21.0 ± 0.4</td>
<td>21.6</td>
</tr>
<tr>
<td>#1 N₂</td>
<td>10.1 ± 0.2</td>
<td>10.5</td>
</tr>
<tr>
<td>CH₄</td>
<td>16.1 ± 0.3</td>
<td>16.8</td>
</tr>
<tr>
<td>H₂</td>
<td>22.6 (by difference)</td>
<td>14.1</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>93.5</td>
</tr>
<tr>
<td>CO</td>
<td>3.06 ± 0.06</td>
<td>3.0</td>
</tr>
<tr>
<td>#2 CO₂</td>
<td>2.93 ± 0.06</td>
<td>2.6</td>
</tr>
<tr>
<td>Air</td>
<td>93 (by difference)</td>
<td>23.9 (O₂ by difference)</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Note: Calculated values for #1 N₂ and #2 CO₂, and the total mole% for Air and 100%.
Devolatilization Procedure for Coal

A coal char sample was produced from Byron Creek Coal in the apparatus shown in Figure F-1 by the following procedure:

1. 200 grams of coal are placed in the furnace tube at room temperature.

2. Nitrogen flow through the tube is started and maintained at 3 L/min.

3. Furnace is turned on and the warm up rate is controlled by dial settings on the Lindberg furnace.
   Start-up: Room Temperature 20°C
   After 8 minutes: Temperature 250°C [30°C/min]

4. Dial Setting is placed at 4. The warm up rate is 7.5°C/min for 40 minutes. (T = 550°C)

5. Dial Setting was placed at 8. The warm up rate is 10°C/min for 25 minutes. (T = 800°C)

6. The sample is kept at 800°C for 20 minutes.
7. The furnace is then turned off but \( \text{N}_2 \) is kept flowing through the apparatus.

8. When the furnace has cooled sufficiently (\( \sim 150^\circ \text{C} \)), the sample is removed, weighed and placed in a sample bottle, purged with \( \text{N}_2 \) and sealed.

This procedure yields approximately 150 grams of char. The temperature time history during charring can be seen in Figure F-2.
Figure F-1  Experimental Setup for Charring

A  Nitrogen cylinder          D  Tar collector
B  Brooks Rotameter          E  Na CO₃ Solution (400 mL H₂O, 150 gm Na CO₃)
C  Lindberg Hevi-Duty 3-zone furnace  F  Fume hood
Derivation of F-curve for N-tanks in Series Model

The exit age distribution of the N-tanks in series model is given as:

\[ E(t) = \frac{1}{\tau} \left( \frac{t}{\tau} \right)^{N-1} \frac{1}{(N-1)!} \exp\left(-\frac{t}{\tau}\right) \]

where \( t = \) time (s)
\( \tau = \) residence time in a single tank (s)
\( N = \) number of tanks in series

Since, \( \dot{E}(t) = d(C/C_0)/dt = dF(t)/dt \), the above expression can be integrated to yield the step response.

\[ \frac{d(C/C_0)}{dt} = \frac{1}{(N-1)!} \left( \frac{t}{\tau} \right)^{N-1} \frac{1}{\tau} \exp\left(-\frac{t}{\tau}\right) \]

\[ C/C_0 = \int_0^\infty \left( \frac{1}{\tau} \right)^{N-1} \frac{1}{\tau} \exp\left(-\frac{t}{\tau}\right) dt \]

\[ C/C_0 = \frac{1}{(N-1)!} \int_0^\infty t^{N-1} \exp(-t/\tau) \, dt \]

The integral is of the form \( \int_0^\infty t^{N-1} \exp(-t/\tau) \, dt \), which can be found in tables to be equal to

\[ \exp(ax) \sum_{r=0}^{m} \frac{(-1)^r m! x^{m-r}}{(m-r)! a^{r+1}} \]
where \( a = -1/\tau \), \( m = N-1 \)

Thus,

\[
\frac{C}{C_0} = \frac{1}{(N-1)!} \left( \frac{1}{\tau} \right)^N \exp \left( -\frac{t}{\tau} \right) \sum_{r=0}^{N-1} \frac{(-1)^r (N-1)!}{(N-1-r)! (1/\tau)^{r+1}} t^{N-1-r}
\]

This can be reduced to a simpler expression:

\[
\frac{C}{C_0} = \left( \frac{1}{\tau} \right)^N \exp \left( -\frac{t}{\tau} \right) \sum_{r=0}^{N-1} \frac{(-1)^r}{(N-1-r)! (1/\tau)^{r+1}} t^{N-1-r}
\]
Derivation of Mixed Model Step Response

