FATE OF COAL NITROGEN

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ABSTRACT

Nitrogen oxides generated from coal nitrogen contribute about a third of the total nitrogen oxides emitted from electric power generation. For coal reserves to be effectively used, methods must be developed to suppress the formation of nitrogen oxides formed from nitrogen in the coal during burning.

Possibilities for suppression of fuel nitrogen conversion to nitric oxide by combustion modification involve alteration of local temperatures, richness, and mixing patterns to increase the regions of the flame where nitrogen compounds are reduced to \( N_2 \). This study has developed fundamental information of fuel nitrogen behavior in the different regions of coal burning. This information can be used to guide development of improved emission control strategies.

Devolutilization of a lignite-A and a hvA bituminous coal was studied at the conditions of a large pulverized coal flame-heating rate of \( 10^4-10^6 \) K/sec, temperatures of 1000-2100 K, and residence times of 2-1000 milliseconds. These experiments were supplemented by experiments on devolutilization of coal maintained at furnace temperature for long times and on the oxidation of coal and devolutilized char.

The devolutilization experiments showed that no nitrogen loss occurred until 10-15\% of the coal had been devolutilized—implying that coal nitrogen is contained mostly in heterocyclic rings. Nitrogen could be completely removed from the char by heating for long times at temperatures above 1750 K, implying that nitrogen does not form condensed stable structures at pulverized flame temperatures as carbon does. After initial fracture, loss of nitrogen and total weight loss are linearly correlated with a nitrogen to carbon slope of 1.25 to 1.50. The pseudo-first order rate constant for initial nitrogen loss was found to be

\[
k = 9.3 \times 10^3 \exp(-22,600/RT) \text{ sec}^{-1}
\]

The efficiencies of volatile nitrogen conversion to nitric oxide, from the experiments on coal and char oxidation, were estimated to be between those of a premixed and a diffusion flame. For the conditions of the present study, volatile nitrogen contributed between 60 and 80\% of the nitrogen oxides produced from fuel nitrogen. Conversions of the fuel nitrogen
to nitrogen oxides in the present experiments agree well with field data at a fuel equivalence ratio of 0.7 and showed that conversions below 10% could be achieved at high fuel equivalence ratios. Percent conversion to nitric oxide of the nitrogen in char was 2-3 times lower than the corresponding values for coal. When the furnace temperature was increased from 1500 to 1750°C, the conversion of fuel nitrogen to nitric dropped by 5-10% absolute, an improvement of a factor of two in some regions, and burnout was essentially complete even at very rich fuel equivalence ratios.

Practical applications of this work are complicated by interaction between volatilization of nitrogen compounds and increase in richness because of increased volatile evolution. One practical suggestion that should be evaluated on a larger scale is to increase the temperature of the first stage of a two stage combustor that is operated as rich as possible consistent with flame stability.

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June 1976

Professor Irving Kaplan
Secretary of the Faculty
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Dear Professor Kaplan:

In accordance with the regulations of the faculty, I herewith submit a thesis entitled "Fate of Coal Nitrogen", in partial fulfillment of the requirements for the degree of Doctor of Science in Chemical Engineering at the Massachusetts Institute of Technology.

Respectfully submitted,

John H. Pohl
ACKNOWLEDGEMENTS

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DEDICATED TO

MY FAMILY
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>1</td>
</tr>
<tr>
<td>AUTHORIZATION PAGE</td>
<td>2</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>3</td>
</tr>
<tr>
<td>LETTER OF TRANSMITTAL</td>
<td>5</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>6</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>8</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>9</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>17</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>21</td>
</tr>
<tr>
<td>I. SUMMARY</td>
<td>22</td>
</tr>
<tr>
<td>I-1. Fuel nitrogen problem</td>
<td>22</td>
</tr>
<tr>
<td>I-2. Control of fuel nitrogen</td>
<td>23</td>
</tr>
<tr>
<td>I-3. Previous work</td>
<td>24</td>
</tr>
<tr>
<td>I-4. Coal flame</td>
<td>25</td>
</tr>
<tr>
<td>I-5. Equipment</td>
<td>26</td>
</tr>
<tr>
<td>I-6. Devolutilization</td>
<td>27</td>
</tr>
<tr>
<td>I-7. Coal burning</td>
<td>29</td>
</tr>
<tr>
<td>I-8. Volatile burning</td>
<td>30</td>
</tr>
<tr>
<td>I-9. Char burning</td>
<td>31</td>
</tr>
<tr>
<td>II. INTRODUCTION</td>
<td>33</td>
</tr>
<tr>
<td>II-1. Fuel nitrogen in fossil fuels</td>
<td>34</td>
</tr>
<tr>
<td>II-1.1 United States energy reserves, uses and policies</td>
<td>34</td>
</tr>
</tbody>
</table>
II-1.2 Potential Coal Use .................................. 35
II-1.3 Nitrogen in Petroleum ................................. 39
II-1.4 The Potential of Oil Shale ......................... 40
II-1.5 Summary of Fuel Nitrogen Prospects ............... 40
II-2. Nitrogen Oxides Produced From Fuel Nitrogen .... 41
   II-2.1 Nitrogen Content of United States Coals .... 41
   II-2.2 Nitrogen Content of Petroleum Products ... 44
   II-2.3 Nitrogen in Shale Oil ............................ 48
II-3. Summary of Fuel Nitrogen ............................. 48
III. PREVIOUS WORK ........................................... 50
   III-1. Coal Systems ...................................... 50
   III-2. Practical Systems ................................ 51
   III-3. Laboratory Burner Systems ....................... 53
   III-4. Fuel Nitrogen Reaction Mechanisms ........... 55
IV. FLAME EQUATIONS ......................................... 57
   IV-1. Flame Equations .................................... 58
      IV-1.1 One Dimensional Flame Equations ............ 61
      IV-1.2 Simplification of the Pressure Tensor ....... 61
         IV-1.2.1 Elimination of Bulk Viscosity ........... 62
         IV-1.2.2 Elimination of the Viscous Terms ...... 62
      IV-1.3 Simplification of the Momentum Equation ... 63
         IV-1.3.1 Elimination of the Buoyant Term ......... 63
         IV-1.3.2 Calculation of the Flame Pressure Drop 64
      IV-1.4 Simplification of the Diffusional Velocity 64
         IV-1.4.1 Thermal Diffusion (Soret Effect) ....... 65
      IV-1.5 The Specie Conservation Equation ........... 66
IV-1.6  Simplification of the Heat Flux Vector ... 68
   IV-1.6.1  Diffusional Heat Flux ............ 68
   IV-1.6.2  Dufour Effect (Temperature Driven Diffusional Flux of Energy) ... 70
   IV-1.6.3  Radiation ...................... 70
      IV-1.6.3.1  Thermal Radiation ........... 70
      IV-1.6.3.2  Cheminluminescent Radiation ... 71
IV-1.7  Simplification of the Energy Equation ... 77
   IV-1.7.1  Elimination of the Kinetic Energy ... 78
   IV-1.7.2  The Pressure Work Term .......... 78
   IV-1.7.3  Elimination of the Gravity Term ... 79
   IV-1.7.4  Expression of the Energy Equation in Terms of Enthalpy .......... 79
IV-1.8  Summary of the Simplified Flame Equations ... 79
IV-2.  Previous Solutions of the Flame Equations ... 82
   IV-2.1  Steady State Flame Equation Approach ... 83
   IV-2.2  Unsteady State Flame Equation Approach ... 85
   IV-2.3  Shvab-Zeldovich Formation of the Flame Equations .................. 86
   IV-2.4  Comparison of Flame Equation Solution Methods .................. 88
   IV-2.5  Solution Method .................... 90
      IV-2.5.1  Introduction of Temperature into the Energy Equation .......... 90
      IV-2.5.2  Von Mises' Coordinates ........... 92
      IV-2.5.3  Other Grid Distribution Methods ... 95
      IV-2.5.4  Introduction of Von Mises' Coordinates into the Conservation Equations ... 98
      IV-2.5.5  Boundary Conditions .............. 99
      IV-2.5.6  Initial Conditions .............. 108
IV-3. Differencing the Flame Equation ........................................ 110
  IV-3.1 Previous Solutions to the Partial
        Differential Flame Equations .................................. 111
            IV-3.1.1 Explicit Solutions to the Flame
                       Equations ........................................... 111
            IV-3.1.2 Implicit Solutions to the Flame
                       Equations ........................................... 113
  IV-3.2 Crank-Nicolson Difference of the Flame
         Equations ................................................................ 115
            IV-3.2.1 The Specie Difference Equation ....................... 116
            IV-3.2.2 The Energy Difference Equation ....................... 127
  IV-3.3 Solution of the Difference Equations ......................... 132
IV-4. Summary of the Flame Equations ..................................... 133
V. EQUIPMENT AND PROCEDURE ................................................. 135
  V-1. Flow Furnace ............................................................. 136
      V-1.1 Laminar Flow Experiment ....................................... 137
      V-1.2 Coal Feeder ......................................................... 139
      V-1.3 Particle Collector ................................................ 140
      V-1.4 Gas Preheater ....................................................... 141
      V-1.5 Suction System ...................................................... 141
      V-1.6 Experimental Procedure ......................................... 142
  V-2. Free Fall Experiment with Bronze Collector .................... 143
      V-2.1 Experimental Procedure ......................................... 144
      V-2.2 Free Fall Experiment with Alumina Collector ............... 144
  V-3. Crucible Experiment .................................................. 147
      V-3.1 Experimental Procedure ......................................... 147
  V-4. Oxidation Experiments ............................................... 147
  V-5. ASTM Proximate Analysis Equipment ............................... 149
VI COAL CHARACTERIZATION ........................................ 152

VI-1. Montana Lignite ............................................. 154
   VI-1.1 Visual Appearances of Montana Lignite .......... 154
   VI-1.2 Size Distribution ..................................... 157
   VI-1.3 Surface Area .......................................... 160
   VI-1.4 Proximate Analysis .................................. 161
   VI-1.5 Heat of Combustion ................................... 163
   VI-1.6 Elemental Analysis ................................... 163
   VI-1.7 Ash Analysis ........................................... 165
   VI-1.8 Functional Group Analysis ......................... 167

VI-2. Pittsburgh Seam #8 Bituminous Coal ................ 168
   VI-2.1 Visual Appearance of Pittsburgh
       Bituminous Coal ........................................ 168
   VI-2.2 Particle Size Distribution ......................... 171
   VI-2.3 Surface Area .......................................... 173
   VI-2.4 Proximate Analysis .................................. 175
   VI-2.5 Heat of Combustion ................................... 175
   VI-2.6 Elemental Analysis ................................... 175
   VI-2.7 Ash Analysis ........................................... 175
   VI-2.8 Functional Group Analysis ......................... 177

VI-3. Physical Properties of Coal .............................. 180

VII. COAL RESULTS ................................................ 182

VII-1. Coal Flame ................................................. 182

VII-2. Devolatilization Results ................................. 186
   VII-2.1 Devolatilization Results from Crucible
       Experiments ............................................... 186
       VII-2.1.1 Pittsburgh Seam #8 hvA Bituminous
       Coal ....................................................... 186
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>VII-2.1.2</td>
<td>Montana Lignite</td>
<td>188</td>
</tr>
<tr>
<td>VII-2.2</td>
<td>Devolutilization of Coal in the Dispersed Phase</td>
<td>190</td>
</tr>
<tr>
<td>VII-2.2.1</td>
<td>Pittsburgh Seam #8 Bituminous Coal</td>
<td>191</td>
</tr>
<tr>
<td>VII-2.2.2</td>
<td>Montana Lignite</td>
<td>195</td>
</tr>
<tr>
<td>VII-2.2.3</td>
<td>Nitrogen Pyrolysis From Lignite and Bituminous Coal</td>
<td>197</td>
</tr>
<tr>
<td>VII-3</td>
<td>Oxidation Results</td>
<td>201</td>
</tr>
<tr>
<td>VII-3.1</td>
<td>Oxidation of Lignite and Bituminous Coal</td>
<td>204</td>
</tr>
<tr>
<td>VII-3.2</td>
<td>Oxidation of Lignite Char</td>
<td>204</td>
</tr>
<tr>
<td>VIII</td>
<td>DISCUSSION OF RESULTS</td>
<td>208</td>
</tr>
<tr>
<td>VIII-1</td>
<td>Discussion of Crucible Results</td>
<td>208</td>
</tr>
<tr>
<td>VIII-1.1</td>
<td>Previous Work on Coal Nitrogen Distribution at Coking Conditions</td>
<td>209</td>
</tr>
<tr>
<td>VIII-1.2</td>
<td>Crucible Results From This Study</td>
<td>219</td>
</tr>
<tr>
<td>VIII-1.3</td>
<td>Models Based on Coking Data</td>
<td>222</td>
</tr>
<tr>
<td>VIII-2</td>
<td>Discussion of Pyrolysis Results</td>
<td>224</td>
</tr>
<tr>
<td>VIII-2.1</td>
<td>Division of Coal Nitrogen Between the Char and Volatile Matter</td>
<td>225</td>
</tr>
<tr>
<td>VIII-2.2</td>
<td>Nitrogen Devolutilized in a Pulverized Coal Flame</td>
<td>226</td>
</tr>
<tr>
<td>VIII-2.2.1</td>
<td>Empirical Correlation of Nitrogen Pyrolysis From Coal</td>
<td>228</td>
</tr>
<tr>
<td>VIII-2.2.2</td>
<td>Empirical Correlation Between Nitrogen Loss and Total Weight Loss</td>
<td>235</td>
</tr>
<tr>
<td>VIII-2.2.3</td>
<td>Prospects for Development of a Coal Nitrogen Pyrolysis Model</td>
<td>241</td>
</tr>
<tr>
<td>VIII-2.2.3.1</td>
<td>Variation of Pyrolysis Rate Constants</td>
<td>244</td>
</tr>
<tr>
<td>VIII-2.2.3.2</td>
<td>Bimolecular and Free Radical Pyrolysis Reaction</td>
<td>246</td>
</tr>
</tbody>
</table>
APPENDIX VII. Surface Areas of Devolatilized Coal . . . 366
APPENDIX VIII. Changes in Physical Structure of Devolatilized Coal . . . . . 370
BIBLIOGRAPHY . . . . . . . . . . . . . . . . . . . . . 385
BIOGRAPHY . . . . . . . . . . . . . . . . . . . . . . 429
<table>
<thead>
<tr>
<th>FIGURE</th>
<th>Description</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-1.</td>
<td>United States energy supply and reserves</td>
<td>36</td>
</tr>
<tr>
<td>II-2.</td>
<td>Nitrogen and sulfur contents of United States coal reserves compared to emission standards</td>
<td>42</td>
</tr>
<tr>
<td>II-3.</td>
<td>Conversion of fuel nitrogen in practical combustors</td>
<td>45</td>
</tr>
<tr>
<td>II-4.</td>
<td>Nitrogen distribution in retined petroleum products</td>
<td>47</td>
</tr>
<tr>
<td>IV-1.</td>
<td>Conditions of an atmospheric pressure flat flame</td>
<td>60</td>
</tr>
<tr>
<td>VI-1.</td>
<td>Scanning electron micrograph of a raw Montanta lignite-A</td>
<td>155</td>
</tr>
<tr>
<td>VI-2.</td>
<td>Photomicrograph of polished raw lignite-A</td>
<td>156</td>
</tr>
<tr>
<td>VI-3.</td>
<td>Rosin-Rammler accumulative size distribution of lignite particles</td>
<td>158</td>
</tr>
<tr>
<td>VI-4.</td>
<td>Lignite particle size frequency distribution</td>
<td>159</td>
</tr>
<tr>
<td>VI-5.</td>
<td>Scanning electron micrograph of raw Pittsburgh seam #8 hvA bituminous coal</td>
<td>169</td>
</tr>
<tr>
<td>VI-6.</td>
<td>Photomicrograph of polished raw Pittsburgh seam #8 hvA bituminous coal</td>
<td>170</td>
</tr>
<tr>
<td>VI-7.</td>
<td>Rosin-Rammler accumulative size distribution of bituminous coal</td>
<td>172</td>
</tr>
<tr>
<td>VI-8.</td>
<td>Bituminous particle size frequency distribution</td>
<td>174</td>
</tr>
<tr>
<td>VII-1.</td>
<td>Schematic of a single coal particle burning in a pulverized coal flame</td>
<td>183</td>
</tr>
<tr>
<td>VII-2.</td>
<td>Crucible devolatilization of Pittsburgh seam #8 hvA bituminous coal</td>
<td>187</td>
</tr>
<tr>
<td>VII-3.</td>
<td>Crucible devolatilization of Montana lignite-A</td>
<td>189</td>
</tr>
<tr>
<td>VII-4.</td>
<td>Element loss with devolatilization of a Pittsburgh seam #8 hvA bituminous coal</td>
<td>192</td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>VII-5</td>
<td>Element loss with devolatilization of a Montana lignite-A</td>
<td>196</td>
</tr>
<tr>
<td>VII-6</td>
<td>Retention of nitrogen in devolatilized lignite and bituminous coal chars</td>
<td>198</td>
</tr>
<tr>
<td>VII-7</td>
<td>Conversion of coal nitrogen as a function of fuel equivalence ratio in a $1500^\circ$K furnace</td>
<td>202</td>
</tr>
<tr>
<td>VII-8</td>
<td>Conversion of coal nitrogen as a function of fuel equivalence ratio in a $1750^\circ$K furnace</td>
<td>205</td>
</tr>
<tr>
<td>VII-9</td>
<td>Conversion of nitrogen as fuel equivalence ratio in a $1500^\circ$K furnace for a lignite char previously devolatilized at $1500^\circ$K for 1 sec</td>
<td>206</td>
</tr>
<tr>
<td>VIII-1</td>
<td>Retention of nitrogen in char versus coking temperature</td>
<td>210</td>
</tr>
<tr>
<td>VIII-2</td>
<td>Distribution of coal nitrogen in coke products</td>
<td>212</td>
</tr>
<tr>
<td>VIII-3</td>
<td>Effect of temperature and heating rate on nitrogen distribution between coke products</td>
<td>215</td>
</tr>
<tr>
<td>VIII-4</td>
<td>The effect of heating rate on coke product nitrogen distribution</td>
<td>218</td>
</tr>
<tr>
<td>VIII-5</td>
<td>Coal nitrogen retention in the char under conditions of asymptotic weight loss</td>
<td>220</td>
</tr>
<tr>
<td>VIII-6</td>
<td>Comparison of rate of nitrogen removal from coal with pyrolysis of model nitrogen compounds and fundamental rate constants</td>
<td>229</td>
</tr>
<tr>
<td>VIII-7</td>
<td>Correlation between nitrogen loss and total weight loss during pyrolysis of coal</td>
<td>237</td>
</tr>
<tr>
<td>VIII-8</td>
<td>Psuedo-first order arrhenius parameters for coal pyrolysis at different extents of reaction.</td>
<td>260</td>
</tr>
<tr>
<td>VIII-9</td>
<td>Equilibrium distribution of nitrogen from devolatilized bituminous coal</td>
<td>283</td>
</tr>
<tr>
<td>VIII-10</td>
<td>Equilibrium distribution of nitrogen from devolatilized lignite</td>
<td>284</td>
</tr>
<tr>
<td>VIII-11</td>
<td>Equilibrium distribution of char nitrogen near burning surfaces</td>
<td>291</td>
</tr>
</tbody>
</table>
VIII-12. Contribution of the oxidation of volatile nitrogen to total nitric oxide .......... 296

VIII-13. Potential reduction of nitric oxide emissions from two stage combustion .......... 300

A-IV-1. Weight loss from Montant lignite-A ........... 319
A-IV-2. Weight loss from hvA bituminous coal .......... 321

A-V-1. Effect of shape factor on velocity and temperature profiles for a furnace temperature of 2100°K .......... 342
A-V-2. Weight loss versus calculated lignite particle temperature. Shape factor of 3 ........ 343
A-V-3. Weight loss versus calculated bituminous particle temperature. Shape factor of 3 .... 344
A-V-4. Correlation between apparent weight loss and weight calculated using ash as a tracer for bituminous coal .......... 346
A-V-5. Correlation between apparent weight loss and weight loss calculated using ash as a tracer for lignite .......... 347
A-V-6. Correlation between ash tracer and measured weight loss for rapid devolatilization of lignite .......... 348
A-V-7. Correlation between ash tracer and measured weight loss for rapid devolatilization of bituminous coal .......... 350
A-V-8. Increase in asymptotic weight loss with time for lignite ........... 352
A-V-9. Increase in asymptotic weight loss with time for bituminous coal .......... 353
A-VI-1. Coalification diagram ............... 361
A-VI-2. Carbonization diagram. 1500°K .......... 363
A-VI-3. Carbonization diagram ............... 365
A-VII-1. Surface area of devolatilized coals .......... 368
A-VIII-1. Particle size of devolatilized lignite .......... 371
A-VIII-3. Particle size of bituminous coal versus weight loss ............... 374
A-VIII-4. Particle size of bituminous coal versus residence time ............... 375
A-VIII-5. Early bubble development in Pittsburgh Seam #8 hvA bituminous coal .......... 376
A-VIII-6. Void development in time for a Pittsburgh seam #8 hvA bituminous coal devolatilized at 1500°K .......... 378
A-VIII-7. Void development of Pittsburgh seam #8 hvA bituminous coal with temperature at asymptotic times .......... 380
A-VIII-10 Electron micrograph of ash obtained on the complete combustion of bituminous coal (top), lignite (bottom) .......... 384
### LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>DESCRIPTION</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>II-1.</td>
<td>Nitrogen in United States crude oils</td>
<td>39</td>
</tr>
<tr>
<td>VI-1.</td>
<td>ASTM coal rank</td>
<td>153</td>
</tr>
<tr>
<td>VI-2.</td>
<td>Lignite coal characterizations</td>
<td>162</td>
</tr>
<tr>
<td>VI-3.</td>
<td>Characterization of Montana-lignite</td>
<td>164</td>
</tr>
<tr>
<td>VI-4.</td>
<td>Ash characterization</td>
<td>166</td>
</tr>
<tr>
<td>VI-5.</td>
<td>Functional group analysis of a lignite</td>
<td>168</td>
</tr>
<tr>
<td>VI-6.</td>
<td>Bituminous coal characterization</td>
<td>176</td>
</tr>
<tr>
<td>VI-7.</td>
<td>Functional group analysis of a high volatile bituminous coal</td>
<td>178</td>
</tr>
<tr>
<td>A-I</td>
<td>Fuel conversion factors</td>
<td>306</td>
</tr>
<tr>
<td>A-II</td>
<td>United States energy supply in 1980 and 1985</td>
<td>307</td>
</tr>
<tr>
<td>A-III</td>
<td>Nitrogen and sulfur contents representative of United States coal reserves</td>
<td>312</td>
</tr>
<tr>
<td>A-IV</td>
<td>Chemical analysis of devolatilized coal</td>
<td>322</td>
</tr>
<tr>
<td>A-VII-1.</td>
<td>Kr surface areas of devolatilized coal</td>
<td>367</td>
</tr>
</tbody>
</table>
I. SUMMARY

I-l. Nitrogen Oxides Emissions From Fuel Nitrogen

The control of the emissions of nitrogen oxides is motivated by concern with their contribution to smog-formation and irritation to the respiratory tract. As part of a program to maintain ambient concentration at acceptable levels, the Environmental Protection Agency has set emission standards for new large stationary sources at 0.7 lbs $\text{NO}_2/10^6$ Btu for coal-fired units, 0.3 lbs/$10^6$ Btu for oil-fired units, and 0.2 lbs/$10^6$ Btu for gas-fired units.

Nitrogen oxide is produced by oxidation of both atmospheric nitrogen and any nitrogen contained in the fuel. The differences in emission standards for gas, oil, and coal largely reflect the contribution of fuel nitrogen to nitrogen oxides emissions. It is estimated that stationary sources contribute about half the nitrogen oxides emitted in the United States and fuel nitrogen accounts for about a third of the emission from stationary sources.

Approximately three quarters of the ultimate energy reserves of the United States are composed of fuels with nitrogen contents sufficiently high to be unacceptable if burned uncontrolled with present emission standards. Shale accounts for the largest fraction of the ultimate reserves and has the highest nitrogen content. Any fuel derived from oil shale if burned without treatment would produce unacceptable emission of nitrogen oxides. Coal accounts for the next
largest fuel reserves and has the next highest nitrogen content. Petroleum reserves are relatively small compared to oil shale and coal reserves. The nitrogen content of most crude oils is low relative to those of coal and shale but some residual oils, such as those derived from California and Alaskan crude oils, may have unacceptably high nitrogen contents. Alaskan proved oil reserves account for approximately 28% of the known United States reserves and California oil reserves for about 10% of the total.

Fortunately, only a fraction of fuel nitrogen is converted to nitrogen oxides averaging about 30% of the fuel nitrogen for a typical practical combustor. This study is aimed at examining the factors influencing fuel nitrogen conversion to nitric oxide in coal flames in order to provide a sound basis for developing improved strategies for reducing the emissions of nitrogen oxides.

I-2. Control Strategies for Reducing the Contributions of $\text{NO}_x$ Emission by the Oxidation of Fuel Nitrogen

Several methods have been developed empirically to control nitrogen oxides emissions from stationary combustion sources. Control strategies for reducing $\text{NO}_x$ emission by reducing flame temperatures have proved to be effective in reducing the fixation of atmospheric nitrogen but have not been as effective in reducing the oxidation of fuel nitrogen, which is relatively temperature insensitive.
Techniques that have been found to be successful in suppressing the conversion of fuel nitrogen to nitrogen oxides depend on the creation in the regions deficient in oxygen where the fuel nitrogen can be converted to molecular nitrogen. Two stage combustion, biased firing, and delayed-mixing flames have been shown in the laboratory and in the field to be capable of reducing the nitrogen oxide emissions contributed by fuel nitrogen by approximately 50%. These methods were developed empirically and a fundamental understanding of the suppression of conversion of fuel nitrogen to nitrogen oxides is needed in order to guide the development of improved control techniques.

I-3. Previous Work

A number of studies conducted on large laboratory units and small flat flame burners suggest that the form of the nitrogen containing compound has little effect on the conversion of fuel nitrogen to nitrogen oxides. In small well-mixed systems, conversion of fuel nitrogen to nitrogen oxides is found to be complete for lean conditions. The production of nitrogen oxides from fuel nitrogen rapidly decreases as the flame becomes rich. The fractional conversion of fuel nitrogen to nitrogen oxide decreases as the nitrogen content of the fuel increases. Diffusion flames show trends similar to those exhibited by premixed flames, although the conversion of fuel nitrogen to nitrogen oxides is lower for
diffusion flames than premixed flames at similar conditions. This is attributed to the presence of rich zones conducive to the formation of the stable nitrogen molecule from fuel nitrogen in diffusion flames.

Practical systems which typically consist of turbulent diffusion flames show trends in fuel nitrogen conversion to nitrogen oxides similar to those observed for laminar diffusion and premixed flames.

Pershing and co-workers have shown that fuel nitrogen contributes about 75-80% of the total nitrogen oxides emission from a small scale coal combustor. No information exists, however, on the contribution of the nitrogen devolatilized from the coal and nitrogen oxidized from the char to total nitrogen oxides emission. In addition, no information is available in the literature on the pyrolysis of nitrogen from coal at pulverized coal flame conditions, although some data is available on the distribution of the nitrogen in coal among pyrolysis products at coking conditions. The coking data, however, is not applicable to pulverized coal flames because of differences in heating rates, final temperature, residence times, and particle interaction.

I-4. Pulverized Coal Flames

Pulverized coal flames are formed by injecting fine coal dust, carried in air through a nozzle into a furnace. The primary stream is surrounded by a preheated secondary air
stream introduced through swirl vanes surrounding the coal-injection nozzle. The particles are injected with about 15-20% of the stoichiometric air requirement and are heated to the ignition temperature in a few milliseconds by a combination of conduction from recirculated gases and radiation from the flame region. As the particles are heated volatile matter is evolved and burns as a diffusion flame surrounding a particle or a cloud of particles. The residual char is subsequently oxidized. The conditions to which pulverized coal particles are subjected in practical flames can be characterized by heating rates of $10^4$ - $10^5$, at maximum temperatures of about $2100^\circ K$ and residence times of tens of milliseconds. Mixing patterns in a pulverized coal flame are very complex.

Combustion modifications change the local temperature, fuel equivalence ratio, and mixing patterns.

I-5 Equipment

The equipment used in this study was designed to simulate the devolatilization and combustion regions of pulverized coal flames.

A hot wall drop tube furnace that can be operated up to $1750^\circ K$ in an oxidizing atmosphere and $2200^\circ K$ in an inert atmosphere is the nucleus of the equipment. Rapid heating rates ($2 \times 10^4$ to $6 \times 10^5$ K/sec) are achieved by conduction to the narrow coal jet from surrounding hot gas and by radiation from the walls. Short residence times are achieved
by using a fast flowing (10 m/sec) plasma heated carrying
gas stream and rapid quenching is obtained by using a water
spray in the collection train. Residence times as short as
2 milliseconds were achieved using this system.

Oxidation experiments were conducted by injecting the
coal through a water-cooled nozzle with an amount of primary
air (simulated by a He/O₂ mixture) representative of large
pulverized coal flames. Secondary air was passed through a
hot flow straightener and was not swirled. Although the
mixing patterns in this system are different from the mixing
patterns expected to exist in pulverized coal flames, the
results on the effects of other variables on the behavior
of coal nitrogen are expected to be generally applicable to
larger units.

I-6. Devolatilization Results

The mechanism and rates of nitrogen devolatilization from
c coal were studied because control of the nitrogen evolution
provides one method of controlling total nitric oxide emissions.
The results from coal slowly heated in crucibles and held at
temperature for long periods of time showed that most of the
nitrogen evolution occurred at temperatures above those used
in the ASTM Proximate Analysis test (1023 °K) but almost all
of the volatile material evolution occurred at temperatures
below that of the ASTM test temperature. At the times at
which the volatile weight loss reached its asymptotic value,
it was found that the nitrogen evolution was essentially
complete at temperatures greater than 1750°K. These results indicate that, in contrast to carbon, nitrogen does not form structures that are stable at pulverized flame temperatures.

Pyrolysis of the nitrogen containing compounds in coal as expected to proceed via a complex series of parallel and sequential competitive reactions. The pseudo-first order rate constant fitted approximately to the early stages of pyrolysis is given by

$$k = 9.3 \times 10^3 \exp(-22,600/RT) \text{sec}^{-1}$$

During the first 10-15% of volatile loss no nitrogen is evolved, supporting the evidence from functional form analysis that the nitrogen in the coal is primarily tied up in heterocyclic rings. A linear correlation was found between fractional total weight loss and fractional nitrogen loss for the two coals studied. After the initial delay in nitrogen loss, nitrogen loss is more rapid than total weight loss. The slope of the nitrogen loss versus total weight loss was 1.25 for the lignite and 1.50 for the bituminous coal studied here. This correlation, if it is found to have general validity provides a base for evaluating the kinetics of nitrogen evolution from that of the more readily determined total volatile evolution.

As an initial step towards developing a kinetic model for interpreting the nitrogen devolatilization kinetics, a complex fundamental radical mechanism was developed.
Unfortunately, kinetic data on the fundamental steps has not yet been compiled to enable a numerical comparison to be made between the proposed model and the data on nitrogen evolution from this thesis. Development of fundamental models for coal pyrolysis is a long range goal of current coal research which when successful will replace the current empirical approaches.

I-7. Coal Burning

The effect of fuel equivalence ratio and temperature on the distribution of the fuel nitrogen among various products will determine the extent to which the emissions of nitrogen oxide can be suppressed by combustion process modification. The conversion of fuel nitrogen to nitrogen oxides and to residual nitrogen in the char and the carbon burnout were studied for a 1500°K furnace temperature over a range of fuel equivalence ratios of 0.2-5. A bituminous hVA bituminous coal and a lignite-A, having nominal particle sizes of 38-45 and 75-90 microns, were studied.

The conversion of fuel nitrogen to nitrogen oxides was found to be 28% at a fuel equivalence ratio of the value typically found in commercial units. This value is in general agreement with results from field surveys. The conversion of fuel nitrogen to nitrogen oxides ranged from about 60% for very lean fuel equivalence ratios to about 5% at fuel equivalence ratios greater than 1.5. However, at the
higher fuel equivalence ratios, 30% of the carbon remained unburned and this residual char contained 45% of the original nitrogen in the coal.

The two coals burned produced about the same conversion of fuel nitrogen to nitrogen oxides. The carbon burnout and amount of nitrogen retained in the residual char were about the same for the two coals up to a fuel equivalence ratio of about 1.5, at higher equivalence ratios, the carbon burnout for the bituminous coal was lower than that for lignite. No effect of particle size was observed over the limited range studied.

For the experiments with pulverized lignite particles conversion of fuel nitrogen to nitric oxide at 1750°K was found to be a factor of two lower than that at 1500°K. At 1750 the carbon burnout was essentially complete even at fuel equivalence ratios above two and very little nitrogen was retained in the residual char.

Increases in flame temperature under fuel-rich conditions, therefore, has the two-fold advantage of reducing the emissions of NOx produced from the oxidation of the fuel nitrogen and of leading to more stable combustion.

I-8. Volatile Burning

It is of interest to know whether the conversion of fuel nitrogen to nitrogen oxides is greater for the volatile nitrogen or for the nitrogen that remained with the chars
since combustion conditions can be altered to change the
distribution of nitrogen between volatiles and chars.
The oxidation of volatile nitrogen to nitrogen oxides, for
the system used in this study, was estimated to contribute
60-80% of the total nitrogen oxides formed. The estimate
was made from the difference in total nitrogen oxides emitted
when burning coal and when burning the char produced at the
same furnace temperature and residence time.

In addition, estimates of the conversion of volatile
nitrogen to nitrogen oxide were found to fall between values
reported in the literature for the conversions of model
nitrogen compounds to nitrogen oxides in premixed and
diffusion flames.

I-9. Char Burning

The production of nitrogen oxides from char was of
interest because it allowed an estimate to be made on the
contribution of volatile nitrogen to nitrogen oxides and
gave an indication whether it was desirable to force fuel
nitrogen into the volatile phase or to allow the fuel nitrogen
to remain in the char. A lignite char, containing approximately
2/3 of the nitrogen content of the raw lignite, was produced
by devolatilizing lignite at 1500\(^\circ\)K for one second. It was
found that the conversion to nitric oxide of the nitrogen
in the char was a factor of two to three lower than the
corresponding value for the raw coal.
The amounts of unburned carbon and nitrogen retained in the residual char was higher for the char combustion than for the coal combustion. The sum of the nitrogen converted to nitrogen oxides and amount of nitrogen left in the char was still about 20% lower for the char compared to the coal.

The relatively low conversion to nitric oxide of the nitrogen in char is thought to be due to the reduction of fuel nitrogen compounds in the fuel-rich boundary layers by both homogeneous and heterogeneous reactions.
II.0 Introduction

Nitric oxides are considered to be hazardous to human health and, consequently, their emissions are being regulated under the provisions of the Clean Air Act Amendments of 1970. Emissions standards have been proposed for both mobile and stationary sources. New source performance standards have already been imposed for steam generating plants with capacities in excess of $250 \times 10^6$ Btu/hr. It is estimated that approximately half of NO$_x$ emissions are from stationary sources and that a little less than half of the stationary contribution is formed by the oxidation of the nitrogen content of the fuel.

The purpose of this thesis is to study the conversion of fuel nitrogen to nitric oxide and other nitrogen compounds under combustion conditions. A fundamental study of the conversion of fuel nitrogen in simple systems is needed if an understanding of the mechanism of fuel nitrogen oxidation is to be obtained. Ultimately the understanding of the kinetics of conversion can be coupled with aerodynamic and heat transfer models to determine fuel nitrogen oxidation in practical systems.

There have been investigations of fuel nitrogen conversion on both industrial and laboratory burners. Both types of studies and the preliminary modeling indicate that fuel nitrogen modeling must be done in more detail. A great deal can be learned about the competitive paths in fuel nitrogen conversion by studying a simple system that can be modeled rather precisely. The system chosen for complete kinetic modeling in this study is the methane-ammonia-oxygen-helium system. This system was chosen because it is the simplest system that involves hydrocarbon combustion with nitrogen in a free form. Additionally,
it is the only system where complete kinetic modeling can be attempted with a reasonable chance of success.

II.1 Fuel Nitrogen in Fossil Fuels

Gas and oil are more convenient to use and produce less pollution than coal. They are also less abundant, however natural gas is essentially free of fuel nitrogen compounds. Poth, et al. (1928) and Ball, et al. (1951) have reported data which shows that crude petroleums found in the United States have nitrogen contents ranging from essentially zero to about one weight percent. Standed (1969), v.5, p.627 reports United States coals have between 0.5 and 2.0 weight percent nitrogen. A number of coal analyses reported in appendix III indicate that bituminous coals will more likely have nitrogen contents between 0.9 and 1.8 weight percent. Standed (1969), v.18, p.5 has reported the nitrogen content of Colorado shale oils produced from various retorting processes. The crude shale oils had nitrogen contents ranging from 1.55 to 3.30 weight percent; the Tosco process had 1.8 percent nitrogen. Tar sands, according to Standed (1969), v.19, p.696, have between 0.3 and 0.6 weight percent nitrogen in the bitumen and about 0.1 percent in the derived crude, but tar sands have little chance of becoming an important energy source in the United States.

II.1.1 U.S. Energy Reserves, Uses, and Policy

It has been proposed that the United States become energy self-sufficient by 1980. Prospects of attaining this goal are very dim. Adelman, et al. (1974) and the National of Engineering (1974) see little opportunity for the United States to be entirely free from imports by 1980 or even 1985. It is unclear what policies if any, the
government will use to help the U. S. achieve energy self-sufficiency. It is, however, clear that many companies are investigating energy sources which would not be economic in their current unsupported status. The primary under-utilized fuels are shale oil, coal, and nuclear power. They all can have significant environmental impact. Coal and shale oil without efforts to regulate pollution could greatly increase the emission of nitric oxide, particulates, and sulfur dioxide. The problems associated with nuclear power are thermal and radioactive wastes. Figure II-1 shows the ultimate reserves, the identified and recoverable reserves, the 1973 uses, and reasonable future fuel supplies for the United States. The ratio of total identified and recoverable reserves to 1973 uses is 85-185, the ratio of coal uses to reserves is 30-60, for petroleum it is 14, for gas 12, and for nuclear power 286. The uses of shale oil and geothermal energy are negligible compared to the reserves. The time to deplete petroleum reserves may seem quite small but the historical crude depletion rate has remained quite constant for many years. The gas depletion rate has been increasing over the last decade. The reserve ratios indicate that the rate of the utilization of coal, oil shale, and nuclear power can be increased substantially without extensive exploration.

II.1.2 Potential Coal Use

Coal use in the United States has been decreasing relative to the use of other fossil fuels. In the decade 1960-1970 coal use increased at a rate of 3.4% compared to increases of 5% for natural gas and 4% for petroleum. Coal has not been extensively used for residential purposes for many years because its utilization is not as convenient as those of natural gas or fuel oil. Coal has found use in the industrial
Figure II-1. United States energy supply and reserves.
and power sectors. The fraction of energy used for power generation has slowly increased in recent years. Utilities used 24.5% of the total energy in 1955, 24.7% in 1970, and 26% in 1973. Coal has maintained its position in power generation relative to the other fossil fuels and will increase in the future as gas is phased out. Coal supplied 54%, 55%, and 54% of the power generated by fossil fuels in 1955, 1970, and 1973 respectively. Coal use has dropped from 20% of the United States energy use in 1970 to 17.9% in 1973. The decrease in coal use has largely been in the industrial sector where coal supplied 42.4% of the fossil fuel energy in 1955 but dropped to 26% in 1970 and 20.8% in 1973.

Coal can not expect to retain its relative small residential base or much of its industrial heating base because it has severe handling and emission problems, but synthetic fuels from coal could become an important source of energy for these uses. Coal could also replace other fossil fuels used in power generation. If this had happened in 1973 coal production would have had to increase about 50% and power generation from this coal without emission control would have nearly doubled the United States nitrogen oxide emissions as well as creating serious increases in both particulate and sulfur oxides levels. A significant fraction of nitrogen oxides produced from coal are due to the oxidation of fuel nitrogen. To make adequate use of our coal reserves and maintain environmental quality requires effective means of controlling fuel nitrogen oxidation.

Coal has also been considered a source of more desirable fuels such as gas and oil. A rather large fraction of the nitrogen contained in coal would likely be converted to molecular nitrogen during gasification but a significant fraction will remain in undesirable forms,
predominantly ammonia (approximately 25%) and hydrogen cyanide (approximately 2%). These compounds can be removed from gas products but their removal would probably require additional steps during processing.

Economic estimates for the cost of gas from coal vary rather widely and are based on uncertain data. Adelman, et al. (1974) has tabulated estimates which indicate a gas selling price of between $1 and $1.50/10^3 \text{ ft}^3. These figures may have to be doubled to encourage private investment. Interstate natural gas prices are controlled at artificially low levels. The most optimistic price rise is from $35/10^3 \text{ ft}^3 in 1973 to $74/10^3 \text{ ft}^3 in 1980. Uncontrolled intra-state gas contracts were being sold at prices of from $75/10^3 \text{ ft}^3 to $1/10^3 \text{ ft}^3 in 1974. There appears little chance that coal gasification will become competitive with natural gas prices particularly if natural gas remains controlled. Coal gasification costs are often cited as being competitive with imported liquid natural gas prices. The current estimated costs are competitive but they would have to be doubled to supply sufficient investment incentive.