The mixed model for the reactor consists of a stirred tank in parallel with a plug flow section which are both preceded by a plug flow section as shown below:

\[ \begin{align*}
V_o & \quad C_{in} \\
V_{PS} & \quad C_1 \\
V_B & \quad C_B \\
(1-R)V_o & \quad V_{PP} \\
C_{in} & \quad C_o
\end{align*} \]

The response of the series plug flow section to a step change in feed composition is given in the time domain by

\[ C_1(t) = C_{in} u_t \left( \frac{V_{PS}}{V_o} \right) = C_{in} u_t \left( T_{PS} \right) \]  
\text{Equation H-1}

and in the Laplace domain by

\[ C_1(s) = C_{in} \exp(-T_{PS}/s) \]  
\text{Equation H-2}

A material balance over the stirred tank section yields:

\[ C_1 - C_B = \frac{V_B}{R V_o} \frac{dC_B}{dt} = \frac{T_B}{R} \frac{dC_B}{dt} ; \quad C_B(t=0) = 0 \]
The solution of this differential equation is given in the time domain by:

\[ C_B(t) = C_{in} \left(1 - \exp\left(R(T_{ps}-t)/T_B\right)\right) u_t(T_{ps}) \]  

Equation H-3

The expression for \( C_B(s) \) can also be found and is given below as:

\[ C_B(s) = \left(C_{in}/s\right) \left((R/T_B)/(s + R/T_B)\right) \exp(-T_{ps} s) \]  

Equation H-4

A material balance over the parallel plug flow section yields:

\[ C_{pp}(t) = C_{in} \left(1(t) \right) u_t(V_{pp}/(v_o(1-R))) \]

\[ C_{pp}(t) = C_{in} u_t(T_{ps}) u_t(T_{pp}/(1-R)) \]  

Equation H-4

In the Laplace domain, this can be described as:

\[ C_{pp}(s) = \left(C_{in}/s\right) \exp(-s(T_{ps} + T_{pp}/(1-R))) \]  

Equation H-5

The composition of the exit stream, \( C_o \), can be found by a simple balance and the use of Equations H-3, H-4.

\[ R v_o C_B + (1-R)v_o C_{pp} = v_o C_o \]

\[ F(t) = C(t)/C_{in} = R(1 - \exp(R(T_{ps}-t)/T_B)) u_t(T_{ps}) \]
\[ + (1-R) u_t(T_{ps} + T_{pp}/(1-R)) \]  

Equation H-6

In the Laplace domain, \( C_o(s) \) is given by:

\[ F(s) = C(s)/C_{in} = \left((R^2/T_B) \exp(-T_{ps} s)/(s + R/T_B)\right) \]
\[ + (1-R) \exp\left(-s(T_{ps} + T_{pp}/(1-R))\right)/s \]  

Equation H-7
APPENDIX I

Derivation of Combined Reactor/Measurement Device Model Step Response

The step response of the combined model for the system can be simply derived by using the Laplace Domain solutions of Appendix H and a material balance over each of the tanks for the measurement device.

For 1 tank,

\[ v_o C_0 - v_o C_1 = V \frac{dC_1}{dt} \]

If \( V/v_o = \tau \), then

\[ C_1(s) = \frac{C_0(s)}{(\tau s + 1)} \]

For 2 tanks,

\[ v_o C_1 - v_o C_2 = V \frac{dC_2}{dt} \]

and

\[ C_2(s) = \frac{C_0(s)}{(\tau s + 1)^2} \]

For \( N \) equal size tanks in series,

\[ C_N(s) = \frac{C_0(s)}{(\tau s + 1)^N} = \frac{1}{\tau^N} \frac{C_0(s)}{(s + 1/\tau)^N} \]

Equation I-1
Substituting Equation H-7 for \( C_0(S) \) yields the required response.

\[
C_N(s) = \frac{1}{\tau^N} \frac{1}{(s + 1/\tau)^N} \left( \frac{(R^2/T_B) \exp(-T_{PS})}{(s + R/T_B + (1-R) \exp(-s(T_{PS} + T_{pp}/(1-R))/s)} \right) \]

Equation I-2
Computer Program for Parameter Estimation

A brief description of the Fortran program is provided below:

**MAIN PROGRAM**
- Calls STAT
- Calls ZXMIN
- Calls RESID
- Calls COVAR
- Writes output

**SUBROUTINE ZXMIN**
- Calls FUNCT
- Calls ZXMJN
- Calls UERTST

**SUBROUTINE COVAR**
- Calls FLINV
- Calls VTPROF
- Calls TANKS
- Calls LINV1F
- Calls LUDATF

**SUBROUTINE FUNCT**
- Calls FLINV
- Calls TANKS

Reads data

Reads initial parameter estimates

Reads final parameter values and calculates partial derivatives

Reads values of parameters of parameters at every iteration

Produces converged values of parameters

Produces Variance-Covariance matrix for parameters

Produces values of $C/C_0$ for both instrument and combined models
Subroutine Name | Description
--- | ---
STAT | - optional, when several values of the dependent variable are available at each time t, this routine calculates the mean and variance for the dependent variable. It also carries out a Bartlett test for equality of variances. (bypassed when IFLAG = 1)
ZXMIN | - IMSL minimization routine used to converge on parameter values (uses a Quasi-Newton method). (ZXMJN, UERTST)
RESID | - routine calculates the weighted or unweighted residual sum of squares. Carries out Derbin-Watson test for serial correlation.
COVAR | - routine that calculates approximate parameter variance-covariance matrix by calculating partial derivative matrix X and subsequently M. Makes use of matrix inversion, matrix multiplication, matrix transposing routines (VTPROF, LINVIF, LUDATF)
FUNCT | - routine that calculates the residual sum of squares, i.e. the function which is being minimized. Uses FLINV to obtain values for the combined model and TANKS to obtain values for the N-tanks in series model.
Subroutine

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLINV</td>
<td>IMSL Laplace inversion routine used to obtain values of $C(t)/C_0$ for the combined model. Algorithm required scaling of both dependent and independent variable.</td>
</tr>
<tr>
<td>TANKS</td>
<td>routine that calculates $F(t)$ for the N-tanks in series model. Maximum number of tanks = 40.</td>
</tr>
</tbody>
</table>

A copy of the program listing is appended.
PROGRAM CONVERGES ON 5 PARAMETERS: T0,T1,P,R,TAU2,TD

IMPLICIT REAL*8 (A-H,O-Z)
EXTERNAL FUNCT
INTEGER NSIG,MAXFN,IOPT
INTEGER NEWTR(25),NEWTS(25),NR,NS,NER,NDS
DIMENSION T(7A),YEXP(150),TI(50)

DIMENSION X(5),H(15),G(5),W(15)
DIMENSION TR(25),YR(25),VR(25)
DIMENSION TS(25),YS(25),VS(25)
DIMENSION P(5),FINV(25),FINS(25),FRACT(5)
DIMENSION ZZ(76),SNAV(25)
DOUBLE PRECISION DIFF(S),AM(5,5),AP(5,5),AMAT(5,5)
DOUBLE PRECISION COV(5,5),CORR(5,5)
COMMON/REACTION/TR,YEXP,FINV,FINS,PCOLS,TC2
COMMON/REACTION/2/NR,NEWTR,NO3
COMMON/REACTION/3/NS,NEWTS,NDS
COMMON/REACTION/4/NR,NEWTR,NO3
COMMON/REACTION/5/NS,NEWTS,NDS
COMMON/MAIN/CO
COMMON/MAIN/NT
CO = 4.000
T0 = 20.000
T0 = T0
IFLAG=1
NP=5
NSIG=4
MAXFN = 500
IOPT=0
WRITE(6,202) NT

202 FORMAT(‘*,’NUMBER OF TANKS IN SERIES=’, I5)
READ(5,100) (X(I),I=1,5)
100 FORMAT(5F10.0)
READ(5,200) NR
200 FORMAT(15)
READ(5,200) NDR
DJ 300 J=1,NR
READ(5,301) T(J),YEXP(J)
T(J) = T0 * T(J)
YEXP(J) = CO * YEXP(J)
WRITE(6,304) T(J),YEXP(J)
FORMAT(‘*,2013,5)

304 CONTINUE
301 FORMAT(2F10.0)
READ(5,302) (NEWTR(L),L=1,NDR)
302 FORMAT(30I1)
READ(5,105) (FRACT(I),I=1,5)
105 FORMAT(3E10.0)
WRITE(6,101)(X(I),I=1,5)
101 FORMAT(‘*,5D13.5)
WRITE(6,201) NR
201 FORMAT(‘*,15)
WRITE(6,201) NDR
WRITE(6,303) (NEWTR(L),L=1,NDR)
303 FORMAT(‘*,4011)