The projections in appendix II show the most optimistic estimate of coal gasification production is about 2.7 trillion \text{ ft}^3 or about 11.5% of the total gas supply in 1980. The gas from coal could increase by a trillion \text{ ft}^3 in the next 10 years and account for 15.7% of the total gas supply in 1985. Many projections, however, predict that synthetic gas will make an insignificant energy contribution by 1985. Federal support of coal gasification development costs is needed so that realistic costs can be assigned to synthetic gas production. The firm economic cost would then either encourage private investment or indicate that government support would be necessary for production of gas.
from coal.

II.1.3 Nitrogen in Petroleum

California petroleum products are a nitrogen oxides emission concern because of high fuel nitrogen contents. Table II-1 lists the proved reserves, the 1972 production, and the average percent nitrogen in the crude petroleums for the states with the largest reserves. The states listed in table II-1 account for 92.6% of the reserves and 88.2% of the production in the United States.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Tex.</td>
<td>12,144 mm bbl 33.4%</td>
<td>1,258 mm bbl 38.3%</td>
<td>0.074</td>
</tr>
<tr>
<td>Alas.</td>
<td>10,096 mm bbl 27.8%</td>
<td>73 mm bbl 2.2%</td>
<td>0.23</td>
</tr>
<tr>
<td>La.</td>
<td>5,028 mm bbl 13.8%</td>
<td>780 mm bbl 23.8%</td>
<td>0.056</td>
</tr>
<tr>
<td>Calif.</td>
<td>3,554 mm bbl 9.8%</td>
<td>346 mm bbl 10.5%</td>
<td>0.49</td>
</tr>
<tr>
<td>Okla.</td>
<td>1,303 mm bbl 3.6%</td>
<td>198 mm bbl 6.0%</td>
<td>0.151</td>
</tr>
<tr>
<td>Wyo.</td>
<td>950 mm bbl 2.6%</td>
<td>139 mm bbl 4.2%</td>
<td>0.183</td>
</tr>
<tr>
<td>N. M.</td>
<td>582 mm bbl 1.6%</td>
<td>106 mm bbl 3.2%</td>
<td>0.082</td>
</tr>
<tr>
<td>U.S. Total</td>
<td>36,339 mm bbl 92.6%</td>
<td>3,281 mm bbl 88.2%</td>
<td>0.148</td>
</tr>
</tbody>
</table>

California crude is about 10% of both reserves and production and most fields have nitrogen concentrations from tenths of a percent up to one percent; the 1955 average for California crude oils was about 0.5%.

The nitrogen compounds have relatively high molecular weights so that the nitrogen tends to concentrate in the higher boiling distillates.
and the residual. This distribution will be shown later but for now it is sufficient to point out that emissions of nitrogen oxides due to oxidation of fuel nitrogen in oils is a problem only for the higher boiling fractions of California crude oil.

II.1.4 The Potential of Oil Shale

The reserves of oil shale are large compared to other United States reserves but the costs of oil shale development have made its use insignificant. Adelman, et al. (1974) has reported the cost of producing shale oil as $5-$8/bbl but thinks that these prices will have to double to attract private investment. At the current imported oil price of about $11/bbl there is a small incentive to produce crude oil from oil shale. For rapid development of this resource the government will need to underwrite the development risk.

Appendix II shows projected oil shale development for 1980 and 1985. The projection of oil shale use are small except for the unrealistic estimate of The Department of Interior. Oil shale could produce as much as 0.1 mbpd or less than 2% of the total crude in 1980. The projected supply of shale oil is not much larger in 1985. Shale oil could supply approximately 2 mbpd in 1985 or still less than 2% of the total crude supply.

II.1.5 Summary of FuelNitrogen Prospects

Coal and heavy California fractions are the only fuels where nitrogen is a current problem. The magnitude of this problem compared to emission standards can be quite large and will be discussed in the next section. The nitrogen compounds contained in coal will continue to be a problem if and when coal is converted to gas and oil, unless a
denitrogenation step is included during processing. Coal conversion should contribute only a moderate fraction of our energy for the next decade. The nitrogen content of shale oil distillates is quite high and ways of controlling the emissions from shale oil combustion must be found to maintain a satisfactory emission level. However, oil shale appears to have little chance of extensive development in the next decade.

II.2 Nitrogen Oxides Produced from Fuel Nitrogen

The previous section indicated which fuels were likely to have large future use and which of these fuels have high nitrogen contents. This section will demonstrate the magnitude of the fuel nitrogen problem for coal, heavy California crude oils, and shale oil.

II.2.1 Nitrogen Content of United States Coals

A number of analyses representative of the United States coal reserves are listed in appendix III. The same data are graphically represented in figure II-2. The data are weighted by relative reserves of each rank of coal, the states which have the largest reserves, and the major reserve areas within the states. The coal reserves of the United States are 46% bituminous mostly in Illinois, West Virginia, and Missouri, 28.4% lignite mainly in North Dakota and Montana, 24.6% subbituminous in Montana, Wyoming, and Alaska, and 1% anthracite almost all in Pennsylvania.

Figure II-2 shows the emission levels of nitrogen oxides and sulfur oxides if all the nitrogen and sulfur in the fuel were converted to the oxides and compares this with the EPA emission standards. It can be seen from figure II-2 that none of the representative coals plotted would be acceptable if conversion were 100%. Fortunately much
Figure II-2. Nitrogen and sulfur contents of United States coal reserves compared to emission standards.
of the nitrogen is converted to molecular nitrogen and some of the
sulfur remains in the ash as sulfur trioxide.

The nitrogen contents of all the coals are close to 0.1%/10^3
Btu (3.28 lb NO_2/10^6 Btu). The lignite and subbituminous coals are
close to this value; the bituminous values are slightly higher.
Bituminous nitrogen concentrations are about 10-20 percent higher than
0.1%/10^3 Btu and anthracite contents are about 30% lower. This trend
can be interpreted in terms of rank, if similar starting materials are
assumed. Nitrogen contents of wood are less than 0.1%, so can not
directly account for the high nitrogen content in coal. Some lower
order organisms have higher nitrogen contents such as bacteria, 13%,
and algae, 4.8%. Kirner (1945) thinks microbial synthesis increased
the nitrogen content during digestion and that the nitrogen compounds
stabilized themselves in the coal and preferentially accumulated.
This would account for the increase in nitrogen content with rank up
to bituminous but not for the lower nitrogen content of anthracite.
Anthracite has, however been subjected to more extreme conditions
than the lower rank fuels. Hendricks (1945) gives the exposure limits
as 600°C for anthracite, 350°C for bituminous, and 100°C for sub-
bituminous and lignite. The higher forming temperatures for anthracite
might indicate that the nitrogen accumulation process has been reversed
at the extreme conditions.

The sulfur content of the representative coals varies much more
widely than the nitrogen content because sulfur can be present in
inorganic forms as well as organic forms. Anthracite, subbituminous,
and lignite tend to have less than 1% sulfur. The sulfur content of
bituminous can vary widely. About half of the eastern bituminous coals
have sulfur contents greater than 1.5%. Almost all the coal from the
interior has sulfur contents above 1.5%. The high sulfur coals plotted in figure II-2 come from one continuous region included in districts 9, 10, 11, and 15 which contain Western Kentucky, Illinois, Indiana, Missouri, and Kansas.

Lignite and bituminous coals seem to have a decrease of about 0.2% nitrogen for each percent increase in sulfur. No pattern was discernable for the subbituminous coals. The decrease in nitrogen content is reasonable because only organic nitrogen is in coal while both organic sulfur and inorganic sulfur are present in coal.

Figure II-3* shows some industrial conversion data for oil and coal fuels of different nitrogen contents compared with emission standards. The solid points represent what little coal data there is available, the points at 1.5% nitrogen are mostly from low temperature fluidized bed combustors and should be interpreted carefully. The data of Pershing, et al. (1973) are the most reliable and show conversions between 25 and 40% at about 1.2 weight % nitrogen. The data at 1.5 weight % shows a conversion of 5 to 20%. Figure II-2 shows that with no thermal fixation fuel nitrogen conversions, less than 15-20% most coals will almost meet the EPA standards.

Nitrogen in the coal is a major source of emissions of nitrogen oxides in coal combustion. Many coals appear to be marginally able to meet current standards. This is not surprising since the standards were set at reasonably attainable goals.

II-2.2 Nitrogen Content of Petroleum Products

Table II-1 listed average nitrogen contents for states that were likely to be major crude producers in the future. The nitrogen content

* Modify with permission from graph prepared by R. C. Flagan.
Figure II-3. Conversion of fuel nitrogen in practical combustors.
is not a good indicator of the magnitude of the fuel nitrogen oxidation problem because nitrogen contents vary in the fuel products from the same crude and emission standards are different for different fuel uses. Figure II-4 shows the distribution of fuel nitrogen in distillate and residual products for a number of different crude oils and for shale oil. The data is plotted as weight percent nitrogen versus end boiling point since nitrogen content increases markedly as the end boiling increases, lines are drawn from the end boiling to the starting boiling point of the fraction since the temperature range of the fraction will also effect the nitrogen content. The boiling range for various commercial products is shown below the abscissa and the emission standards for stationary and mobile sources are shown on the ordinate.

It is immediately apparent that no crude oils, even at 100% conversion will have trouble meeting the mobile source standard if thermal fixation is excluded. Kerosene and the light distillate fuel oils appear to have nitrogen contents that would yield emissions that might barely meet the stationary source standard, even for catalytically cracked California crude oils. Standards have not as yet been set for aircraft or home heating emissions which are the light distillates end uses. Diesel fuels derived from California crude oils will exceed the 1976 NOx standard of 0.4 g/mile from fuel nitrogen alone if used in light duty vehicles. Light duty diesel vehicles are a small fraction of the total light duty vehicles and the total vehicles that use diesel fuel. Standards have not as yet been set for heavy duty vehicles.

Heavy fuel oil produced from California crude oil will most likely produce nitrogen oxides at a level incompatible with the
Figure II-4. Nitrogen distribution in refined petroleum products.
emission standards. Figure II-3 shows that most liquid fuels that contain greater than 0.25 weight % nitrogen will exceed the emission standard when thermal nitrogen oxides are included. All the heavy fuel oils from California are greater than 0.25 weight % and the residual fuel oil produced from Kuwait crude is marginal at 0.3 weight % nitrogen.

II-2.3 Nitrogen in Shale Oil

Figure II-4 shows that any fuel derived from oil shale will have too high a nitrogen content to meet the emission standards regardless of how it is used. The shale oil points are solid in figure II-4 and the symbol shape represents different retorting processes. Shale oil use will demand either that the fuel be chemically cleaned, a difficult task, or that combustion conditions must be drastically modified, or more likely both, if its use is not to cause degradation of local environments.

II-3 Summary of Fuel Nitrogen

The major under-utilized fossil fuel reserves in the United States are coal and oil shale. Both fuels must have greater use if the United States is to minimize its reliance on imported energy. Coal has a nitrogen content that makes it only marginally acceptable as a fuel with current emission standards. Shale oil has such a high nitrogen content that it would be environmentally unacceptable for any use without control. Possible development of oil shale reserves look favorable for the distant future but oil shale will probably not be a significant energy source until after 1985. Heavy fractions derived from California crude oil will have a serious problem meeting the nitrogen oxide emission standards. Conversion of coal to alternate
fuels will not be significant until after 1985 and the problem of emissions from units burning coal will still have to be resolved.
III. PREVIOUS WORK

Limited studies of the mechanism and effects of fuel nitrogen conversion to nitrogen oxides have appeared in the literature over the past ten years. These studies while not definitive of all the problems associated with the conversion of fuel nitrogen to undesirable products, provide a valuable basis for this work. The studies can be largely divided into three types: study of the conversion of fuel nitrogen compounds to nitrogen oxides in practical systems and other systems that have similar mixing limitations, study of the behavior of fuel nitrogen compounds where simple hydrocarbons burned in premixed or diffusion flames, and study of reactions, more or less in isolation, that are thought to be important in the conversion of fuel nitrogen to final products.

III-1. Coal Systems

Limited data is available on the behavior of fuel nitrogen in coal systems. Jonke, et al., (1970) first showed that conversion of fuel nitrogen to nitrogen oxides was a major source of emissions in coal combustion, when nitrogen oxide did not decrease when air argon-oxygen mixture was substituted for air in fluidized combustion. The low operating temperature of a fluidized bed precludes significant formation of nitrogen oxides from atmosphere nitrogen so this study showed that fuel nitrogen was the major contributor to nitrogen oxide emissions for fluidized beds but didn't present conclusive
evidence that oxidation of fuel nitrogen contributed a significant fraction of the emission from a pulverized coal flame.

Pershing, et al., (1973), Pershing and Wendt (1967a and b) have shown that oxidation of fuel nitrogen contributes approximately 75-80% of the nitrogen oxides emitted from pulverized coal flames. Pershing and Wendt (1967b) have, also, shown that the conversion of fuel nitrogen to nitrogen oxides is insensitive to temperature increases except at temperatures above 2400°K where the conversion of fuel nitrogen to nitrogen oxides increases.

Haynes and Kirov (1974) have monitored nitrogen oxide concentrations from a fixed bed of coal burning. Their results showed levels of nitrogen oxides are high early in the burning process where volatile burning in this region is followed by a sharp drop in nitrogen oxides concentration. The lower level was associated with char burnout.

Periera, et al., (1975) investigated the behavior of nitrogen oxides in a fluidized bed. The results showed that volatile nitrogen contributed very little to nitrogen oxides emissions at 1000°K but contributed 2/3 of the nitrogen oxides emitted at 1200°K. They also found strong indication the nitric oxide could be efficiently reduced by char in a fluidized bed.

III-2. Practical System

The study of fuel nitrogen in turbulent flames has been
restricted to the measurement of conversion of various fuel nitrogen compounds to nitric oxide as a function of various control variables. The efforts are aimed at developing efficient control strategies to suppress nitrogen oxide emissions.

The investigations on the effect of form of the fuel nitrogen compounds on overall conversion to nitrogen oxides have generally indicated that the form of the fuel nitrogen compound has little effect on the ultimate nitrogen oxides emissions. Martin, et al., (1970) studied the effect of aliphatic amines, cyclic amines, arene amines, and heterocyclic nitrogen compounds, in fuel oil combustion and found little differences between the conversion of different fuel nitrogen compounds to nitrogen oxides. In a similar study, Martin, et al., (1970) found only minor differences in the conversion of pyridine, piperdine, and quinoline to nitrogen oxides in oil fired systems, although the conversion of quinoline to nitrogen oxides appeared to be slightly lower. Turner, et al., (1972) found no difference in conversion of a large number of nitrogen compounds to nitrogen oxides in an oil fired unit, except, very low boiling compounds which had lower conversion to nitrogen oxides which was attributed to handling losses. Turner studied the effect of 9 primary amines, 4 secondary amines, 2 tertiary amines, and 5 heterocyclic nitrogen compounds. Data from premixed systems to be presented later in this section also shows that the form of the nitrogen compound
has little effect on the conversion of the nitrogen contained in the fuel to nitrogen oxides.

A large number of studies on conversion of fuel nitrogen compounds to nitrogen oxides are tabulated in Figure II-3. The general conclusions are: (i) the conversion of fuel nitrogen to nitrogen oxides decreased as the content of the fuel nitrogen increases (ii) burning lean increases the conversion of fuel nitrogen compounds to nitrogen oxides (iii) for typical operating conditions, an oil fired unit will have 40 to 60% and a coal fired unit will have 20 to 40% of the fuel nitrogen converted to nitrogen oxides. Again, these results are collaborated by results produced on laboratory premixed and diffusion flames.

Data on operating utility plants collected by Crawford et al., (1975) and Selker (1975) confirm the results of the smaller units, presented above, and indicate that current combustion modifications can reduce uncontrolled emissions by 50%.

III-3. Laboratory Burner Systems

It is much easier to investigate kinetic mechanisms in systems that have uniform mixing, consequently much laboratory work has been done on the conversion of simple nitrogen compounds in gaseous hydrocarbon flames. The earliest study, performed by Shaw and Thomas (1965), is only historically significant and the data must be reinterpreted to include
in the fuel equivalence ratio the amount of oxygen necessary to burn the nitrogen additive.

The form of the nitrogen compound used to simulate fuel nitrogen does not effect the conversion of the fuel nitrogen compound to nitrogen oxides. Fenimore (1972) studied conversion to nitrogen oxides of ammonia, methacrylonitrile, methyl amine, and pyridine in a flat flame system and found no difference between the additives. De Soete (1973a) found little difference in conversion of fuel nitrogen added as ammonia, ethylenediamine, dibutylamine, and triethylamine. Triethylamine appeared to have slightly lower conversion to nitrogen oxides than the other nitrogen compounds. Merryman and Levy (1975) found conversion of pyridine and piperdine to be about equal for methane flames with a fuel equivalence ratio of about 0.7. Methylamine was about twice as easily converted into nitrogen oxides as pyridine and piperdine under similar conditions. In another study Merryman and Levy found NO, NH$_3$, and C$_2$N$_2$ to have approximately the same conversion to fuel nitrogen. Synder (1975) found HCN and NH$_3$ to have similar conversions to nitrogen oxides for methane flames.

The conversion of all fuel nitrogen compounds investigated in flat flames appear to have near complete conversion to nitrogen oxides in fuel lean conditions but lower conversion of fuel nitrogen to nitrogen oxides in conditions with less than stoichiometric oxygen. This trend is most clearly shown in Fenimore, et al., (1972) and Sarofim, et al., (1975).
Sarofim et al., (1975) have reported the conversion of \( \text{NH}_3 \), \( \text{CH}_3\text{NH}_2 \), pyridine, and NO added to the fuel side of a diffusion flame. The conversion of all nitrogen additives to nitrogen oxides was similar but the conversion of fuel nitrogen to nitrogen oxides in a diffusion flame is about half that produced in premixed flames.

III-4. Fuel Nitrogen Reaction Mechanisms

The competitive mechanism between conversion of fuel nitrogen to nitrogen oxides and other nitrogenous compounds including molecular nitrogen is obscure. Fenimore proposed that an unidentified intermediate either reacted with oxygen compounds, particularly OH, to form nitrogen oxides or with NO to form molecular nitrogen. De Soete and Queraud (1973) have identified hydrogen cyanide as a transient intermediate in the conversion of fuel nitrogen to nitrogen products and developed global rate expression for oxidation of fuel nitrogen to nitrogen oxides or reaction of fuel nitrogen to produce molecular nitrogen. The mechanism is more complicated than either Fenimore or De Soete imply.

The complete competitive mechanism will not be presented in this thesis but remains for future work and publication. The mechanism is based on the mechanism partially developed in the literature for oxidation of ammonia and hydrogen cyanide. The reactions of nitrogen fragments with hydrocarbon fragments and reduction reactions of nitrogenous species are added to
complete the mechanism. In the reactions to produce molecular nitrogen only atomic nitrogen and nitrous oxide are species that can lead directly to molecular nitrogen.
IV FLAME EQUATIONS

The flame equations for a simple one-dimensional flat flame burner were developed at a time when it was anticipated that kinetics of fuel nitrogen reactions in the gas phase would be investigated. This proved to be too ambitious an undertaking.

The standard equations for heat and species conservation were carefully evaluated for the types of flame and conditions encountered in a typical laboratory burner of the type that would be used to study kinetics of flames. The final equations differed from other developments because order of magnitude estimates indicated that terms usually ignored were important for the types of flame situations studied. A computer program was developed based on the differencing procedure presented but has not, as yet, been completely validated. Because of time limitations the portion of program which calculates species concentrations has been evaluated but has not yet been coupled with the heat balance equations. This remains as future work for the author and others.

While the portion of this thesis dealing with solution of the flame equations has not been completed, it is thought valuable to present the development and evaluation of the flame equation system as a basis for future work.
IV-1. Flame Equations

The flame equations were originally written by Hirschfelder and Curtiss (1949). This first approach assumed that radiational energy transport and the secondary transport—Soret (thermal diffusion) and Dufour (diffusion thermo) were negligible. Hirschfelder, et al. (1954) p. 698 later wrote the complete flame equations. The flame equations have appeared since then in various modified forms; two useful references are Williams (1965) p. 2 and Pristrom and Westenberg (1965) p. 47. This presentation will generally follow Hirschfelder, et al. (1954) and Williams (1965).

The flame equations have been developed from continuum considerations and from molecular considerations by Williams (1965), appendices C and D. The equivalence of the two approaches has been demonstrated by Williams (1965), appendix D. The general flame equations, after Williams (1965) with some modifications, can be written as

overall continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (IV-1)$$

continuity of species

$$\frac{\partial Y_i}{\partial t} + \mathbf{v} \cdot \frac{\partial Y_i}{\partial \mathbf{r}} = \frac{w_i}{\rho} - \left[ \nabla \cdot \left( \frac{\rho Y_i \mathbf{v}_i}{\rho} \right) \right] \quad (IV-2)$$

momentum

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = -\left( \frac{\nabla \cdot \mathbf{P}}{\rho} \right) + \sum_{i=1}^{N} Y_i \mathbf{F}_i \quad (IV-3)$$

energy

$$\rho \frac{\partial}{\partial t} (u + 1/2 \mathbf{v}^2) + \rho \mathbf{v} \cdot \nabla (u + 1/2 \mathbf{v}^2) = -\nabla \cdot q - \frac{\mathbf{P} \cdot \mathbf{v}}{\rho} + \rho \mathbf{v}_i \mathbf{F}_i \quad (IV-4)$$
where the pressure tensor is

$$\mathbf{p} = [\rho + (2/3n - \kappa)(\nabla \cdot \mathbf{v})\nabla - n[(\nabla \cdot \mathbf{v}) + (\mathbf{v} \cdot \nabla)\nabla]$$  \hspace{1cm} (IV-5)

the heat flux vector is

$$\mathbf{q} = -\lambda\nabla T + \rho L_{i=1}h_i n_i \nabla v_i + \frac{RT\Sigma_{i=1}^n}{\Sigma_{j=1}^n} \mathbf{x_j} \frac{D_{T_i}}{m_i} (T_i - T_j) + \mathbf{q}_r$$  \hspace{1cm} (IV-6)

where \(\mathbf{q}_r\) is the radiational part of the heat flux vector and the diffusional velocity is

$$\mathbf{v}_i = \left(\frac{\rho}{n_i}\right)^2 \sum_j m_{j} D_{ij} d_{i} - \frac{i}{n_i m_i} D_{T_i} \nabla T$$  \hspace{1cm} (IV-7)

The mass rate of production of species is defined generally as

$$w_i = m_i \Sigma_{k=1}^m (v'_{i,k} - v_{i,k}) A_k e^{-\frac{(E_k/RT)}{RT}} \mathbf{P} \sum_{j=1}^N \frac{x_i^j}{RT} v_j^j k$$

The nature of the flame problem allows the general flame equations to be greatly simplified. The laboratory flat flame can be approximated as a steady reacting one dimensional flow system. The stabilizing surface used in flat flames provides a flame with a central core that has essentially no radial gradients. As an example, an atmospheric methane-air flame stabilized on a one inch diameter porous disc has a central, flat region of approximately one-half inch in diameter at a distance of one-half centimeter downstream from the flame region. This distance usually includes all the regions of interest in flame investigations. The Reynolds number of atmospheric flat flames are typically on the order of 100 which gives an entrance length of about 25 cm which is again much beyond the region of interest.

The flat flame that will be used for order of magnitude analysis is shown in figure IV-1.1.
\[ v = 150 \text{ cm/sec} \]

\[
\begin{array}{l}
\bar{N} = 1 \times 10^{-5} \text{ g mole/cc} \\
\bar{\rho} = 5 \times 10^{-4} \text{ g/cc} \\
\bar{\eta} = 5 \times 10^{-4} \text{ g/cm sec} \\
\lambda = 1.4 \times 10^{-4} \text{ cal/cm sec } ^{\circ}\text{K} \\
\n\nu_0 \sim 20 \text{ cm/sec}
\end{array}
\]

Burnt Gas

\[
\begin{array}{l}
T = 2000^{\circ}\text{K} \\
\rho = 10^{-4} \text{ g/cc} \\
\eta = 10^{-3} \text{ g/cm sec} \\
\lambda = 2 \times 10^{-4} \text{ cal/cm sec } ^{\circ}\text{K} \\
N = 6 \times 10^{-6} \text{ g mole/cc}
\end{array}
\]

Unburnt Gas

\[
\begin{array}{l}
T = 300^{\circ}\text{K} \\
\rho = 10^{-3} \text{ g/cc} \\
\eta = 2 \times 10^{-4} \text{ g/cm sec} \\
\lambda = 7 \times 10^{-5} \text{ cal/cm sec } ^{\circ}\text{K} \\
N = 4 \times 10^{-5} \text{ g mole/cc}
\end{array}
\]

Figure IV-1

Figure IV-1.1 is for an atmospheric flat flame but we will also be concerned with subatmospheric flames. The overall methane flame reaction has been shown by Westenberg and Fristom (1961) to be approximately bimolecular. The pressure effects on flame variables have been discussed by Fristrom and Westenberg (1965) p. 336 and Hirschfelder, et al. (1954) p. 765. The pressure effects on transport properties are discussed in Reid and Sherwood (1966). Both effects have been summarized by Pohl (1973). Pressure has the following effects for a flame dominated by bimolecular reactions

\[ v \neq f(p) \quad \text{(IV-9)} \]

\[ T \neq f(p) \quad \text{(IV-10)} \]

for reduced pressure less than 10

\[ \eta \neq f(p) \quad \text{(IV-11)} \]

for gases in the ideal range

\[ D_{i}^{T} \neq f(p) \quad \text{(IV-12)} \]
for pressures up to 1000 atmospheres

\[ \lambda \neq f(p) \]  
\[ x \propto l/p \]  
\[ \rho \propto l/p \]  
\[ \sigma_{ij} \propto l/p \]  

**IV-1.1 One Dimensional Flame Equations**

The first approximation to the flame equations is to consider the one dimensional flame. This simplification leads to

**overall continuity**

\[ \frac{\partial \rho}{\partial t} + \frac{\partial (\rho v)}{\partial x} = 0 \]  

**continuity of species**

\[ \frac{\partial Y_i}{\partial t} + v \frac{\partial T_i}{\partial x} = \frac{w_i}{\rho} - \frac{1}{\rho} \frac{\partial}{\partial x} (\rho Y_i V_i) \]  

**momentum**

\[ \frac{\partial v}{\partial t} + v \frac{\partial v}{\partial x} = \frac{1}{\rho} \frac{\partial}{\partial x} (\rho P + (2/3 \eta - \kappa) \frac{\partial}{\partial x} v - 2n \frac{\partial v}{\partial x}) + \sum_{i=1}^{N} Y_i F_i \]  

**energy**

\[ \frac{\partial (\rho u + 1/2 \rho v^2)}{\partial t} + v \frac{\partial}{\partial x} (\rho u + 1/2 \rho v^2) = \frac{\partial}{\partial x} [\lambda \frac{\partial T}{\partial x} + q_R] \]  

\[ + \rho \sum_{i=1}^{N} h_i Y_i V_i + RT \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{x_j}{m_i \sigma_{ij}} (V_i - V_j) \]  

\[ - \frac{\partial}{\partial x} [Pv + (2/3 \eta - \kappa) \frac{\partial v}{\partial x} - 2n \frac{\partial v}{\partial x}] + \rho \sum_{i=1}^{N} Y_i F_i V_i \]  

**IV-1.2 Simplification of the Pressure Tensor**

The one dimensional components of the pressure tensor can be simplified by neglecting the bulk viscosity as well as the shear viscosity terms.
IV-1.2.1 Elimination of Bulk Viscosity

The bulk viscosity, $\kappa$, is related to the relaxation times for transfer of translation energy to internal energy. The bulk viscosity term is rarely important in combustion systems, (see Williams (1965) p. 435). Its importance is apparent when one considers the dense gas development given in Hirschfelder, et al. (1954) p. 644 where the bulk viscosity is defined as

$$\frac{\kappa}{\eta} = 1.002 \frac{[\left(\frac{\bar{F}^N}{RT}\right) - 1]}{\nu} b_0$$  \hspace{1cm} (IV-21)

where $b_0/\nu$ for dilute gas conditions is much less than one. In combustion systems the gases are essentially ideal; therefore the bulk viscosity is unimportant compared with the shear viscosity.

IV-1.2.2 Elimination of the Viscous Term

Once the bulk viscosity term has been eliminated compared with the shear viscosity terms the shear viscosity terms can be neglected compared with the pressure term. The pressure term is

$$p = p \cdot 1.33 \times 10^3 \text{ g/cm sec}^2/\text{torr}$$

$$= 1 \times 10^6 \text{ g/cm sec}^2$$

when the pressure is one atmosphere. The one dimensional viscous terms in the pressure tensor are

$$2\eta \frac{dv}{dx} - \frac{2}{3} \eta \frac{dv}{dx} = \frac{4}{3} \eta \frac{dv}{dx}$$  \hspace{1cm} (IV-23)

At one atmosphere pressure, equation (IV-23) has the magnitude

$$\frac{4}{3} \eta \frac{dv}{dx} = \frac{4}{3} (5 \times 10^{-4} \text{ g/cm sec} \frac{130 \text{ cm/sec}}{0.2 \text{ cm}}) = 0.43 \text{ g/cm sec}$$

Since low pressure flames and atmospheric pressure flames will be of interest in this study, order of magnitude elimination of terms must also be justified at low pressures. Equation (IV-14) predicts a flame thickness of 7.6 cm at 20 torrs. Flame zones are never this thick in
practice but are more typically about one-two cm's thick. Consequently
a flame thickness of a 20 torr flame will be assumed to be 2 cm for
this order of magnitude analysis. Low pressures will reduce the pressure
and viscous terms by the same factor, thus leaving their relative
importance unchanged. It follows from equations (IV-22) and (IV-23) that
viscous terms are unimportant compared with the pressure effects for
flames investigated in this study. The pressure tensor for one dimen-
sional flow has reduced to only the hydrostatic pressure.

IV-1.3 Simplification of the Momentum Equation

The momentum equation can be reduced to a simple equation between
the rate of change of momentum and the pressure drop across the flame
front. The pressure drop calculated from the simplified equation is
very small, thus justifying the common assumption that the flame is at
constant pressure.

IV-1.3.1 Elimination of the Buoyant Term

The buoyant force term will be compared with the rate of change
of the momentum term. The transient term will be ignored temporarily
because the flame can be expressed by time independent equations.
The time dependent term has been carried through this development
because it makes solution of the flame equations somewhat easier.

The momentum term is

$$\frac{\partial}{\partial x} \left( \frac{3v}{2} \right) = 85 \frac{\text{cm}}{\text{sec}} \left( \frac{130 \text{ cm/sec}}{0.2 \text{ cm}} \right) \approx 5 \times 10^4 \frac{\text{cm/sec}^2}{\text{}}$$

(IV-24)

The buoyant force term is

$$\sum_{i} F_i = 980 \text{ cm/sec}^2$$

(IV-25)

Reduction of the flame pressure to 20 torrs will not change the
magnitude of the buoyant term but will reduce the momentum term by about a factor of ten because of the expanded flame region. The buoyant term is unimportant for atmospheric pressure flames but could have a minor effect on low pressure flames. The buoyant term will, for the time being, be ignored for both high and low pressure flames. The buoyant term has always been ignored in previous flame modeling work.

IV-1.3.2 Calculation of the Flame Pressure Drop

The pressure drop across the flame front can be estimated from the simplified steady state momentum equation. The pressure drop across the flame is

\[ \nabla \frac{\partial v}{\partial x} = \frac{1}{\rho} \frac{\partial P}{\partial x} \]  

(IV-26)

\[ \Delta P = \rho v \Delta v \approx 5 \times 10^{-4} \frac{g}{\text{cc}} \frac{85}{\text{sec}} \frac{\text{cm}}{\text{sec}} 130 \frac{\text{cm}}{\text{sec}} = 5.5 \frac{g}{\text{cm sec}^2} \]

\[ = 5.5 \frac{g}{\text{cm sec}^2} \cdot 9.9 \times 10^{-9} \frac{\text{atm}}{g/\text{cm sec}^2} = 5.5 \times 10^{-6} \text{ atm} \]

The pressure drop across the flame decreases proportionally with pressure. The relative change in pressure drop across a flame front is nearly independent of flame pressure. The pressure drops across flame fronts are so small compared to flame pressures that they can be ignored.

IV-1.4 Simplification of the Diffusional Velocity

The diffusional velocity is expressed in equation (IV-7) after Hirschfelder, et al. (1954) p. 479. The one dimensional diffusional driving force, \( d_j \), is

\[ d_j = \frac{d}{dx} \left( n_j \right) + \left( \frac{n_j}{\rho} - \frac{\rho_j \cdot d \ln \rho}{dx} - \frac{\rho_j}{\rho} (\mathbf{F}_j - \sum_{i=1}^{\infty} \frac{\rho_i}{\rho} \mathbf{F}_i) \right) \]  

(IV-27)
The diffusional driving force will reduce to only the concentration driving force for flame conditions. The concentration driving force for flames is

\[
\frac{\partial}{\partial x} \left( \frac{n_j}{n} \right) = \frac{10^{-2}}{0.2 \text{ cm}} = 5 \times 10^{-2} \text{ l/cm} \tag{IV-28}
\]

The concentration driving force will be reduced by a factor of ten for a 20 torr flame.

The pressure gradient contribution to the driving force is negligible. The pressure gradient term, evaluated approximately for CO\textsubscript{2} is

\[
\left( \frac{n_j}{n} - \frac{\rho_j}{\rho} \right) \frac{1}{P} \frac{dP}{dx} = \frac{n_j}{n} \left( 1 - \frac{\rho_j}{\rho} \right) \frac{1}{P} \frac{3P}{\partial x}
\]

\[
\approx -0.1(0.6) \frac{1}{1} \frac{5 \times 10^{-6}}{0.2 \text{ cm}} = 1.5 \times 10^{-6} \text{ l/cm} \tag{IV-29}
\]

where the pressure gradient has been calculated from equation (IV-26).

The pressure driving force will be reduced by a factor of ten at 20 torrs; therefore its relative importance is unchanged by pressure variations.

The driving force caused by differences in external forces acting on individual molecules is also unimportant. The external force gradient is

\[
\frac{\partial}{\partial x} \left( \frac{F_j}{P} - \Sigma \frac{\rho_i}{\rho} F_i \right) = \frac{\rho_j}{P} \left( \rho_j - \Sigma \rho_i \right) = 0 \tag{IV-30}
\]

When the only external force acting is gravity, which is the same for all molecules, the external force contribution is zero.

**IV-1.4.1 Thermal Diffusion (Soret Effect)**

Concentration driven diffusion must still be compared with thermally driven diffusion. Concentration driven diffusion for hydrogen in nitrogen has the magnitude of
\[
\frac{n_i^2}{n_i \rho} \sum_{j \neq i} d_{ij} \frac{d n_j}{d x} \sim \frac{1}{x_i^m} m_j N_2 \frac{\partial}{\partial x} \frac{d(x_j)}{dx} = \frac{1}{0.01 \text{ cm}^2 \cdot 0.01 \text{ cm}} = 50 \text{ cm/sec}
\]

The thermal diffusion coefficient is more complicated than the ordinary diffusion coefficient. The thermal diffusion coefficient depends on the mixture concentration, the relative mass and size of the interacting species, and has a very complex temperature dependence. Grew and Ibbs (1952), p. 128 gave \( \alpha \), the thermal diffusion factor, for a binary \( \frac{k_T}{X_1 X_2} \); and \( \frac{D_T}{n_i \rho} \sim \frac{12}{X_1} \frac{k_T}{X_1} \) for a trace component. \( D_T \), for \( H_2 \) in \( N_2 \), is about 0.003. This value gives the magnitude of thermally induced diffusion of

\[
\frac{D_T}{n_i \rho} \sim \frac{1 \frac{dT}{dt} \cdot 0.003(10 \text{ cm}^2/\text{sec})}{0.01} \frac{1}{1700 \text{K}} = 21 \text{ cm/sec}
\]

At atmospheric pressures the thermal diffusion term will be on the same order as the concentration driven diffusion term. At a flame pressure of 20 torrs the concentration driven velocity will be increased by a factor of 4 while the thermal diffusion velocity will be reduced by about a factor of 10. Thermal diffusion will be less important than concentration diffusion for low pressure flames but can be about equally important for atmospheric flames.

**IV-1.5 The Specie Conservation Equation**

The specie conservation equation cannot be reduced in complexity by eliminating the remaining diffusion, chemical reaction, or convective terms. The convective term for \( H_2 \) has the order

\[
\frac{\partial^2 V_i}{\partial x} = 130 \frac{\text{ cm}}{\text{ sec}} \frac{(0.01)}{2 \text{ g/gmole}} \frac{28 \text{ g/gmole}}{0.2 \text{ cm}} = 0.46 \frac{1}{\text{ sec}}
\]

This value is to be compared with the diffusional term, here evaluated for \( H_2 \) in \( N_2 \). The magnitude of the diffusional term is

\[
\frac{1}{\rho} \frac{3}{3} (Y_i \rho V_i) = \frac{0.9 \times 10^{-3}}{5 \times 10^{-4}} \frac{\text{ g/cc}}{\text{ g/cc}} \frac{(0.01)}{2 \text{ g/gmole}} \frac{28 \text{ g/gmole}}{0.2 \text{ cm}} = 0.45 \frac{1}{\text{ sec}}
\]
The chemical reaction term is known to be important but is more difficult to estimate than the other terms. For the purposes of this analysis one moderately fast reaction will be evaluated in isolation. The reaction chosen for evaluation is

\[ \text{H}_2 + \text{O} = \text{OH} + \text{O} \]  

(IV-35)

which is one of the slowest of the fast interchange reactions of the \text{H}_2 - \text{O}_2 systems. The rate constant used for reaction (IV-35) is from Baulch, et al. (1968-1970). The chemical reaction term will be altered by participation of all other reactions involving \text{H}_2, but this analysis will show that in general chemical reaction speeds are fast compared to other important terms in the specie conservation equation. The rate of reaction (IV-35) in isolation is

\[
\frac{w_i}{\rho} = \frac{k[0][\text{H}_2]}{\rho m_i} \cdot \frac{3\times10^{11} \text{ cc/gmole sec}}{5\times10^{-4} \text{ g/cc}} \cdot \frac{1 \text{ atm}}{82 \text{ cc-atm} \cdot 1200^\circ \text{K}} \cdot \frac{1}{[0.01][0.01]} \cdot \frac{2 \text{ g/gmole}}{\text{mole} \cdot ^\circ \text{K}} 
\]

(IV-36)

\[ \cdot 2 \text{ g/gmole} = 12 \text{ l/sec} \]

The above analysis indicates that the chemical reaction term can be large compared to the convective and diffusion terms. This is a function of the way in which the analysis was performed because three terms must balance. If the chemical reaction rate is initially rapid and depletes reactants faster than they can be supplied by convection and diffusion, the reaction must slow down because the rate of reaction is directly proportional to the concentration of reactants.

The specie conservation equation can not be greatly simplified and retain its accuracy for all species in all regions of the flame. The convective and reaction terms will approximately balance each other with significant contributions from the diffusion terms under certain conditions.
In a 20 torr flame the convective term will be reduced by a factor of 10, the diffusion term will be reduced by a factor of 2, and the chemical reaction term will be reduced by a factor of 2000. The same terms are in important in the reduced pressure case as in the atmospheric pressure flame; however, the diffusion term has become relatively more important.

IV-1.6 Simplification of the Heat Flux Vector

The heat flux vector expressed in equation (IV-6) can be reduced to a conduction, two radiation, and one diffusion term for the flames of interest. The conduction term will be used for comparison purposes because it is the most important term. The conduction term can be written as

\[
\frac{\partial T}{\partial x} \sim 1.4 \times 10^{-4} \frac{\text{cal}}{\text{cm sec} \ \text{K}} \frac{1700 \ \text{K}}{0.2 \ \text{cm}} \cdot 4.2 \times 10^7 \frac{\text{g cm}^2}{\text{sec}^2} = 5 \times 10^7 \frac{\text{g}}{\text{sec}^3}
\]

(IV-37)

The conduction term will be reduced by approximately an order of magnitude for a 20 torr flame.