C
READ(5,200) NS
READ(5,200) NDS
WRITE(6,201) NS
WRITE(6,201) NDS
DJ 400 J=1,NS
K=NR+J
READ(5,301)TI(J),YEXP(K)
TII(J)=TII(J)+TII(J)
YEXP(K)=C0*YEXP(K)
WRITE(6,304)TI(J),YEXP(K)
400 CONTINUE
READ(5,302)(NEWTS(L),L=1,NDS)
WRITE(6,303)(NEWTS(L),L=1,NDS)
IF(IFLAG.EQ.1)GOTO 769
CALL STAT(T,YEXP(1),NR,NDR,NEWTR,TE,YR,VR,PCOLR,CR)
DO 450 J=1,NDR
WRITE(6,500)TR(J),YR(J),VR(J)
450 CONTINUE
500 FORMAT(13D13.5)
WRITE(6,550)PCOLR,CR
550 FORMAT(13D13.5,1D13.5,1D13.5,1D13.5)
CALL STAT(T,YEXP(NR+1),NS,NDS,NEWTS,TS,YS,VS,POOLS,CS)
DO 600 J=1,NDS
WRITE(6,500)TS(J),YS(J),VS(J)
600 CONTINUE
WRITE(6,550)PCOLS,CS
IF(IFLAG.EQ.0)GOTO 790
700 DO 750 K=1,NDS
READ(5,751)VS(K)
750 CONTINUE
DO 760 K=1,NDR
READ(5,751)VR(K)
760 CONTINUE
751 FORMAT(E10.5)
769 CONTINUE
DO 770 K=1,NR
TR(K)=T(K)
770 CONTINUE
DO 780 K=1,NS
TS(K)=TI(K)
780 CONTINUE
1 DO 1 I=1,NR
VR(I)=0.0
1 CONTINUE
2 DO 2 I=1,NS
VS(I)=0.0
2 CONTINUE
CALL ZMIN(FUNCT,NP,NSIG,MXFN,IOPT,X,H,G,F,W,IER)

CALCULATING RESIDUALS
CALL RESID(TR,VR,F INV,YEXP(1),NDR,AR,NEWTR)
CALL RESID(TS,VS,F INS,YEXP(NR+1),NDS,NS,NEWTS)

P(1)=X(1)*X(1)
P(2)=X(2)*X(2)
P(3)=EXP(-X(3)*X(3))
P(4)=(DSIN(X(4)**2/1.57079D-04))**2
P(3)=X(5)

5050 DD,5050 K=1,NP
   DIFF(K)=FRACT(K)*P(K)
   IF(DIFF(K) LT 1.0E-10)DIFF(K)=FRACT(K)
   CONTINUE

CALL CDVAR(P,DIFF,F,AM,AP,AMAT,CCV,CCRF,NP)
WRITE(6,9001)(R(1),I=1,NP)

900 FORMAT(* PARAMETERS ARE*,5D15.7)
WRITE(6,9011)(DIFF(I),I=1,NP)
WRITE(6,8031)
WRITE(6,9041)((AM(I,J),J=1,NP),I=1,NP)
WRITE(6,9042)((AP(I,J),J=1,NP),I=1,NP)
WRITE(6,9044)
WRITE(6,9045)((AMAT(I,J),J=1,NP),I=1,NP)
WRITE(6,9046)
WRITE(6,9047)((CCV(I,J),J=1,NP),I=1,NP)
WRITE(6,9048)
WRITE(6,9049)

901 FORMAT(* T10,'DELTAS',5D13.5)
904 FORMAT(* ,5D13.5)
903 FORMAT(* ,T10,'PRODUCT OF X TRANSFCE X',
1'RESPONSE 1 THEN RESPONSE 2',/
804 FORMAT(* ,T10,'M MATRIX,XTX+XTX',/
805 FORMAT(* ,T10,'APPROXIMATE PARAMETER VAR-CCV MATRIX',/
806 FORMAT(* ,T10,'PARAMETER CORRELATION MATRIX',/

STOP
END

SUBROUTINE SUPPLIED FOR ZMIN

SUBROUTINE FUNCT(N,X,SS)
IMPLICIT REAL*8 (A-H,O-Z)
INTEGER N, NSIG, KMAX, IER
INTEGER NEWTR(25), NEWTS(25), NR, NS, NTR, NDS
DIMENSION X(S), YEXP(150), T1(60)
DIMENSION TR(25), YR(25), VR(25)
DIMENSION TS(25), YS(25), VS(25)
DIMENSION FINV(25), FINS(25)
COMPLEX*16 F, TB, R, TAU2, TD, TP, DCPLX
COMMON/REACT1/TR, YEXP, FINV, VR, PCCLR, TOT1
COMMON/SENSE1/TS, YS, FINS, NDS, TOT2
COMMON/REACT2/NR, NEWTR, NDR
COMMON/SENSE2/NS, NEWTS, NDS
COMMON/PLACE/ TB, TAL2, TD, TP, R
DATA FACT / 1. 570796 - 04 /

EXTERNAL F

TB = DCPLX(X(1)**2, 0. * 0D0)
TP = DCPLX(X(2)**2, 0. * 0D0)
R = DCPLX(DEXP(-X(3)**2), 0. * 0D0)
TAU2R = (DSIN(X(4)**2 * FACT) * ** 2.
TAU2 = DCPLX(TAU2R, 0. * 0D0)
TD = DCPLX(X(5), 0. * 0D0)

NSIG = 6
KMAX = 200
ALPHA = 0. * 0D0
WRITE(6, 230)(X(I), I = 1, 5)
WRITE(6, 200)TB, TAU2, TD
WRITE(6, 200)TP, R
200 FORMAT(5D13.6)
CALL FLINV(F, NDR, TR, ALPHA, NSIG, KMAX, FINV, IER)
CALL TANKS(TS, NDS, TAU2R, 0. * 0D0, FINS)

DO 75 J = 1, NDR
IE = TR(J), LT, X(5) FINV(J) = 0. * 0D0
75 CONTINUE

CALCULATING WEIGHTED SUM OF SQUARES
JJ = 0
TOT1 = 0. * 0D0

DO 100 K = 1, NDR
KK = NEWTR(K)
DO 90 J = 1, KK
TOT1 = TOT1 + (FINV(K) - YEXP(J + JJ)) ** 2
90 CONTINUE
JJ = JJ + KK
100 CONTINUE

WRITE(6, 101) TOT1
COMMON/SENSE1/TS, VS, FINS, POOLS, TCT2
COMMON/REACT2/NB, NEWNR, NDR
COMMON/SENSE2/NS, NEWTS, ND2
COMMON/PLACE/TB, TAU2, TD, TP, R
EQUIVALENCE (FNEW(1), TB), (PNEW(2), TAU2), (FNEW(3), TD)
EQUIVALENCE (PNEW(4), TP), (PNEW(5), R)

NSIG = A
KMAX = 200
ALPHA = 0.000
PNEW(1) = DCMPLX(P(1), 0.000)
PNEW(4) = DCMPLX(P(4), 0.000)
PNEW(5) = DCMPLX(P(5), 0.000)
PNEW(2) = DCMPLX(P(2), 0.000)
PNEW(3) = DCMPLX(P(3), 0.000)

NE = NR
DO 20 J = 1, NEW
   IF(J LE NDR) TALL(J) = TR(J)
   IF(J GT NDR) TALL(J) = TS(J - NDR)
   CONTINUE
20 CALL FLINV(F, NEW, TALL, ALPHA, NSIG, KMAX, FO, IER)

DO 50 I = 1, NP
   PNEW(1) = PNEW(1) + DCMPLX(DIFF(I), 0.000)
   IF(I LE I1) PNEW(I-1) = DCMPLX(P(I-1), 0.000)
   CALL FLINV(F, NEW, TALL, ALPHA, NSIG, KMAX, FUNC, IER)
   DO 40 J = 1, NEW
      A(J, I) = (FUNC(J) - FO(J)) / DIFF(I)
40 CONTINUE
50 CONTINUE

DO 55 I = 1, NP
   JJ = 0
   DO 54 K = 1, NEW
      IF(K LE NDR) KK = NEWTR(K)
      IF(K GT NDR) KK = NEWTS(K - NDR)
      DO 53 J = 1, KK
         AX(J+JJ, I) = A(K, I)
53 CONTINUE
54 JJ = JJ + KK
55 CONTINUE

CALL VTPROF(A, NR, NF, 150, ATA)