IV-1.6.1 Diffusional Heat Flux

An average diffusional velocity is required to evaluate heat transfer caused by diffusion. The comparison between the conduction and diffusion terms can be made by estimating the diffusional flux of heat as the diffusional fluxes times the enthalpies of the three major flame components, \( \text{CO}_2, \text{H}_2\text{O}, \) and \( \text{CO} \). The diluent will not contribute much to the diffusional flux because of its very low concentration gradient. Other species such as \( \text{H}_2 \) which have high diffusional fluxes but low absolute concentrations and enthalpies will not contribute significantly to the heat transferred by diffusion. The major contributions to diffusional heat flux are
for $\text{CO}_2$

$$V_{\text{NX}, H_i^+} \sim 2 \frac{\text{cm}^2}{\text{sec}} \cdot 0.1 \frac{\text{cm} \times 0.1}{\text{cm} \times 0.1} \cdot 10^{-5} \frac{\text{g moles}}{\text{cc}} \cdot 0.05(-94 \times 10^3 \frac{\text{cal}}{\text{g mole}}).$$

$$4.2 \times 10^7 \frac{\text{g cm}^2}{\text{sec} \cdot \text{cal}} = +2.0 \times 10^7 \frac{\text{g}}{\text{sec}^3} \quad \text{(IV-38)}$$

for $\text{CO}$

$$V_{\text{NX}, H_i^+} \sim -4 \frac{\text{cm}^2}{\text{sec}} \cdot 0.01 \frac{\text{cm} \times 0.01}{\text{cm} \times 0.01} \cdot 10^{-5} \frac{\text{g moles}}{\text{cc}} \cdot 0.005(-27 \times 10^3 \frac{\text{cal}}{\text{g mole}}).$$

$$4.2 \times 10^7 \frac{\text{g cm}^2}{\text{sec} \cdot \text{cal}} = +1.0 \times 10^6 \frac{\text{g}}{\text{sec}^3} \quad \text{(IV-39)}$$

for $\text{H}_2\text{O}$

$$V_{\text{NX}, H_i^+} \sim -4 \frac{\text{cm}^2}{\text{sec}} \cdot 0.2 \frac{\text{cm} \times 0.2}{\text{cm} \times 0.2} \cdot 10^{-5} \frac{\text{g mole}}{\text{cc}} \cdot 0.1(-43 \times 10^3 \frac{\text{cal}}{\text{gmole}}).$$

$$4.2 \times 10^7 \frac{\text{g cm}^2}{\text{sec} \cdot \text{cal}} = 3.6 \times 10^7 \frac{\text{g}}{\text{sec}^3} \quad \text{(IV-40)}$$

for $\text{H}_2$

$$V_{\text{NX}, H_i^+} \sim -8 \frac{\text{cm}^2}{\text{sec}} \cdot 0.01 \frac{\text{cm} \times 0.01}{\text{cm} \times 0.01} \cdot 10^{-5} \frac{\text{gmole}}{\text{cc}} \cdot 0.005(-6.4 \times 10^3 \frac{\text{cal}}{\text{gmole}}).$$

$$\cdot 4.2 \times 10^7 \frac{\text{g cm}^2}{\text{sec} \cdot \text{cal}} = 5.4 \times 10^4 \frac{\text{g}}{\text{sec}^3} \quad \text{(IV-41)}$$

The total diffusional flux of heat is then approximately the sum of the $\text{CO}_2$ and $\text{H}_2\text{O}$ contributions which is $5.5 \times 10^7 \frac{\text{g}}{\text{sec}^3}$. The diffusional flux of heat is on the same order as the conduction heat flux and therefore must be retained in the equation for the heat flux vector. The low pressure flame will have diffusional heat fluxes reduced by a factor of ten compared with the atmospheric flame. The relative importance of the diffusional term will, therefore, remain unchanged with pressure changes.
IV-1.6.2 Dufour Effect (Temperature Driven Diffusional Flux of Energy)

The amount of enthalpy transferred due to thermally driven diffusion is quite small compared to other terms in the heat flux vector equation and can be neglected. The Dufour effect has the magnitude in flames of

\[ \sum_{i=1}^{n} \sum_{j=1}^{\infty} \frac{X_i D_i}{t_i} (V_i - V_j) \sim 8.3 \times 10^7 \frac{g \text{ cm}^2}{\text{g mole sec}^2 \text{K}}. \]

\[ (0.01) \frac{6 \times 10^{-6}}{2} \frac{g/\text{cm sec}}{\text{g/gmole}} \frac{50 \text{ cm/sec}}{10 \text{ cm}^2/\text{sec}} \sim 1.5 \times 10^4 \frac{g/\text{sec}^3}{.} \]

The Dufour effect is so small that pressure effects need not be considered.

IV-1.6.3 Radiation

Radiational loss of energy can be by either thermal or chemiluminescent radiation. Both terms appear to be important modes of heat loss from the flame region. Previous investigations have neglected thermal radiation and in most cases have not considered chemiluminescent radiation at all.

IV-1.6.3.1 Thermal Radiation

Thermal radiation is caused by a species in an energy level dropping to a lower energy level and emitting the difference in energy as a photon of specific energy. This radiation occurs in a system that has essentially a Boltzmann energy distribution. The emitted photon usually leaves the system under combustion conditions, thus causing a new Boltzmann distribution at a lower system energy level. Most of the thermal radiation from flames is emitted in the infrared region of the spectrum. The major contributors to thermal radiation in flames are H₂O and CO₂. Minor species such as CO, CH₄, and contribute to
flame radiation primarily dependent on their composition but also dependent on their spectrum. See Hottel and Sarofim (1967) chap. 6 for more information. The radiation from CO$_2$-H$_2$O mixtures is well documented and will be used as an approximation to the total thermal radiation from the flame. Neglected species will have low flame concentrations except for CO in rich flames. The actual radiation may then be 10-30% higher than that estimated here but will not be in error by as much as a factor of two.

Total radiational losses from the flame are important enough to temporarily retain the radiation term in the heat flux vector equation. The radiational losses of energy from a one inch diameter burner are

$$\varepsilon \sigma T^4 \sim 0.008 (1.3 \times 10^{-12}) \frac{\text{cal}}{\sec \ cm^2 \ ^oK^4} \times 3.7 \times 10^{12} \ ^oK^4 x$$

$$4.2 \times 10^7 \frac{g \ cm^2}{\sec^2 \ \text{cal}} = 1.6 \times 10^6 \ g/\sec^3 \quad \text{(IV-43)}$$

This term will be decreased by a factor of about 35 for the low pressure flame while the conduction term will only be decreased by a factor of 10. The thermal radiation term is moderately important for the atmospheric pressure flame but rather unimportant for the low pressure flame.

**IV-1.6.3.2 Chemiluminescent Radiation**

Chemiluminescent radiation results from the decrease in energy level by photon emission of a specie that has been excited by chemical reaction. Emission of CO$_2^*$, CH*$_2$, and C$_2^*$ have been identified by Child and Wohl (1959) as contributing to chemiluminescent radiation from flames. Carrington (1959) and Fissan (1972) have identified excited hydroxyl radicals as contributors to flame radiation. Early work on coal gas explosions by Garner and Johnson (1928) and Johnson
and Garner (1928) indicate that, while chemiluminescent radiation is a small part of the total radiation loss, chemiluminescent radiation is a major part of the heat lost during explosion.

Typically chemiluminescent reactions are highly exothermic processes, such as association reactions, that can result in products that have energy internally stored. The following chemiluminescent reactions are suspected to be important causes of flame radiation.

\[
\begin{align*}
\text{C}_2\text{OH} &= \text{CO} + \text{CH}^* & \Delta H_f^{298} &= -94.0 \text{ k cal/gmole} \\
\text{H} + \text{OH}^* &= \text{H}_2\text{O} & \Delta H_f^{298} &= -119.3 \\
\text{H} + \text{OH} + \text{OH}^* &= \text{H}_2\text{O} + \text{OH}^* & \Delta H_f^{298} &= -119.3 \\
\text{CO} + \text{O} &= \text{CO}_2^* & \Delta H_f^{298} &= -127.2
\end{align*}
\]

where the enthalpies are for the analogous reaction to ground state products. Reactions for production of excited \( \text{C}_2^* \) have not been identified but, as we will see later, this reaction does not significantly contribute to the radiation loss. Once the excited species are formed in reactions (IV-44) - (IV-47) they can lose their excess energy by spontaneous photon emission, which would reduce the energy of a transparent system, or they can transfer their energy to another specie by collision in which case the energy is redistributed inside the system. The fraction of the excited specie that is quenched by collisions and the fraction that loses energy by photon emission are rather difficult to specify at the moment. First, some reaction rate constants for chemiluminescent reactions are derived from measurements of flame emission. These values are values for the efficiency of photon emission for the particular experimental conditions. Other data are reported for the rate of excitation and a quenching efficient must be applied to these values to obtain the rate of light emission.
By CF* will be unimportant compared to other heat transfer terms at a conservative estimate. The flux of energy out of the flame system will have the following magnitude due to the chemiluminescent reaction (IV-44) will have the following magnitude.

Equation (IV-48) clearly shows that chemiluminescent radiation produced by CF* at 1 atm, 1600 K, 2.0 x 10^12 photon/cc/gmole x 1.0 x 10^-27 g/cm^2 photon/sec x 3 x 10^-10 cm/phot/sec x 52 cc atm gmole x 10^4 K/cm^2 = 40 g/sec.

Porter et al. (1967) support CF* production by reaction (IV-44) a rate constant of about 3.6 x 10^11 cc/gmole sec for the 2 state with a very little temperature dependence in the range 875-1650 K. This rate constant was derived without considering quenching reactions other than photon emission and therefore must be considered as a lower limit. At the low pressure (6mm Hg) used the quenching rate constant would have to be approximately 10^7 times larger than the emission rate constant for the 2 to the ground state with emission at 4309A. Porter et al.'s (1967) value of 2 x 10^9 mole fraction of C_2 is probably representative of the entire emission process. The strongest CF* quenching to be important. The rate constant can then be taken as

\[ \frac{d[NH]}{N} \]
atmospheric conditions. At low pressures production of CH* will be reduced by the square of the pressure and the quenching efficiency will tend to zero, i.e. all excited molecules will lose energy by photon emission. The quenching factor used in this analysis was only ten so that the photon emission rate can only be increased by a maximum factor of ten at low pressures. This increase will be greatly over shadowed because the rate of production of CH* will be decreased by a factor of 1400 for a 20 torr flame. The volume to surface ratio will be increased only by a factor of four for the low pressure case, therefore reaction (IV-44) is an unimportant mode of energy loss for all cases.

Definite reactions producing C2* have not been identified. Chemiluminescent radiation from C2* will not be important because according to Kushida and Wohl (1958) it is less important than radiation from CH* which has just been shown to be unimportant.

Padley (1960) has supported reaction (IV-45) as the cause of the faint blue radiation from hydrogen flames. He reported that reaction (IV-45) had a continuum extending from 2200-6000°A with a flat maximum in the region of 4500°A. Padley claimed that reaction (IV-45) proceeded at a rate 1/100 of the rate of the corresponding three body non-radiating reaction. He assumed a quenching factor of 10 which is probably somewhat low at atmospheric pressure. Using Padley's values and Baulch, et al.'s (1968-1970) rate constant for the three body reactions yields

\[
\frac{\sqrt{hP^C}}{S} \frac{d(H_2O^*)}{\lambda L} = \frac{1}{10} \frac{1.1 \text{ cm}^3}{11 \text{ cm}^2} \times \frac{6.6 \times 10^{-27} \text{ g cm}^2/\text{sec photon}}{4 \times 10^{-5} \text{ cm}} \times 3 \times 10^{10} \text{ cm/sec} \times 6 \times 10^{23} \text{ photon/gmole}^* \times \frac{1}{100} \frac{1.2 \times 10^{16}}{1 \text{ atm} \frac{82 \text{ cc atm}}{\text{g mole} \circ K}} \left[ \frac{1200 \circ K}{.01} \right]^3 = 3.5 \times 10^5 \text{ g/sec}^3
\]  

(IV-49)

Chemiluminescent radiation produced by reaction (IV-45) could be
marginally important at atmospheric conditions although it contributes only 1/4 as much heat loss as thermal radiation and is only 1/100th of the conductive heat flux. The chemiluminescent radiation will again be reduced by a factor of about 35 for the 20 torr flame. Energy loss caused by chemiluminescent radiation of reaction (IV-45) will be ignored for all flame of this study.

Kaskan (1959a) has suggested that reaction (IV-46) among others might account for chemiluminescent radiation of OH* in flames. Hinck, et al. (1965) have considered reaction (IV-46) as a radiation source in several different flames. Zeegers and Alemade (1965) have shown reaction (IV-46) to be the most important reaction for production of excited hydroxyl radicals and have measured a rate constant of $7 \times 10^{14}$ cm$^6$/gmole sec, consistent with Kaskan's (1959) value. The rate constant was measured based on the difference in predicted thermal emission and measured emission. The rate constant derived in this manner already has the quenching efficiency of an atmospheric flame included.

The heat loss by chemiluminescent radiation from reaction (IV-46) has the value

$$\sqrt{\frac{h}{S}} \frac{c_L}{\lambda_L} N_{AV} \frac{d(OH^*)}{dt} = \frac{1.1 \text{ cm}^3}{1 \text{ l cm}^2} \frac{6.6 \times 10^{-27} \text{ g cm}^2/\text{photon sec}}{3 \times 10^{-5} \text{ cm}} \times$$

$$3 \times 10^{10} \text{ cm/sec} \times 6 \times 10^{23} \text{ photon/gmole} \times 7 \times 10^{14} \text{ cm}^6/\text{gmole sec} \times$$

$$\left[ \frac{1 \text{ atm}}{82 \text{ cc atm}} \right] \left[ \frac{1600^\circ K}{0.01} \right] \left[ \frac{3.8 \times 10^5}{\text{ g/sec}^3} \right] \quad \text{(IV-50)}$$

This value is about the same as the radiation lost through reaction (IV-45) and so will be ignored. The radiation from the low pressure flame will be reduced more than the radiation produced by the other reactions because it is termolecular while the other reactions are bimolecular.
Reaction (IV-47) has long been identified (see Kaskan (1959b)) as the source of the broad continuum in hydrocarbon flames that produces the characteristic blue color. The molecularity of the reaction as well as its emission states are still uncertain. The rate constants measured for reaction (IV-47) are in reasonable agreement but there are still many unresolved features of this reaction. The general evidence tends to favor a three body reaction for reaction (IV-47) (see Clyne and Thrush (1963)). Measurements of the rate constant for reaction (IV-47) at low temperatures, Kondrat'ev and Ptichkin (1961) and Clyne and Thrush (1963), find an activation energy of several kcal, but high temperatures measurements, Brabbs and Belles (1967), and from dissociation measurements of CO₂, Davies (1965), show the small negative temperature dependence typical of three body reactions. It seems reasonable to adopt Brabbs and Belles (1967) upper limit of 1x10¹⁴ cm⁶/mole sec for reaction (IV-47) at flame conditions. No quenching correction is necessary since the rate constant was derived from emission data at pressures from 8.8 to 22.6 atmospheres.

Reaction (IV-47), under low resolution, appears to produce continuum emission from 2500 Å to 7000 Å which reveals an underlying fine structure under higher resolution. Myers and Bartle (1967) have investigated the emission distribution. Weight averaging their distribution shows that reaction (IV-47) emits photons of average energy associated with a wave length of 3750 Å. The amount of radiation as energy emitted through a transparent gas by reaction (IV-47) can be estimated as

\[
\frac{\sqrt{\frac{h_p c}{\lambda L}}}{N_{AV}} \frac{d(CO_2^*)}{dt} \approx 1.1 \frac{cm^3}{11 \ cm^2} \times 6.6 \times 10^{-27} \frac{g \ cm^2}{photon \ sec} \times \frac{6x10^{23} \ photon/gmole}{3.75 \times 10^{-5} \ cm} \times 3 \times 10^{10} \ cm/sec \times 6 \times 10^{23} \ photon/gmole \times 1 \times 10^{14} \ cm^6/gmole^2/sec \times
\]
The magnitude of the chemiluminescent radiation caused by reaction (IV-47) is about an order of magnitude lower than the conductive flux and slightly higher than the thermal radiation flux. The chemiluminescent term will be further decreased compared to the conductive flux at low pressure and will thus be less important in the low pressure flames.

The above analysis shows that chemiluminescent radiation from hydrocarbon fragments will be very small compared to other modes of heat transfer, chemiluminescent radiation from excited water and hydroxyl radicals will be approximately two orders of magnitude smaller than the conductive heat flux and can be neglected, and only the energy loss by excited carbon dioxide can be an important mode of chemiluminescent heat loss and its magnitude is about one-tenth that of the conductive heat flux. Thermal radiation is also about one order of magnitude smaller than the conductive flux and as a first estimate all radiation fluxes can be ignored. It should be remembered that a 10% heat loss from the flame will result in a 10% reduction in temperature. At flame temperatures around 2000°C a 10% reduction in flame temperature would be an intolerable error. The radiational terms can be ignored only as a first approximation but must usually be included in atmospheric flame solutions for acceptable answers. Radiation appears to be a moderately important term in the heat flux vector for atmospheric pressure flames but not to be important for flames that have pressures in the tens of torr range.

IV-1.7 Simplification of the Energy Equation

The kinetic energy term and the term involving work against
gravity forces can be neglected in the energy equation compared with the heat flux vector term and the convective term.

**IV-1.7.1 Elimination of the Kinetic Energy**

The convection of internal energy term has the magnitude

\[
u \sim \frac{16 \times 10^3 \text{ cal/gmole}}{16 \text{ g/gmole}} \times (0.1) \times \frac{16}{28} \times 4.2 \times 10^7 \frac{\text{g cm}^2/\text{sec}^2}{\text{cal}}\]

\[= 2.4 \times 10^{10} \text{ cm}^2/\text{sec}^2 \quad (\text{IV-52})\]

while the kinetic energy term has the approximate value of

\[
\frac{1}{2} v^2 \sim \frac{1}{2} (130 \text{ cm/sec})^2 = 8.4 \times 10^8 \text{ cm}^2/\text{sec}^2 \quad (\text{IV-53})
\]

The internal energy and kinetic terms decrease in the same manner with decreasing pressure so that their relation remains unchanged for low pressure flames.

**IV-1.7.2 The Pressure Work Term**

The pressure tensor has previously (section IV-1.2) been reduced to only the one dimensional hydrostatic pressure. The pressure work term is to be compared with the heat flux vector term. The heat flux vector has the magnitude

\[
\frac{\partial q}{\partial x} \sim \frac{5 \times 10^7 \text{ g/sec}^3}{0.2 \text{ cm}} = 2.5 \times 10^8 \text{ g/cm sec}^3 \quad (\text{IV-54})
\]

The heat flux term will be reduced by a factor of 100 in a 20 torr flame. The pressure work term has the value of

\[
p \frac{\partial v}{\partial x} \sim 1 \times 10^6 \text{ g/cm sec} \times \frac{130 \text{ cm/sec}}{0.2 \text{ cm}} = 6.5 \times 10^8 \text{ g/cm sec}^3 \quad (\text{IV-55})
\]

The pressure work term is on the same order as the heat flux term and can not initially be eliminated, although it will not appear in the energy equation when the equation is expressed in terms of enthalpy instead of internal energy. The pressure work term will be reduced by
a factor of 400 in the low pressure flame. The slight change in the relative order of the two terms does not alter the conclusion of this analysis.

**IV-1.7.3 Elimination of the Gravity Term**

The term expressing work against gravity forces in the energy equation is very small compared to the important terms in the energy equation and can be neglected. The gravity work term has the magnitude

\[ \rho \Sigma Y_i F_i V_i = 5 \times 10^{-5} \frac{g}{cc} \times 980 \text{ cm/sec}^2 \times 1 \text{ cm/sec} = 0.05 \frac{g}{cm \text{ sec}^3} \]  

(IV-56)

The gravity work term will be reduced by a factor of 400 for a 20 torr flame, but is negligible in any case.

**IV-1.7.4 Expression of the Energy Equation in Terms of Enthalpy**

The energy equation has, until now been expressed in terms of internal energy. It is more convenient to express the energy equation in terms of enthalpy for flame situations. This can easily be accomplished by converting internal energy to enthalpy via

\[ u = h - \frac{P}{\rho} \]  

(IV-57)

Substitution of equation (IV-57) and the continuity equation (IV-17) in to the simplified energy equation and neglecting terms involving pressure gives

\[ \rho \frac{\partial h}{\partial t} + \rho \frac{\partial h}{\partial x} = \frac{\partial q}{\partial x} \]  

(IV-58)

which is the one dimensional energy equation for flame systems expressed in terms of enthalpy without radiation.

**IV-1.8 Summary of the Simplified Flame Equations**

The experimental evidence on flat flames is good enough to support
expression of the flame equations as one dimensional. The flame equations for a flat flame burner could have been written as steady state equations but they were written in the more general unsteady state form because it has some solution advantages.

Order of magnitude analysis of the complete flame equations for atmospheric and low pressure flames has resulted in great simplifications to the flame equations. All the terms neglected have been neglected by all previous investigators. An additional set of terms that could become important under certain conditions have been retained. Some of these terms have been previously retained by various authors but some terms have not as yet been included in any solution of the flame equations. The terms that have been neglected in common with other authors are

- bulk viscosity
- viscous terms
- pressure driven diffusion
- external force driven diffusion
- temperature driven diffusional energy flux (Dufour effect)
- kinetic energy
- work against gravity forces

See Campbell, et al. (1966) for another discussion of simplification of the flame equations.

Thermal diffusion appears to be moderately important in atmospheric pressure flames but only marginally important in low pressure flames. The Dufour effect has been retained in the flame equations only by Dixon-Lewis (1968), (1970b). Dixon-Lewis (1968) found that inclusion of thermal diffusion in the flame equations gave better agreement
between a flame solution and experiments for rich atmospheric $\text{H}_2-\text{O}_2-\text{N}_2$ flames. Inclusion of thermal diffusion in the flame equations improved the agreement with experiment approximately 10% for the $\text{H}_2$ profile but made little difference in either the nitrogen or oxygen profile.