K = 0
DO 60 I = 1, NP
   DO 59 J = 1, I
      AM(I, J) = ATA(K)
      IF(I GT NE, J) AM(J, I) = AM(I, J)
59 CONTINUE
60 CONTINUE
DO 100 I=1,NP
   DO 95 J=1,NP
      A(J,1)=0.000
      IF(1,N.E.2)GOTO 91
      DELTA=0.000
      PARM=P(2)
      CALL TANKS(TALL,NEW,PARM,DELTA,F1)
      CALL TANKS(TALL,NEW,PARM,DIFF(2),F2)
      A(J,1)=(F2(J)-F1(J))/DIFF(1)
   CONTINUE
91   *CONTINUE
100  CONTINUE

C
DO 300 K=1,NP
   J=0
   DO 299 K=1,NP
      IF(K .GT. NDR) K=NEWTS(K-NDR)
      AX(J+J,K)=1
      J=J+K
299  CONTINUE
300  CONTINUE

C
CALL VTPROF(AX,NR,NP,150,ATA)

C
   K=0
   DO 65 I=1,NP
      DO 65 J=1,NP
         AP(I,J)=ATA(K)
         IF(I,N.E.1) AP(J,J)=AP(I,J)
   65  CONTINUE
67   CONTINUE

C
DO 150 I=1,NP
   DO 125 J=1,NP
      AMAT(I,J)=AM(I,J)/(TOT1/(NR-NP)) + AP(I,J)/(TOT2/(NS-NP))
      AJUNK(I,J)=AMAT(I,J)
125  CONTINUE
150  CONTINUE

C
CALL LINVF(AJUNK,NP,NP,COV,0,WKAREA,IER)

C
CALCULATING THE PARAMETER CORRELATION MATRIX

C
DO 200 I=1,NP
   DO 90 J=1,NP
      CORR(I,J)=COV(I,J)/DSQRT(COV(I,I)*COV(J,J))
90   CONTINUE
200  CONTINUE

C
RETURN
END

C
SUBROUTINE STAT(T,YEXP,ND,NN,NEW,TT,Y,VAR,POHLS,CHI)

C
IMPLICIT REAL*8 (A-H,O-Z)
DOUBLE PRECISION T(ND),YEXP(ND),TT(NN),Y(NN),VAR(NN)
INTEGER NEWT(NN)
CALCULATION OF DIFFERENT TIME VALUES
CALCULATION OF THE MEAN AND VARIANCE AT EACH TIME

PREV = -1.000
KJ=0
DO 450 J=1,ND
   IF(T(J).NE.PREV)GO TO 450
   KJ=KJ+1
   T(T(J))=T(J)
   PREV=T(J)
450 CONTINUE

JJ=0
DO 460 K=1,NN
   KK=NEWT(K)
   TOT=0.
   DO 455 J=1,KK
      TOT=TOT + YEXP(J+JJ)
   455 CONTINUE
   Y(K)=TOT/KK
   JJ=KK+JJ.
460 CONTINUE

JJ=0
DO 470 K=1,NN
   KK=NEWT(K)
   TOT=0.
   DO 465 J=1,KK
      TOT=TOT + (YEXP(JJ+J)-Y(K))**2
   465 CONTINUE
   VAR(K)=TOT/(KK-1)
   IF(VAR(K).LE.1.0D-03)VAR(K)=1.0D-05
   JJ=JJ+KK
470 CONTINUE

BARTLETT'S TEST FOR EQUALITY OF VARIANCES

SUM=0.
TOT=0.
DO 1001 J=1,NN
   TOT=TOT + NEWT(J)
   SUM=SUM + (NEWT(J)-1)*VAR(J)
1001 CONTINUE

TOT=TOT-NN
POCLS = SUM/TOT

C=1. + (TOT-1./TOT)/(J.*((NN-1))

TOT = 0.
DO 1002 J=1,NN
   TOT = TOT + NEWT(J) * DLOG(VAR(J)/POCLS)
1002 CONTINUE

CHI = -TOT/C

RETURN
END
SUBROUTINE RESIU(TT,VAR,F,YEXP,ND,NCDATA,NEWT)
IMPLICIT REAL*8 (A-F,O-Z)

DIMENSION ZZ(100),TT(ND),VAR(ND),F(ND)
DIMENSION YEXP(NDATA), SAV(100)
INTEGER NEWT(ND)

WRITE(*,690)
FORMAT(' 20X,'TIME(S),8X,'VARIANCE',8X,'PRED.',
1' VALUE',15X,'EXP VALUE',15X,'RESIDUALS')/j
J=0
DO 550 K=1,ND
K=NEWT(K)
WRITE(6,690) TT(K),VAR(K),F(K)
DO 525 J=1,KK
ZZ(J+JJ)=YEXP(J+JJ)-F(K)
WRITE(6,601)YEXP(J+JJ),ZZ(J+JJ)
525 CONTINUE
JJ=JJ+KK
550 CONTINUE
500 FORMAT(' 15D15.6,15D15.6,15D15.6,15D15.6,15D15.6')
501 FORMAT(' 15D15.6,15D15.6,15D15.6,15D15.6,15D15.6')
C
DO 900 J=1,2
C DERBIN WATSON TEST FOR SERIAL CORRELATION
KK=I-NEWT(J)
DC 850 K=1,ND
SAV(K)=ZZ(K+NEWT(K))
950 C
KK=KK+NEWT(K)
CONTINUE
C
SUM=0.0D0
TOT=0.0D0
J=ND-1
DO 800 K=1,J
SUM=SUM + (SAV(K+1)-SAV(K))**2
TOT=TOT + SAV(K)**2
800 CONTINUE
C
TOT = TOT + SAV(ND)**2
D=SUM/TOT
C
WRITE(6,998) D
FORMAT(' 15D15.6,DERBIN WATSON TEST, D=',D14.7)
900 C
RETURN
END

C SUBROUTINE TANKS(T,N,TAU,DELTA,F)
C SUBROUTINE PREDICTS OUTPLT FROM NT TANKS IN SERIES WITH EQUAL
C TIME CONSTANTS
C NT=NUMBER OF TANKS
C
IMPLICIT REAL*8 (A-H,O-Z)
DOUBLE PRECISION T(K),SMALL,TAU,F(N)
COMMON/MAIN/C0
COMMON/MAIN/NT
DATA ONE/1.0D0/,SMALL/1.0D-04/
C OUTER LOOP CORRESPONDS TO INDIVIDUAL DATA POINTS
C
IFLAG=0
DO 100 J=1,N
F(I)=0.0D0
Q=T(I)/TAU + DELTA)
100 CONTINUE
IF(0. GE. 1.78) IFLAG = 1
IF(IFLAG .EQ. 1) GOTO 75

DENOM = 1.0D0

C

P = DEXP(-Q)
DO 50 J = 1, NT
    L = J - 1
    IF(J .NE. 1) DENCM = DENCM * L
    IF(L .GE. 25) GOTO 30
    R2 = 1.0D0
    R1 = 0. * M
    GOTO 35
  30 CONTINUE
    M = L / 2
    M1 = L - M
    M2 = M
    R1 = 0. * M1
    R2 = 0. * M2

  35 F(I) = F(I) + R1 / DENCM * R2
    CONTINUE
  50 CONTINUE

C

F(I) = F(I) * P
IF(F(I) .LT. SMALL) IFLAG = 1
CONTINUE
    F(I) = CQ * (CNE - F(I))

100 CONTINUE
C
RETURN
C
END
APPENDIX K

Void Volume Estimates of Char Bed

Estimates of the fractional voids in packed beds are found in Figure 5-53 in Perry's Chemical Engineers Handbook (5th Ed.).

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>( \frac{D_p}{D_t} )</th>
<th>Spheres</th>
<th>Granules</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 - 0.4 mm</td>
<td>0.019</td>
<td>0.333</td>
<td>0.42</td>
</tr>
<tr>
<td>0.4 - 1.0 mm</td>
<td>0.044</td>
<td>0.358</td>
<td>0.45</td>
</tr>
<tr>
<td>1.0 - 1.4 mm</td>
<td>0.074</td>
<td>0.36</td>
<td>0.45</td>
</tr>
</tbody>
</table>

The volume of the annular char bed can be calculated as

\[
V = \frac{\pi(D_2^2 - D_1^2)h}{4} \quad D_1 = 0.125 \text{ in} \\
D_2 = 0.625 \text{ in} \\
V = 14.5 \text{ cm}^3 \\
h = 3 \text{ in}
\]

The volume occupied by the particles is therefore \((1-\epsilon)V\). The range for these volumes is tabulated below:

<table>
<thead>
<tr>
<th>Particle Size</th>
<th>Estimated Volume Occupied by char (cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 - 0.4</td>
<td>8.41 &lt; ( V_p ) &lt; 9.67</td>
</tr>
<tr>
<td>0.4 - 1.0</td>
<td>7.98 &lt; ( V_p ) &lt; 9.31</td>
</tr>
<tr>
<td>1.0 - 1.4</td>
<td>7.98 &lt; ( V_p ) &lt; 9.28</td>
</tr>
</tbody>
</table>
APPENDIX L

Approximate Pressure Drop Calculation for Internal Recirculation Reactor

A simplified view of the reactor internals is given below:

Assuming the gas experiences negligible resistance from the end of the impeller shaft to the bottom of the packed bed, one can get an estimate of the pressure head developed by the impeller and available for gas flow.