The buoyant term in the momentum equation has been neglected by previous investigators. The order of magnitude analysis of equations (IV-24) and (IV-25) shows that the buoyancy force is approximately 50 times smaller than the momentum term in an atmospheric flame and can therefore be neglected. The buoyant term is, however, only 5 times smaller than the momentum term in a 20 torr flame. Neglecting the buoyancy force term in the low pressure flame could make about a 7% difference in the velocity. In view of other inherent errors involved in solution of the flame equations and the complication introduced by retaining the momentum equation, the buoyancy term will be neglected for all flames. The term may be introduced in later developments but it hardly seems worth the effort in the first analysis.

Radiational energy losses have not been previously considered in solution of the flame equations. The order of magnitude analysis in equations (IV-37), (IV-43), and (IV-51) shows that radiational losses are approximately 10% of the conduction term in the atmospheric pressure flame and very much smaller in the low pressure flame. The amount of heat lost through radiation is only about 5% of the total heat release. Ignoring radiational heat loss could lower the temperature sufficiently so that the chemical rate of reaction would be decreased by about 25% at 2000°K for a reaction with an activation energy of 20 kcal. The error in the rate of reaction caused by ignoring radiational heat loss is insignificant compared with errors usually associated with rate
constants. The radiational terms will not be included in the flame equations solved in this study.

The order of magnitude analysis has justified solution of the usual simplified flame equations with the possible exception of the buoyancy term in low pressure flames, which has not previously been included in the flame equations, and the Dufour effect in atmospheric flame, which has previously been retained in the flame equations by Dixon-Lewis (1968) and (1970b).

The simplified one dimensional, unsteady state flame equations can then be expressed as

\[ \frac{\partial Y_i}{\partial t} + v \frac{\partial Y_i}{\partial x} = \frac{W_i}{\rho} - \frac{1}{\rho} \frac{\partial}{\partial x} (\rho Y_i V_i) \]  \hspace{1cm} (IV-59)

**Conservation of energy**

\[ \rho \frac{\partial h}{\partial t} + \rho v \frac{\partial h}{\partial x} = - \frac{\partial q}{\partial x} \]  \hspace{1cm} (IV-60)

where

\[ V_i = \left( \frac{2}{n_i \rho} \right) \Sigma_{j} m_{ij} D_{ij} \left( \frac{n_i}{n} \right) - \frac{1}{n_i m_i} D_{i} \frac{\partial lnT}{\partial x} \]  \hspace{1cm} (IV-61)

and

\[ q = -\lambda \frac{\partial T}{\partial x} + \rho \Sigma_{i=1}^{n} h_{i} V_{i} V_{i} \]  \hspace{1cm} (IV-62)

where the continuity and momentum equations have not been included because the only new information they add is the flame pressure drop which is not an important flame variable.

**IV-2. Previous Solutions of the Flame Equations**

Work began in the late 1940's on an exact numerical solution of simplified flame equations. The early work was hampered by difficulties
in obtaining a numerical solution to the flame equations and by the very poor quality of the input data. The field has advanced to the point where numerical solutions to rather complete sets of flame equations can be generated. There have also been advances in the quality of the input data. Most notably there has been a marked improvement in the accuracy of the physical property data. There have also been improvements in the accuracy of the rate data, but large uncertainties are still attached to many important rate constants. It is not unusual for a rate constant to be uncertain by a factor of 10, occasionally rate constants have even larger uncertainties.

IV-2.1 Steady State Flame Equation Approach

The flame equations are most naturally, from a physical point of view, written as steady state equations. The early investigators worked at finding numerical solutions to various simplified forms of the first order steady state flame equations written in terms of mass flux. This work is best typified by Hirschfelder and his co-workers at the University of Wisconsin. For instance, see Curtiss and Hirschfelder (1949), Hirschfelder and Curtiss (1949a), Henkel, et al. (1949a), Hirschfelder and Curtiss (1949b), Henkel, et al. (1949b), Hirschfelder and Curtiss (1951), Hirschfelder, et al. (1953a), Hirschfelder, et al. (1953b), Giddings and Hirschfelder, et al. (1956), Klein (1957), Campbell (1957), Campbell, et al. (1963), and Campbell (1965a), (1965b), (1966). Other unrelated workers have also used what might be termed the Hirschfelder approach; these are Wilde (1954), Spalding (1957a), (1957b), Adler (1959), (1961), Dixon-Lewis (1968), (1970), and Dixon-Lewis, et al. (1973).

The general Hirschfelder approach was to write simplified first
order steady state flame equations in terms of mass flux and then attempt to numerically solve these equations for very simple, idealized flame systems. Hirschfelder usually expressed the diffusion coefficients in a reasonably precise manner first presented in Hirschfelder and Curtiss (1949a). This method of expressing mixture diffusion coefficients is exact for a binary mixture or for a trace element in a diluent. It gives mixture diffusion coefficients that are entirely satisfactory for almost all combustion systems of interest. Hirschfelder usually made all the justified simplifications to the flame equations discussed in section IV-1. He also eliminated the thermal diffusion contribution, radiational heat losses, and buoyance forces. Some of the usually neglected terms were investigated in Hirschfelder, et al. (1953a). They concluded that the usually neglected terms were unimportant for their simple system. Hirschfelder, et al. (1953b) justified ignoring the thermal diffusion term in the hydrazine decomposition flame but conceded that radiational energy loss might be important. The early work of the Hirschfelder group is adequately summarized in Hirschfelder and Curtiss (1961).

The first order steady state equations as used by Hirschfelder and co-workers are difficult to solve for realistic problems. The numerical contributions in the Hirschfelder series are summarized by Klein (1957). The steady state flame equations have been solved by Hirschfelder and co-workers for a number of very simple kinetic problems. The steady state equations have also been successfully solved by Bailey (1969) and Bittker and Scullin (1972) for more difficult kinetic problems where the flow condition allows elimination of the second order diffusion and conduction terms. Dixon-Lewis (1970) and Dixon-Lewis, et al. (1973) have successfully solved the first order steady
state equations for the \( \text{H}_2\text{-O}_2 \) system with the flame equations written in terms of the mass flux. Dixon-Lewis used a solution to the simplified transport property, unsteady state equations as a starting values for the solution to the steady state flame equations.

IV-2.2 Unsteady State Flame Equation Approach

Spalding (1956) rendered the flame equations solvable for complex systems by writing the equations in the unsteady state form and introducing the Von Mises' cooreinate transformation. Papers from the Spalding group leading to and using the unsteady approach are Spalding (1953), (1956), Stephenson and Taylor (1970), Spalding and Stephenson (1971a), (1971b), and Stephenson and Taylor (1973). Other investigators who have also used the Spalding approach are Zeldovich and Barenblatt (1959), Adams and Cook (1959), Dixon-Lewis and Williams (1963), Dixon-Lewis (1967), Lovachev and Kaganova (1969), Lovachev, et al. (1970), Eberius, et al. (1971), and Bledjian (1973).

The basic method of the Spalding approach is to write the flame equations in the unsteady state form. This physically corresponds to either a one dimensional flame propagating through a stagnant media of mixed combustible gases or a flame holder moving through the same combustible mixture at the speed with which the gases would issue through the holder if the holder were stationary. Either of these conditions are expressed by the same set of flame equations although the boundary conditions are different. The unsteady state equations are then solved in time as the flame or flame holder propagates through the mixture. The steady state solution is the solution to the unsteady state equations as time approaches infinite.

The Von Mises' coordination transformation allows the coordinate system to be stretched in the direction of propagation so that equal
spacings of the transformed coordinate corresponds to very tight spacings in the initial region where changes occur most rapidly and rather loose spacing in the later regions were changes occur more slowly. Spalding further refined the flame equations by making his transformed space coordinate dimensionless which allowed him to restrict his solution to only a specified space region provided he could properly specify the boundary conditions for the reduced space region. The boundary conditions are then specified in terms of entrainment rates and their relation to the transformed space variable. This part of Spalding solution procedure is described in Patankar and Spalding (1967) for boundary layer flows and is adapted to solution of the flame equation in Stephenson and Taylor (1970) and Spalding and Stephenson (1971a).

Spalding used very simplified physical properties until Spalding and Stephenson (1973) and Stephenson and Taylor (1973). The basic physical property simplification made in much of the early work is that the Lewis number is one. The Lewis number is the ratio of the thermal diffusivity to the molecular diffusivity \( \lambda/\rho C_p D_L \). Hirschfelder (1960) has shown that the approximation of the unit Lewis number coupled with the common assumptions of equal diffusivities and constant heat capacities leads to constant enthalpy throughout the flame. These assumptions allow the energy conservation equation to be replaced with an algebraic equation. The validity of the unit Lewis number approximation will be discussed later. The later Spalding work uses the Hirschfelder diffusion model along with mixture thermal conductivities and individually variable heat capacities.

IV-2.3 Shvab-Zeldovich Formulation of the Flame Equations

Many of the previous simplifications take the form of a modified
Shvab-Zeldovich formulation of the flame equations. See Williams (1965), p. 9 and Zeldovich (1951). In addition to eliminating bulk viscosity, viscous terms, pressure driven diffusion, external force driven diffusion, temperature driven diffusion (Dufour effect), kinetic energy, and work against gravity forces discussed in section IV-1, the formulation also neglects thermal diffusion (Soret effect), radiation, and buoyancy. The physical properties are simplified by assuming all the diffusion coefficients are equal and the Lewis number is one. These assumptions are less restrictive than those necessary to reduce the energy equation to an algebraic expression.

The diffusion coefficients in flame situations can vary by almost a factor of ten but more usually only by a factor of 2. The very light H and H₂ diffuse very much faster than other substances in the flame. The light species will have concentrations on the order of 1% so that underestimating their diffusion rate will not directly have a significant effect on the energy equation. However, H and H₂ are very important for chemical reactions and hence concentration profiles. In rich systems most of the fuel will initially react with H atoms. Errors in the concentration of H atoms can therefore cause both the concentration profiles and temperature profiles to be skewed.

The Lewis number is reasonably close to one in combustion situations and is not a strong function of temperature. The Lewis number in an unburnt stoichiometric methane-air mixture varies between 1.2 based on CO₂ and 0.18 based on H. Values of the Lewis number in a burnt mixture of the same gas are 1.39 for CO₂ and 0.20 for H. The errors caused by the assumption of unit Lewis number will not greatly effect the calculated profiles except through errors in the reaction term caused by erroneous diffusion coefficients. Campbell (1966) has
investigated deviations from unit Lewis number and found little differences in ozone flame velocities for a system with some Lewis numbers equal to 1/2 and systems with some Lewis numbers equal to 10. However, modern computers and better physical properties have all but eliminated the computational advantage gained by assuming a unit Lewis number, therefore individual physical properties and their variation with temperature will be used in this investigation.

IV-2.4 Comparison of Flame Equation Solution Methods

Several authors have included in their papers short reviews of previous attempts to solve the flame equations. The best of these are Von Karman (1957), Zeldovich and Barenblatt (1959), Hirschfelder and Curtiss (1961), and Eberius, et al. (1971). One author (Wilde (1972)) has made direct comparison of different solution methods and one author (Dixon-Lewis (1967), (1968), (1970a), (1970b) and Dixon-Lewis, et al. (1973)) has used both the steady and unsteady state methods, but Dixon-Lewis has not made a detailed comparison. It is Eberius, et al.'s (1971) contention that solution of the steady state equations is unattractive because the equations are inherently unstable when integrated from the cold boundary and the boundary conditions must be very accurately perturbed (estimated to be one part in a billion) when the integration is started at the hot boundary.

Wilde (1972) has compared numerical methods of solution to the flame equations formulated in three different ways for the O$_3$-O$_2$, H$_2$-Br$_2$, and H$_2$-O$_2$ flame systems. The flame equations can be formulated as time independent first order ordinary differential equations if they are written in terms of mass flux instead of composition. This approach has been used successfully by Dixon-Lewis (1968), (1970) and Dixon-Lewis,
et al. (1973). This formulation requires either that the mass fluxes are specified or that they are specified in the form of additional equations if a solution is to be in the form of concentration profiles. The flame equations can also be formulated as steady state second order ordinary differential equations. This approach so far has not been widely used. The third method of formulating the flame equations is as unsteady state second order partial differential equations. This approach has been used to solve real flame problems by Spalding (1971a) and Stephenson and Taylor (1973).

The first order differential equations consist of s variables and equations for both the fractional mass fluxes and the compositions and one variable and one equation for both the temperature and burning velocity. This formulation leads to a well posed problem containing 2s+1 variables. Wilde (1972) solved this set of equations by linearizing the derivatives about a previously calculated value. The matrix of partial derivatives involved in the linearization causes numerical problems when it has either large positive or large negative roots. Both large positive and negative roots appear in solutions to the flame equations. This problem can now be overcome with numerical techniques outlined in Wilde (1972). The time independent s+1 second order differential equations were linearized in a manner similar to that of the first order linearized equations and solved by matrix inversion. The s+1 partial differential equations were solved by expanding and averaging the chemical rate term and using an implicit formulation for the second derivative.

Wilde (1972) concluded from his comparison of the different numerical methods that "...the second-order time-independent equations
was faster per iteration than that for the first-order equations, but required closer initial estimates and more iterations to converge. The partial differential equations program was longer running than the other two but was surer in converging." Wilde did his calculations on an EMR/ASI 6020 with a floating-point multiply time of 330 microseconds. The run times, using simplified physical properties, took as long as 8 hours. The IBM 370 has a multiply time of 0.78 microseconds. Run times for solution to realistic flame problems will probably take on the order of one to two minutes at a cost per run of 10-20 dollars.

There is very little evidence to support a choice as to the best way to formulate and solve the flame equations. It appears that the unsteady-state formulation has advantages in solution of general problems while the steady state formulations can have computational advantages for specific problems. The approach to be used in this study is the unsteady state formulation of the flame equations because a program surer of convergence is desired for the problem in this study where there is rather limited a priori knowledge.

IV-2.5 Solution Method

It has been implied through much of the preceding material that the Spalding approach was favored as a method of solving the flame equations. This author thinks there are many numerical advantages attached to working with the unsteady-state flame equations as opposed to the steady state flame equations. The author however can not clearly see the advantage of some of the procedures used in the complete Spalding approach to solving the flame equations.

IV-2.5.1 Introduction of Temperature into the Energy Equation

Prior to discussing the solution procedure, the flame equations
expressed in equations (IV-59) – (IV-62) need some minor rearrangements. First the energy equations is most conveniently written in terms of mean heat capacities and temperature. The heat capacities can be introduced into the energy equation by

\[
h_i = h_i^{298} + \int_{298}^{T} C_{pi} \frac{dT}{T} = h_i^{298} + \frac{C_{pi}}{T} (T-298)
\]

(IV-63)

The energy equation can be written in its final form by substituting for the enthalpy from equation (IV-63), the heat flux vector by equation (IV-62), and the diffusional velocity by equation (IV-61). The continuity equation can be cancelled from the resulting equation and the specie balance equations can be used to introduce the chemical rate of production of specie i. The final set of flame equations to be solved is N specie equations of the form

\[
\frac{\partial Y_i}{\partial t} + v \frac{\partial Y_i}{\partial x} = \frac{\sum w_i}{\rho} - \frac{1}{\rho} \frac{\partial}{\partial x} (\rho Y_i \left( \frac{n_i}{n_{\infty}} \right) \sum_j D_{ij} \frac{\partial (n_j/n)}{\partial x}) - \frac{1}{n_i m_i} \frac{D_{T_i}}{\partial x} \left( \frac{\partial \ln T}{\partial x} \right)
\]

(IV-64)

where one species concentration may be found from the difference from the sum of the mass fractions and one, and one equation for temperature

\[
\sum_i \left[ \rho Y_i \left( \frac{n_i}{n_{\infty}} \right) \frac{\partial C_{pi} T}{\partial t} + \rho v Y_i \frac{\partial C_{pi} T}{\partial x} \right] - \frac{\partial}{\partial x} \lambda \frac{\partial T}{\partial x}
\]

\[+ \sum_i Y_i \frac{\partial}{\partial x} \left( \frac{n_i}{n_{\infty}} \right) \sum_j D_{ij} \frac{\partial (n_j/n)}{\partial x} - \frac{D_{T_i}}{n_i m_i} \frac{\partial \ln T}{\partial x}
\]

(IV-65)

\[= -\Sigma h_i^{298} w_i + \sum j \frac{C_{pi}}{T} (T-298) \frac{\partial \ln T}{\partial x}
\]

The velocity can be found from the ideal gas equation of state if buoyancy forces are unimportant and the flame pressure is constant. Radiation losses have been neglected in equation (IV-65).
IV-2.5.2 Von Mises' Coordinates

Spalding (1956) introduced Von Mises' coordinate into flame work. The Von Mises' transformation takes the form

\[
\frac{\partial \psi}{\partial x} = \rho \quad \text{(IV-66)}
\]

\[
\frac{\partial \psi}{\partial t} = -\rho v \quad \text{(IV-67)}
\]

which satisfies the continuity equation and will eliminate the convective terms from the specie and energy conservation equations. The transformation was originally used for solving boundary layer problems where it is advantageous to have fine resolution near the fixed boundary where changes occur most rapidly and course resolution near the free boundary where changes are slow. The transformation also allows a constant number of grid points to be used as the boundary layer expands. The effect of the Von Mises' transformation in flames is to expand the spacial coordinate in the direction of flame propagation. This results in small grid spaces near the cold boundary and expanded grid spacings through the flame and post flame region where the density is decreasing. This transformation is advantageous for numerical solution of flames that have a cold constant temperature surface which allows flow only in the direction of flame propagation. Flames that are freely propagating or flames that are stabilized without benefit of a cold surface are handled better by a transformation that gives the smallest grid spacings approximately in the middle of the flame region instead of near the cold boundary.

Spalding and Stephenson (1971) later superimposed an "S" shaped grid spacing over the grid spacing given by the Von Mises' transformation. They first defined a dimensionless space function by
where \( \psi_H \) and \( \psi_C \) represent the space function defined in equation (IV-66) at the hot and cold boundaries. The value of \( \psi_C \) for a stabilized burner surface is the mass flux of material through the burner surface. The value of \( \psi_H \) depends on time and is equal to the mass flux through the cold boundary at infinite time. A specie balance at infinite time when no material is allowed to cross the boundaries by diffusion gives

\[
\rho S_j \equiv G_C = -G_H = \frac{\int_{w_j}^H w_j \, dx}{Y_{jH} - Y_{jC}} \tag{IV-69}
\]

where \( S_j \) is the flame speed evaluated for specie \( j \) and \( G \) is the mass flux. Spalding and co-workers retain the same form for the mass flux at times less than infinite. The mass crossing the hot boundary at any time in a stabilized system is specified as

\[
G_H = G_C \left[ \frac{Y_{j,H} - Y_{j,HH}}{Y_{j,H} - Y_{j,C}} \right] \times 100 \tag{IV-70}
\]

where HH represents a point inside but close to the hot boundary. Equation (IV-70) is equivalent to specification of the profile of one specie near the boundary. The fractional concentration change between the point HH and the hot boundary is usually, in Spalding's work, specified as 1%. With this specification of the specie profile, the fractional change is 1% when \( G_H = G_C \) and the procedure has converged. If, however, the fractional concentration change is greater than 1% then \( G_H < G_C \) and the grid spacing will contract. If the fractional change is less than 1% then the grid spacing will expand to conserve computer time. The value of \( \alpha \) is usually specified at 0.1 or 0.25, any larger value gave Spalding and Stephenson (1971) oscillating
flame speeds.

Two points should be noted about the above computational procedure. First the specification of the mass flux through the hot boundary is used as a parameter to aid efficient convergence. Second, one of the specie profiles has now been specified at the hot boundary at a finite but small value instead of zero. Stephenson and Taylor (1970) have claimed that inaccurate specification of the hot boundary condition does not greatly effect the flame solution. They have stated this as "... although the I[cf. H] boundary conditions are only approximate, it has been found...that the flame is insensitive to the downstream conditions...".

The advantage of using the Von Mises' transformation is that the coordinate system expands into the flame which is desirable when the maximum rate of change of the important independent parameters is at the burner surface. The advantage of using the dimensionless space variable is that the region of interest is now confined between values of w of 0 and 1. The disadvantage of the Von Mises' transformation is that the second derivative of the important independent variable must always be negative if the coordinate is to give economic grid distribution. Flames propagating in a free environment or flames that have little interaction with the flame holder have decided "s" shaped curves where the second derivative of the temperature and stable species problems have values of zero around the middle of the flame region and values of zero on either end of the flame region. The disadvantage of using the dimensionless space variable is that the hot boundary conditions for stabilized flames and, both boundary conditions for unstabilized flames are no longer specified precisely. One must introduce a new convergence parameter that is somewhat arbitrarily defined and one
specie profile must be specified at the boundary.