A simple Bernoulli equation ignoring any potential energy changes in the system is given below:

\[
\frac{1}{2} \frac{v^2}{g_c} + \frac{\Delta P}{\rho} = 0
\]

\[g_c = 32.17 \text{ lb-ft} \left(\frac{1 \text{ ft}}{1 \text{ lb}_f s^2}\right) ; \quad v = \frac{r \omega}{25.4 \text{ mm/in}} = 17 \text{ mm} \left(\frac{1 \text{ ft}}{12 \text{ in}}\right) \left(\frac{2 \pi \text{ rev}}{1 \text{ min}}\right) \left(\frac{1 \text{ min}}{60 \text{ s}}\right)
\]

\[v = 10.5 \text{ ft/s}
\]

\[\rho = \frac{P}{RT} = \frac{1 \text{ atm}}{82.05 \text{ cm}^3 \text{ atm}(298) \text{ K}} = 4.1 \times 10^{-5} \text{ mol/cm}^3 = 32.3 \text{ lb/ft}^3
\]
Substituting these values into the equation gives

\[ \frac{(10.5)^2}{2(32.2)} + \frac{\Delta P}{32.2} = 0 \]

\[ \Delta P = 55.3 \text{ lb/ft}^2 = 0.382 \text{ psi} \]

This is a very small pressure head.

The Ergun equation can be used to calculate the velocity through the drierite/ascarite-bed (8 mesh) for this pressure

\[ \frac{\Delta P}{L} = 150 \frac{(1-\epsilon)^2}{\phi_s d_p^2} \frac{\mu v}{g_c \epsilon^3} + 1.75 \frac{(1-\epsilon)}{\phi_s d_p^2} \frac{\rho v^2}{g_c \epsilon^3} \]

where \( \epsilon \sim 0.4 \)
\( \phi_s \sim 0.75 \)
\( L = 0.25 \text{ ft} \)
\( d_p = 7.75 \times 10^{-3} \text{ ft} \)
\( \Delta P = 55.3 \text{ lb/ft}^2 \)

The linear fluid velocity in the empty bed is found to be

\[ v = 0.321 \text{ ft/s} \]

This velocity is not substantially greater than the inlet fluid velocity which is

\[ v_{in} = 4000 \text{ cm}^3/\text{min} \times \frac{1}{(\pi \frac{0.375}{4} 2.54^2 30.48^{0.6})} = 0.29 \text{ ft/s} \]

This would indicate that there isn't sufficient circulation through the bed.
Experimental Data From Mixing Tests

Particle Size
Gas Flowrate 1000 cm³/min
Impeller Speed 1800 rpm

<table>
<thead>
<tr>
<th>Elapsed Time [s]</th>
<th>Measurement</th>
<th>Combined Response C/C₀</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Device Response C/C₀</td>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
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<td>0</td>
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<tr>
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<td>0.8</td>
<td>0</td>
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<td>0.909</td>
<td>0</td>
</tr>
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<td>0.936</td>
<td>0.04167</td>
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</table>
Particle Size \(1.0 - 1.4 \text{ mm}\)
Gas Flowrate \(1000 \text{ cm}^3/\text{min}\)
Impeller Speed \(1800 \text{ rpm}\)

<table>
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<tr>
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<th>Measurement Device Response (C/C_0)</th>
<th>Combined Response (C/C_0)</th>
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<td>0</td>
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Particle Size: 1.0 - 1.4 mm
Gas Flowrate: 1000 cm$^3$/min
Impeller Speed: 500 rpm

<table>
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<th>Combined Response C/C$_0$</th>
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Particle Size 0.4 - 1.0 mm  
Gas Flowrate 750 cm³/min  
Impeller Speed 900 rpm  

<table>
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<tr>
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<th>Measurement Device Response C/C₀</th>
<th>Combined Response C/C₀</th>
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**Particle Size**: 0.4 - 1.0 mm  
**Gas Flowrate**: 750 cm$^3$/min  
**Impeller Speed**: 900 rpm

<table>
<thead>
<tr>
<th>Elapsed Time [s]</th>
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Gas Flowrate 500 cm³/min
Impeller Speed 500 rpm

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