IV-2.5.3 Other Grid Distribution Methods

In flame situations three types of profiles are common. The reactants have decreasing "S" shaped profiles, the temperature and stable products have increasing "S" shaped profiles, and the intermediate species have profiles that exhibit maximums. The "S" shapes are quite strong in freely propagating flames or in flames stabilized in the manner of Dixon-Lewis, et al. (1970). The "S" shaped profiles are truncated at the burner surface when that surface strongly interacts with the flame. Profiles that exhibit the truncated behavior have been reported by Eberius, et al. (1971), Sarofim and Pohl (1973), and Peeters and Mahnen (1973). All three types of profiles in the unstabilized case can be best handled by a distribution of grid points that has a maximum in the central region of the flame. Truncated profiles can be adequately handled by the Von Mises' transformation.

For solution of flames that are not stabilized strongly it is advantageous to have a space coordinate that is stretched at small and large distances. This could be accomplished by introducing a functional coordinate transformation with the property that equal spacings in the new coordinate system correspond to the desired space stretching in the original coordinate system. The same effect can be obtained if the original coordinate system is retained and the stretching is introduced in the numerical solution by specifying a variable grid system that has the desired functionality. The most appropriate function for the grid spacing appears to be the temperature profile function using equal increments of ΔT which will produce the desired variation in the space coordinate. The temperature profile is chosen because all compositions
are a strong function of the temperature, the temperature profile can be initially specified with relative ease and accuracy, and, with some limiting assumptions, the differential energy equation can be replaced with an algebraic expression. This simplification of the energy equation will allow the solution for the temperature profile to approach the true temperature profile with relative ease in the early stages of computation.

The temperature profile calculated from a previous time can be used to specify the grid spacings. This method gives as good a grid distribution as can be obtained when different independent variables have different positions of maximum change. A starting value for the temperature profile must be specified after which time the solution will generate its own grid distribution.

The temperature profile for the unstabilized case should be specified as an "S" shaped curve. Two functions have been previously recommended to produce "S" shaped curves. Spalding, et al. (1971) recommended a fifth order polynomial as a starting profile for product concentrations and Wilde (1972) recommended the hyperbolic tangent function to generate a variable grid distribution for solution to the flame problem.

The polynomial function can be written as

\[ T = 10^{-3} - 15x^4 + 6x^5 \]  

(IV-71)

where \( T \) and \( x \) represent dimensionless quantities that have values between 0 and 1. The dependent variable could be either dimensionless temperature or dimensionless concentration. It is obvious that the nature of equation (IV-71) forces both the first and second derivatives to be zero at the origin. This is undesirable as it implies that an equal spacing of the dependent variable at the origin gives an infinite grid
spacing in terms of the independent variable. This problem can be avoided numerically by retaining a constant grid spacing when the independent variable approaches either zero or one. Equation (IV-71) has an inflection point at \( \bar{x} = 0.5 \) where the slope is equal to 7.5.

Wilde (1972) has used a hyperbolic tangent function to generate an "S" shaped curve. The hyperbolic tangent has values of -1 at \(-\infty\) and +1 at \(+\infty\) but it has a value of 0.964 when the argument is equal to 2. An "S" shaped curve can be generated by shifting the coordinate zero. The generating function then takes the form

\[
\bar{T} = 0.5 + 0.5187 \tanh (4\bar{x} - 2) \tag{IV-72}
\]

Equation (IV-72) generates an "S" shaped curve between \( \bar{x} \) equals 0 and 1 and has an inflection point at \( \bar{x} = 0.5 \) where the slope is equal to 2. The slope of the curve generated by equation (IV-72) has non-zero values at both \( \bar{x} = 0 \) and \( \bar{x} = 1 \). The hyperbolic tangent function can be used to generate a starting curve for the highly stabilized flame if only the positive portion of the curve is used. The generating function then takes the form

\[
\bar{T} = 1.0373 \tanh (2\bar{x}) \tag{IV-73}
\]

Equation (IV-73) has no inflection points and slopes of 2.07, 1.307, and 0.1465x at \( \bar{x} = 0, 0.5, \) and 1.0 respectively.

"S" shaped curves suitable as starting points for solution of the flame equations can be generated by either a polynomial function such as equation (IV-71) or a hyperbolic tangent function such as equation (IV-72). The polynomial function gives a greater concentration of grid points in the central region. A slope of 7.5 compared to 2, but must be handled specially at the end points. Since the generation curve will only be used to start the computational procedure the hyperbolic function appears to be easier to use for the unstabilized flame.
Equation (IV-73) could be used to generate starting values for strongly stabilized flames but the Von Mises' transformation has several advantages over the hyperbolic function. The Von Mises' transformation eliminates some terms from the conservation equations and exactly specifies a grid spacing that varies with the temperature profile without further interpretation. For unstabilized flames it is recommended that the grid spacing be in equal increments of the dependent variable $T$ with the initially temperature profile specified by the hyperbolic tangent function of equation (IV-73). For stabilized flames the Von Mises' transformation is recommended.

### IV-2.5.4 Introduction of Von Mises' Coordinates into the Conservation Equations

Von Mises' coordinate will now be introduced into the conservation equations because the transformation gives the proper grid distribution with minimum effort for the stabilized flame situation. Most laboratory flat flames are strongly stabilized so that the Von Mises' coordinate system is appropriate for solution of the flame equations of this study.

The Von Mises' transformation is defined in equations (IV-66) and (IV-67). It is easy to see that these definitions satisfy the continuity equation by introducing them in equation (IV-17) which gives

$$\frac{\partial \psi}{\partial x \partial t} - \frac{\partial \psi}{\partial \psi \partial x} = 0$$ (IV-76)

which according to the Maxwell relations is an identity. The transformation of the conservation equations takes the form of a transformation from $(x,t)$ coordinates to $(\psi,t)$ coordinates. The space transformation is just

$$\frac{\partial}{\partial x} |_{t} = \rho \frac{\partial}{\partial \psi} |_{t}$$ (IV-75)
because both the partial derivatives with respect to \( x \) and \( \psi \) are evaluated at constant time. The time derivative transformation is a little more complicated because the old coordinate time and derivative is evaluated at constant \( x \) while the new coordinate time derivative is evaluated at constant \( \psi \). The transformation then takes the form

\[
\frac{\partial}{\partial t} \bigg|_x = -\rho v \frac{\partial}{\partial \psi} \bigg|_t + \frac{\partial}{\partial t} \bigg|_\psi
\]  

(IV-76)

Introduction of equations (IV-75) and (IV-76) into the specie conservation equation, (IV-59) gives

\[
\frac{\partial Y_i}{\partial t} = \frac{w_i}{\rho} - \frac{\partial}{\partial \psi} \left( \rho Y_i \times \left( \frac{n_i^2}{n_i} \Sigma_{j} m_{ij} D_{ij} \frac{\partial (n_j/n)}{\partial \psi} \right) - \frac{D_{T_i}}{n_i m_i \rho} \frac{\partial \ln T}{\partial \psi} \right)
\]  

(IV-77)

and into the energy conservation equation, (IV-65) gives

\[
\Sigma_i \left( \rho Y_i \frac{\partial \bar{C}_{Pi}}{\partial t} \right) - \rho \frac{\partial}{\partial \psi} \lambda \rho \frac{\partial T}{\partial \psi} + \Sigma_i Y_i \rho \frac{\partial}{\partial \psi} \bar{C}_{Pi} \frac{T \left( \frac{n_i^2}{n_i} \Sigma_j m_{ij} \frac{\partial (n_j/n)}{\partial \psi} \right)}{n_i} - \frac{D_{T_i}}{n_i m_i \rho} \frac{\partial \ln T}{\partial \psi} = -\Delta h_f \frac{w_i}{298} + \Sigma_j \bar{C}_{Pi} (T-298) w_i
\]  

(IV-78)

**IV-2.5.5 Boundary Conditions**

Two boundary conditions are needed, for each variable appearing in the steady state flame equations, to properly specify the problem. Additionally, one initial condition is needed if the flame equations are written in the unsteady state form. The boundary conditions are customarily divided into the hot boundary conditions and the cold boundary conditions. The hot boundary conditions are at the end of the flame region of interest and the cold boundary conditions are at the surface of a stabilized flame and at some unstream position that
encompasses the region of interest in the unstabilized flame. The hot boundary conditions can be specified adequately in a number of ways but there is some question as to the proper method of specifying the cold boundary conditions for stabilized flames.

The hot boundary conditions are specified to be just outside the region of interest to minimize computation time. At this point the concentration and temperature gradients can be specified as zero as was done by Hirschfelder and Curtiss (1949), Campbell, et al. (1965), Bledjian(1971), and Spalding and Stephenson (1971). Other authors such as Dixon-Lewis (1967), (1970), Eberius, et al. (1971), and Wilde (1972) have chosen to specify the hot boundary conditions as an equilibrium mixture at the adiabatic flame temperature. Adams and Cook (1959) specified the concentration at the hot boundary condition in a hydrazine decomposition flame as a burnt stoichiometric mixture. Various combinations of boundary conditions can be used at the hot boundary. Stephenson and Taylor (1970) and Spalding, et al. (1971) have used zero concentrations for the reactants and zero gradients for temperature and the remaining compositions.

The cold boundary condition is easy to specify for the unstabilized flame. Hirschfelder and Curtiss (1949) have specified the unburnt gas composition as the cold boundary condition for unstabilized flames. Campbell, et al. (1965) has justified this specification for the idealized case. Others have also specified the unburnt gas composition including Adams and Cook (1959), Dixon-Lewis (1967), (1970), Stephenson and Taylor (1970), and Spalding, et al. (1971). Bledjian (1973) specified the gradients to be zero at the cold boundary.

The cold boundary conditions for the stabilized flame are more difficult to specify because the burner surface interacts with the flame.
The idealized stabilizing surface is impenetrable to back diffusion, allows unimpeded unburnt gas flow, and is maintained at a constant temperature. The cold boundary condition is usually specified as a constant temperature surface with zero specie fluxes. The concentration condition at the cold boundary could be stated as the rate of a material transported into the flame region is equal to the vector sum of the material transported to the burner surface by diffusion and by convection of the unburnt gas. This specification of the cold boundary conditions has been used by Spalding and Stephenson (1971) and Wilde (1972).

Eberius, et al. (1971) have suggested that radical recombination on the burner surface must be considered at the cold boundary. They specified no details of how radical destruction on the burner surface was to be included. The implication was that all radical that struck the surface were completely destroyed.

A more general approach to the cold boundary conditions can be obtained by writing a material balance around the surface of the burner. This balance yields

\[(\rho v_{1_u}) \cdot u - (V_{1_i} \rho) \cdot s - w_{is} = (\rho v_{1_i}) \cdot s\]  

(IV-79)

where \(u\) refers to the unburnt gas, \(s\) refers to the burner surface, \(w_{is}\) is the net rate of destruction of specie \(i\) on the burner surface per unit area. \((\rho v_{1_i})\) will be zero for components that are not reactants.

A great deal of work on surface reactions has shown that the rate of surface reactions depends strongly on the surface material, because the surface material forms an intermediate with the reacting material. Wise and Wood (1967) reviewed surface reaction data and reported recombination coefficients (the fraction of the material that strikes a saturated surface that recombines) ranging from \(10^{-4}\) for glass surfaces
up to about 0.5 for clean noble metal surfaces. The reaction mechanism can be either the Eley-Rideal mechanism, where a gas phase molecule reacts with a chemisorped molecule to form a gas phase product and one vacant surface site, or the Langmuir-Hinshelwood mechanism, where two chemisorbed molecules react on the surface to form a gas phase product and two vacant sites. Most surface atom recombinations appear to follow the Eley-Rideal mechanism.

The kinetic evidence for surface reactions is obtained for combinations of atoms that diffuse from a low gas phase concentration to a surface that has only been exposed to a low concentration of the active mixture. Active mixtures might typically contain atoms and molecules composed of the same elements. The data is reported as the fraction of atoms that diffuse to the surface that react. The surface is usually considered to be covered by chemisorbed active species.

In a flame situation a number of active specie are present simultaneously, such as H, O, OH, HO₂, H₂O₂, and more stable species. The burner surface is almost always made out of copper or one of the common copper alloys. Only reactions that involve highly mobile light species diffusing back to the burner will be important. The following reactions might be important on a burner surface.

\[
\begin{align*}
H + H + \text{wall} &= H₂ + \text{wall} \\
O + O + \text{wall} &= O₂ + \text{wall} \\
O + H + \text{wall} &= OH + \text{wall} \\
OH + OH + \text{wall} &= H₂O₂ + \text{wall} \\
H + OH + \text{wall} &= H₂O + \text{wall} \\
H + O₂ + \text{wall} &= HO₂ + \text{wall} \\
OH + OH + \text{wall} &= H₂O + O + \text{wall} \\
OH + H₂ + \text{wall} &= H₂O + H + \text{wall}
\end{align*}
\]
\[ \text{O} + \text{H}_2 + \text{wall} = \text{OH} + \text{H} + \text{wall} \]  

Smith (1943) has speculated that reactions (IV-83, 86, and 87) take place on surfaces. Wood (1971) claims that reaction (IV-82) occurs with unit efficient on gold surfaces and that reaction (IV-88) does not take place on gold surfaces at 300\(^\circ\)K and \(10^{-3}-10^{-5}\) torr. Ponec, et al. (1965) has shown that molecular hydrogen is not adsorbed on copper at 273\(^\circ\)K and \(10^{-3}\) torr. His finding supports Wood's finding that reaction (IV-88) does not proceed under these conditions. Pritchard and Tompkins (1960) had shown earlier that the failure of many surfaces to adsorbed molecular hydrogen under low temperature and pressure conditions was because of unfavorable thermodynamics. Since \(\Delta S\) is negative for adsorbtion processes is follows that adsorption of molecular hydrogen is more favorable at higher temperatures. Adsorption of molecular hydrogen can occur on copper surfaces at one atmosphere pressure and 400\(^\circ\)K, but the adsorption is probably dissociative and incomplete. Ponec, et al. (1965) also observed that \(\text{H}_2\) did not react with preadsorbed \(\text{O}_2\). The \(\text{O}_2\) is probably also dissociatively adsorbed so that reactions that involve molecular hydrogen such as (IV-87) and (IV-88) will not be important reactions at the burner surface.

Ponec, et al. (1965) observed that molecular oxygen does not react with previously adsorbed atomic hydrogen, nor will atomic hydrogen react with adsorbed hydroxyl radicals. These two observations allow reactions (IV-84) and (IV-85) to be ignored.

There is no data available for reactions of the hydroxyl radical reactions on other surfaces. Smith (1943) reported the efficiency of hydroxyl radical and atomic hydrogen recombination on pyrex. The efficiency of hydroxyl recombination was \(8 \times 10^{-5}\) and the hydrogen efficiency was \(1.9 \times 10^{-5}\) at room temperature. Panfilov (1962) reported
the efficiencies of radical recombination on K$_2$Br$_4$O$_7$ coated walls surrounding a very low pressure hydrogen flame. The efficiency of hydroxyl radical recombination was 4x10$^{-2}$ and the efficiency of hydrogen recombination was 10$^{-4}$ at 600°C. Wise, et al. (1964) measured the efficiency of hydroxyl radical recombination as 5x10$^{-6}$ compared to 2.8x10$^{-3}$ for atomic hydrogen on quartz walls at room temperature.

Although the measured recombination coefficients appear to be quite different for hydroxyl and hydrogen radicals there is reason to assume that hydroxyl radical recombination efficiency will be much closer to the efficiencies of oxygen atom recombination. Avramenko and Kolesnikova (1964) assumed that the surface rates of hydroxyl radical destruction and oxygen atom destruction were the same. Warren (1953) has concluded from explosion data that "Surfaces show themselves to be for the most part unselective in their activity towards the three chain carriers." (c.f. H, OH, O). Greaves and Linnett (1959) have reached similar conclusions for oxide surfaces.

Warren (1953) has claimed that hydrogen peroxide is made on the walls in explosions. Hydrogen peroxide is not an important species in flames. Peeters and Mahnen (1973) found no hydrogen peroxide in lean methane flames with a lower detection limit of 10$^{-5}$ mole fraction. Reaction (IV-83) can be eliminated because H$_2$O$_2$ is not an important flame specie and the attack of one hydroxyl radical on another surface bound hydroxyl radical radical is geometrically unfavorable. Additionally, if H$_2$O$_2$ was formed in small quantities at the surface it will rapidly decompose to form active centers probably initially in the form of hydroxyl radicals. The surface reaction in this case would form a closed loop neither creating nor destroying hydroxyl radicals.

Surface reactions to be considered are then reactions (IV-80),
(IV-81), (IV-82), and (IV-86). There is considerable rate data for recombination of atomic hydrogen and oxygen on copper and copper oxide surfaces. Sato (1959) reported a 0.2 efficiency for hydrogen atom recombination between room temperature and 200°K on clean copper surfaces. Sato claimed the activation energy was small, between 0 and 3 kcal/g mole. Wise and Wood (1961) reported a similar efficiency of hydrogen atom recombination. Their value for the efficiency of recombination of hydrogen atoms was 0.12 independent of temperature for the temperature range 333-693°K. There appears to have been no measurements of hydrogen atom recombination rates on oxidized copper surfaces.

There is more data available for surface recombination of oxygen atoms than for hydrogen atoms. There are several independent measured recombination efficiencies for oxygen atoms on copper surfaces. The data has been reviewed by Wise and Wood (1967). Greaves and Linnett (1958) measured a room temperature efficiency of 0.17 and Hartunian et al.'s value is reported as the recombination efficiency of oxygen atoms on oxidized copper surfaces. His experimental procedure, however, corresponds to what other authors have called recombination on clean surfaces. His measurement will be considered as the efficiency of recombination on clean surfaces.

The efficiencies of oxygen atom recombination on oxidized surfaces are slightly smaller than the corresponding value for clean surfaces. Greaves and Linnett (1958) reported, at room temperature, a 0.02 efficiency of oxygen atom recombination on oxidized copper. A later measurement, Greaves and Linnett (1959), gave a slightly higher value of 0.043. Dickens and Sutcliffe (1964) reported recombination efficiency of oxygen atoms on Cu₂O between 294 and 540°K could be expressed as

$$\gamma = e^{1,300/RT}$$

(IV-88)
and for CuO between 330 and 540°K as
\[ \gamma = 9.1e^{-3.206/RT} \] (IV-90)

Expression (IV-89) gives efficiencies on Cu₂O of 0.11 at 300°K and 0.19 at 400°K and (IV-90) gives efficiencies of 0.042 at 300°K and 0.16 at 400°K on CuO. The efficiencies expressed by equation (IV-90) agree well with the room temperature value of Greaves and Linnett (1959).

While the measurements of surface reactions are not complete nor accurate, they are as accurate as most of the gas phase rates that will be used for the bulk of the input data. There is no direct measurement of the rate of reaction (IV-80) on oxidized copper alloys. An efficiency of 0.15 at 400°K will be chosen based on the similarity between O and H recombination efficiencies on clean copper surfaces and the data on oxygen atom recombination on oxidized copper surfaces.

There is data available on the efficiency of reaction (IV-81) on oxidized copper surfaces. The efficiency of reaction (IV-81) will be taken as 0.15 at 400°K based on the data of Dickens and Sutcliffe (1964) for oxidized surfaces.

Reaction (IV-82) will be taken as 100 percent efficient for either adsorbed H or O atoms based on Wood (1971) evaluation of this reaction of gold surfaces.

There is no data for reaction (IV-86), but Smith (1943) indicated that the reaction might take place on a variety of surfaces. Reaction (IV-86) will be assumed to be of very low efficiency based on Ponce, et al. (1965) observation that H does not react with adsorbed OH and the similarity of the intermediates in reactions (IV-86) and (IV-84).

The approximate mechanism of burner surface recombination is
\[ H + H + \text{wall} = H_2 + \text{wall} \] (IV-80)
\[ O + O + \text{wall} = O_2 + \text{wall} \] (IV-81)
\[ O + H + \text{wall} = OH + \text{wall} \]  \hspace{1cm} (IV-82)

The first two reactions are taken to have 0.15 efficiencies at 400\(^\circ\)K and the last reaction is assumed to occur at every collision. The efficiencies reported are for surfaces saturated with one of the reactants. If the reactants compete for the same surface site then the efficiencies would be proportionally reduced when sites are occupied by species that will not participate in one of the reactions.

The cold surface boundary conditions will be altered for species that appear in reactions (IV-80) through (IV-82). The boundary condition for H atom will be

\[
(Y_{Hs} Y_{80} + Y_{O_s} Y_{82} - 1) (\rho \frac{m H}{m} \frac{\partial Y_{H}}{\partial \psi} - \rho \frac{D_{T}}{H} \frac{\partial T}{\partial \psi}) + Y_{Hs} Y_{O_s} Y_{82} \rho \gamma_{82} - \rho v_{Y_{Hs}} = 0
\]  \hspace{1cm} (IV-91)

where \( s \) refers to evaluation of the subscripted terms at the surface.

The boundary conditions for \( H_2, O, O_2, \) and \( OH \) are similarly expressed as

\[
\rho \frac{m H_2}{m} \frac{\partial Y_{H_2}}{\partial \psi} + \rho \frac{D_{T}}{T} \frac{\partial Y_{H_2}}{\partial \psi} - Y_{80} Y_{Hs} \rho \gamma_{82} Y_{Hs} = \rho v_{Y_{H_2s}}
\]  \hspace{1cm} (IV-92)

\[
(Y_{O_s} Y_{81} + Y_{Hs} Y_{82} - 1) (\rho \frac{m O}{m} \frac{\partial Y_{O}}{\partial \psi} - \rho \frac{D_{T}}{O} \frac{\partial T}{\partial \psi}) + Y_{82} Y_{O_s} Y_{Hs} Y_{P_{Hs}} = (\rho v_{Y_{O_s}})
\]  \hspace{1cm} (IV-93)

\[
(\rho v_{Y_{O_2s}}) = u (V_{O_2} Y_{O_s} + Y_{81} Y_{O_s} Y_{0^2}) = \rho v_{Y_{O_2s}}
\]  \hspace{1cm} (IV-94)

and

\[
-(V_{OH} Y_{OH} - \gamma_{82} Y_{Hs} Y_{O_s} (V_{O_s} + V_{Hs})) = (\rho v_{Y_{OH}})
\]  \hspace{1cm} (IV-95)

The remaining boundary conditions are easily written with \( w_{is} = 0 \) and \( \rho v_{Y_i} = 0 \) if the specie is not a reactant and equal to its value in the unburnt gas if it is a reactant.
The reaction mechanism for surface reactions will lower the O and H radical concentration at the surface and raise the \( \text{H}_2^* \) and \( \text{O}_2^* \) and OH concentration at the surface. The hydroxyl radical concentration will be increased the most because of the high efficiency chosen for reaction (IV-82). The generation of hydroxyl radicals at the surface is in apparent agreement with the OH profiles measured by Eberius, et al. (1971). These OH profiles were measured by absorption on rather large burners so that probe disturbance was not a problem. Absorption measurements, however, do require that the flame be essentially one dimensional - this condition is expected to be met for the large burners used, 7.5-19. cm diameter, close to the surface. The OH profiles from this study show distinct minimums in the prereaction zone. This strongly implies that OH is produced at the burner surface and is then partially consumed in fuel oxidation and then exhibits a strong maximum as it becomes equilibrated with other O-H species in the flame region prior to radical recombination.

IV-2.5.6 Initial Conditions

Use of the time dependent partial differential flame equations requires initial conditions in addition to the boundary conditions outlined in section IV-2.5.5. The initial conditions are specified as the value of all dependent variables everywhere in the flame region at time zero.

The dependent variable specification at time zero can be arbitrary but computer time is saved if care is used in selecting the initial conditions. Dixon-Lewis (1967), Spalding, et al. (1971), Wilde (1972), and Bledjian (1973) have all claimed that the initial dependent variable profiles can be specified arbitrarily. Dixon-Lewis (1967) and Bledjian (1973) claim that radical concentration must be specified at
a sufficient level to cause ignition. However, Spalding, et al. (1971) has apparently successfully solved the flame equations starting with a zero initial radical concentration. If this was a proper specification of the initial conditions the convergence must have been very slow because the rate of all chemical reactions involving radicals (the vast majority of the important reactions) must have initial rates of zero. The only mechanism for production of the radicals is by dissociative reactions which are not physically important in flame situations.

Computer time can be saved by more accurately specifying the initial profiles. Dixon-Lewis (1967) has recommended that rather steep initial radical profiles be specified to save computation time. Bledjian (1973) specified smooth "S" shaped profiles asymptotic to the boundary conditions and assumed intermediate species concentrations as his initial conditions. Spalding, et al. (1971) specified "S" shaped profiles for the stable species by an equation of the form (IV-71) and initial radical concentration as zero.

Initial dependent variable profiles will be specified in this study with analytical functions that give the approximate profile shape and maximum value of the variable. Product concentrations including radicals and temperature will be specified by the truncated "S" shaped profile given in equation (IV-73). Reactant profiles will be specified by the complement of equation (IV-73).

\[ \bar{C} = 1.0 - 1.0373 \tanh (2\bar{X}) \]  

(IV-96)

Intermediate species profiles will be specified as a gamma function distribution. The reciprocal gamma function produces a curve with a broad maximum skewed towards the origin and a long tail. This function has the approximate shape of an intermediate specie profile. The maximum can be shifted more towards the origin and the tail shortened.
by increasing the multiple in the gamma function argument. The tail can be further truncated while only slightly shifting the maximum by introducing the decreasing exponential. A function of this type is

$$C = 3.700 \frac{e^{-6x}}{\Gamma(4x)}$$  \hspace{1cm} (IV-97)

This function gives a maximum at $x \approx 0.15$ and has a normalized value at $x = 1.0$ of 0.0015. This function is of the approximate but not necessarily the optimum shape for specification of intermediate profiles.

**IV-3.0 Differencing the Flame Equations**

It was chosen to write the flame equations as time dependent partial differential equations in the previous section. The flame equations to be numerically solved are a species equation for each species, present in the flame, except one, of the form

$$\frac{\partial Y_i}{\partial t} = \frac{w_i}{\rho} - \frac{\partial}{\partial \psi} \left( \rho Y_i \frac{2}{n_i} \sum_j D_{ij} m_j \frac{\partial (n_j/n)}{\partial \psi} - \frac{D_{ii}}{n_i m_i} \rho \frac{\partial \ln T}{\partial \psi} \right)$$  \hspace{1cm} (IV-77)

and one energy equation of the form

$$\frac{\partial C_p}{\partial t} \frac{T}{v_i} = \sum_i \left( \frac{\partial}{\partial \psi} \left( \rho Y_i \frac{2}{n_i} \sum_j D_{ij} m_j \frac{\partial (n_j/n)}{\partial \psi} - \frac{D_{ii}}{n_i m_i} \rho \frac{\partial \ln T}{\partial \psi} \right) - \frac{D_{ii}}{n_i m_i} \rho \frac{\partial \ln T}{\partial \psi} \right) = -E_i h_i \frac{C_p}{298} w_i$$  \hspace{1cm} (IV-78)

with initial conditions specified by

$$T = 1.037 \tanh (2x)$$  \hspace{1cm} (IV-73)

for temperature, product species, and radical concentration. Initial reactant concentrations will be specified by the complement of equation (IV-73)

$$\bar{x} = 1 - 1.037 \tanh (2 \bar{x})$$  \hspace{1cm} (IV-98)
and initial intermediate concentrations will be specified by a gamma function distribution of the form

\[
\bar{X} = \frac{e^{-6\bar{X}}}{\Gamma(4\bar{X})}
\]  

(IV-97)

At the hot boundary the gradients of all the dependent variables will be specified as zero. The cold boundary conditions will be specified as temperature and a material balance for each specie of the form

\[
(pvY_i)u - (V_i Y_i \rho)_s - w_{is} = (pvY_i)_s
\]  

(IV-79)

IV-3.1 Previous Numerical Solutions to the Partial Differential Flame Equations

The first attempt to solve the partial differential flame equations was Spalding's (1956) graphical integration technique. The graphical integration was followed quickly by explicit numerical approximations by Zeldovich and Barenblatt (1959) and Adams and Cook (1959). Dixon-Lewis (1967) and Bledjian (1973) then used modifications of the original explicit technique. Following Douglas's (1958) work on the stability of numerical methods for solution of quasi-linear parabolic partial differential equations, von Rosenberg, et al. (1962) used an implicit numerical technique to solve a simplified reacting system. Lovachev and Kaganova (1969) and Lovachev, et al. (1970) used an implicit numerical technique to solve the flame equations for the Br₂-H₂ and H₂-O₂ flames. Spalding and co-workers have solved the flame equations by using a numerical technique developed by Patankar and Spalding (1967) for solution to boundary layer problems. This technique was successfully modified for solution to the flame equations by Stephenson and Taylor (1970).

IV-3.1.1 Explicit Solutions to the Flame Equations
Zeldovich and Barenblatt (1959) reported the first computer solution to the partial differential flame equations but the numerical details were not reported. Adams and Cook (1959) solved the partial differential equations for a hydrazine decomposition flame using an explicit differencing technique to extrapolate from the old time to the new time. The space derivative was approximated by a central difference formula and the source term was evaluated entirely at the old time. Adams and Cook found a satisfactory ratio, $\Delta t/\Delta \psi^2$, of $1/6$ which gives the minimum truncation error for the heat conduction equation without source terms.

Dixon-Lewis (1967) used the same differencing technique as Adams and Cook (1959) for the solution of the flame equations for the hydrogen-oxygen system. They found that the step size ratio, $D_{H_2}/D_{O_2} \Delta t/\Delta \psi^2$, less than $1/2$ was not controlling for the parabolic equations with a source term. Dixon-Lewis found that, $D_{H_2}/D_{O_2} \Delta t/\Delta \psi^2 = 1/6$ which corresponds to $\Delta t/\Delta \psi^2 \sim 1/30$ gave stable solutions.

Bledjian (1973) has solved the partial differential flame equations for both the hydrazine and ozone flame by writing the spatial derivatives as their central difference analog and solving the resulting ordinary differential equation by a standard fourth order Runge-Kutta extrapolation in time using step size control. He claims that his method of solution is faster per iteration but is less sure of convergence than the implicit method. There was no direct comparison of the explicit and implicit solutions in this paper.

Explicit techniques are usually "...least efficient of all the possible equations which can be used." according to von Rosenberg (1969) p. 18. Bledjian (1973), however, points out that the comparisons
have only been made between the crudest explicit techniques and im-
licit techniques. Additionally generalizations are based on compari-
son of the two techniques on relative simple equations which may yield
results different from those of real problems. The explicit techniques
usually give a second order correct difference equation for the space
coordinate and a first order correct difference for the time derivative.
The correctness of the time derivative can be improved as Bledjian
(1973) has done by using a high order Runge-Kutta method for the time
derivative. Additionally the explicit methods have a rather restric-
tive stability criteria in terms of time step size. The stability
criteria of the ratio $\frac{\Delta t}{\Delta \psi} < 1/2$ has been found too lax for stable
solutions to the flame equations. In general the implicit techniques
appear to hold more promise for solution to the general flame equations
for unknown systems.

IV-3.1.2 Implicit Solutions to the Flame Equations

The foundation for implicit solution of the partial differential
flame equations was established by Douglas (1958). Douglas investigated
stability and convergence criteria for various numerical methods applied
(1962) applied implicit numerical techniques to a simple reacting
system. The system was a two dimensional fixed bed reactor with a
single first order irreversible reaction changing composition and
releasing heat. This system resulted in two coupled quasi-linear
parabolic differential equations. The equations were solved by a
Douglas linearization of the source term and calculation of the composi-
tion in terms of a previously determined temperature and then using the
newly found compositions to calculate new temperatures. Von Rosenberg,
et al. found that iteration to find new values of composition in terms of the new temperature was not necessary for their system.

Lovachev and Kaganova (1969) have solved the partial differential equations for the hydrogen bromine flame. From later work by Lovachev, et al. (1970), they appear to have used an implicit numerical technique. Lovachev, et al. (1970) solved the partial differential flame equations for the hydrogen-oxygen system by an implicit method similar to the one to be used in this study. Lovachev, et al. wrote a second order correct difference formula for the time coordinate about \( t + 1/2 \) and a second order correct spatial difference about \( i \) evaluated at time \( t + 1 \). The heat capacity was assumed constant, the thermal conductivity was evaluated at the old time level, but the diffusivity was evaluated at the future time level by corrective iteration. The source term was linearized by extrapolation of the derivative of the function from the old time level instead of extrapolating the dependent variables to the new time level and evaluating the source term in terms of the extrapolated dependent variables. The boundary conditions were also similar to those proposed for this study. The hot boundary conditions were specified as zero gradients of all the dependent variables. The cold boundary conditions were specified as the entering temperature plus the temperature rise due to conduction and a similar balance was used for the concentrations. Surface reactions were not included in the species balance at the cold boundary.

Wilde (1972) has used a modified implicit numerical technique to solve the flame equations. He implicitly represented the second spatial derivatives by a central difference formula at the new time and linearized the source term by a Douglas extrapolation of the function to the future.
time and averaged it with the value at the old time. Wilde evaluated the spatial derivative entirely at the future time because results showed that to be slightly superior to averaging the derivatives at the old and new times.

IV-3.1.3 Spalding Numerical Approach (Integration Over Finite Volumes)

Spalding and co-workers (Stephenson and Taylor (1970), Spalding and Stephenson (1971), Spalding, et al. (1971), and Stephenson and Taylor (1973)) have used an approach that is slightly different from previous approaches but gives similar difference formulas. The approach is outlined in Patankar and Spalding (1967) p. 34 for solution to boundary layer flow and modified by Stephenson and Taylor (1970) for solution to the flame equations.

Spalding writes his differences for a control volume in two dimensional space. The control volume is one time step by one space step with the node centered in the space direction. The two dimensional control volume extends from time = n to n + 1 and from \( \psi = i - 1/2 \) to \( i + 1/2 \). The difference equations are written in terms of integrated averages of the differential terms over the control volume. The dependent variable is assumed to be linear with spatial distance; this corresponds to a Crank-Nicholson difference formulation about the half node. The dependent variable is assumed to be constant through the control volume at its future time value. The Spalding procedure amounts to the spatial derivative being evaluated at the half node and the time derivative being evaluated at the future time. This is similar to the procedure used by Wilde (1972) to evaluate the partial differential flame equations. The Spalding approach has the additional advantage of assuring that invariants are conserved in each control volume instead of only over the entire system. The source term is evaluated at the
future time by a linear extrapolation from the old time.

**IV-3.2 Crank-Nicholson Differencing of the Flame Equations**

The partial differential flame equations ((IV-77) and (IV-78)) are quasi-linear parabolic partial differential equations. Numerical techniques for solving this type of equations have been reviewed by Douglas (1958). The method chosen for solution of the flame equations is the Crank-Nicholson procedure with Douglas linearization of the source terms and coefficients. This method was chosen because it is second order correct in both space and time and when linearized results in easy to solve linear algebraic difference equations. Without linearization of the source term the difference equations would be non-linear. Linearization of the source term however introduces a restriction on the step size not present in the non-linear difference formulation.

**IV-3.2.1 Step Size Restriction on Linearized Crank-Nicholson Difference Equations**

The flame equation in the generalized form used by Douglas (1958) is

\[
\frac{\partial}{\partial x} \left( P(x,t) \frac{\partial u}{\partial x} \right) - q(x,t,u) = r(x,t,u) \frac{\partial u}{\partial t}
\]  

(IV-99)

Reference to equation (IV-77) shows the following correspondence between the nomenclature of equation (IV-77) and equation (IV-99)

\[
P = \rho \sum_{i}^{2} \frac{n_i \Sigma_j D_{ij} m_j}{m_i}
\]  

(IV-100)

\[
r = 1.0
\]  

(IV-101)

\[
q = - \frac{w_i}{\rho}
\]  

(IV-102)
where \( p \) has been taken to be the most important coefficient term since the most restrictive condition is for large \( p \). Douglas defines a term \( a_i \) as

\[
a_i = -\frac{1}{r} \left[ \frac{\partial q}{\partial u} - \frac{\partial r}{\partial u} \frac{\partial u}{\partial t} \right] \quad (IV-103)
\]

where the maximum value of \( a_i \) appears in the step size restriction and there are different step size restrictions depending on the sign of \( a_i \). The source term in the flame equations can be approximated as a sum of kinetic rates of disappearance of specie \( i \) that are dependent on \( Y_i \) to the first power. This approximation is valid because any kinetic terms that do not involve \( Y_i \) will have zero derivatives with respect to \( Y_i \) and kinetic terms involving higher order \( Y_i \) terms are not as important as those involving a first order dependence. The maximum value of \( a_i \) can then be approximated as

\[
a_{i\text{ max}} = -\frac{1}{\rho} \left( \frac{P}{RT} \right)^2 \Sigma_j k_j Y_j \quad (IV-104)
\]

where all terms are positive, therefore \( a_i \) will always be negative in the species balance equations.

Douglas (1958) has reported the step size restriction as

\[
\frac{\Delta t}{\Delta \psi} < \left( \frac{P}{-a_{\text{max}} r} \right)^{1/2} \quad (IV-105)
\]

when \( a_i \) is less than zero. Equation (IV-105) is dimensionally inconsistent because \( p \) has the units of \( g^2/cm^4 \text{-sec} \), \( r \) has no units, \( a_i \) has units of \( 1/\text{sec} \), and \( \Delta t/\Delta \psi \) has units of \( cm^2/\text{sec}/g \). Brian (1968) agrees with Douglas assessment of the step size limitation for positive \( a_i \) but claims that the difference formula has no restriction for negative \( a_i \). Therefore there is no step size restriction of the species balance difference equations.

Terms in the energy equation can be designated in a manner similar
to the specie balance equations. The important parameters in Douglas's (1958) nomenclature are

\[ r = \frac{C_p}{\rho} \]  
\[ P = \lambda \rho \]  
\[ q = \frac{1}{\rho} \sum_i h_i^f 298 w_i \]

(IV-106)  
(IV-107)  
(IV-108)

where the energy equation (IV-78) has been divided by \( \rho \). The mean heat capacity will be assumed independent of temperature to simplify the analysis. The approximate \( a_i \) is then

\[ a_i \sim -\frac{1}{C_p} \frac{\partial q}{\partial u} \]

(IV-109)

and the \( q \) term is

\[ q = \frac{1}{\rho} \sum_i m_i h_i^f 298 A_i e^{-E_i/RT} Y_i Y_j \left( \frac{P}{RT} \right)^2 \]

(IV-110)

where all terms except the heat of formation are positive. The \( a_i \) term can then be expressed as

\[ a_i \sim \frac{P}{C_p \rho m_i} \sum_i m_i \left( h_i^f 298 \right) A_i e^{-E_i/RT} Y_i Y_j \left( \frac{E_i}{RT} - 1 \right) \]

(IV-111)

Since the maximum value of \( RT \) is about 4 kcal the activation energies will be larger than this hence the bracketed term is always positive. The \( a_i \) term is therefore always positive and subject to the original Douglas restriction,

\[ \frac{\Delta t}{\Delta \psi} < \left( \frac{r}{aP} \right)^{1/2} \]

(IV-112)

Substituting the approximate flame values into (IV-112) considering the average rate of reaction is about \( 1.0^{11} \) g-mole/cc-sec with a heat release of about 150 kcal/g-mole. These figures are expected to give a more restrictive step size limitation than will be encountered in actual practice but it provides a safe starting point for parametric investi-
gation of step size limitations for the linearized energy equation. The analysis shows the step size limitation should be

$$\frac{\Delta t}{\Delta \psi} < 2.5 \times 10^{-2}$$  \hspace{1cm} (IV-113)

This severe restriction on the time step size is caused by linearization of the source term in the energy equation. Since only the steady state solution is of interest it might be better to evaluate the energy equation source term at the old time level which would not introduce any step size limitations.

Lovachev and Kaganova (1969) found that, in units of $t \sim$ sec and $\psi \sim g/cm^2$, the time step must be less than $10^{-7}$ sec for accurate solutions of the Br$_2$-H$_2$ flame. They used a space coordinate of about $5 \times 10^{-5} g/cm^2$. The ratios for several cases studied were $\frac{\Delta t}{\Delta \psi} = 1.6 \times 10^{-2}$ and $1.3 \times 10^{-2}$ in reasonable agreement with the criteria of equation (IV-113).

Spalding and Stephenson (1971) have been able to significantly increase the time step size for the flames solved by Lovachev and Kaganova by not linearizing the source term in the energy equation. For one case where Lovachev and Kaganova used a step size of $8 \times 10^{-8}$ sec Spalding and Stephenson were able to start with a step size of $2 \times 10^{-6}$ sec and increased the step size through the calculation to $3 \times 10^{-4}$ sec.

Evaluating the source term in the energy equation at the old time level instead of extrapolating it to the half time level appears to allow much larger time step sizes. Evaluating the energy source term in terms of the old time values has been adopted as the initial procedure in this study.
IV-3.2.1 The Specie Difference Equations

The Crank–Nicholson differencing procedure involves differences written about the half node. These differences can be expressed in terms of the values at the half node if they are known or as the average of values at the full nodes.

The Crank–Nicholson difference for the flux of material $i$ by thermal diffusion is

$$\frac{\partial}{\partial \psi} \left( \frac{\rho D_T}{T} \frac{\partial T}{\partial \psi} \right) \approx \frac{1}{2 \Delta \psi} \left[ \left( \frac{\rho D_T}{T} \right)_{x=i+1/2} \frac{T_{x=i+1} - T_{x=i}}{t=n+1/2, t=n+1} \right]$$

$$- \left( \frac{\rho D_T}{T} \right)_{x=i-1/2} \frac{T_{x=i} - T_{x=i-1}}{t=n+1/2, t=n+1} + \left( \frac{\rho D_n}{T} \right)_{x=i+1/2} \frac{T_{x=i+1} - T_{x=i}}{t=n+1/2, t=n+1}$$

$$(T_{x=i+1} - T_{x=i}) - \left( \frac{\rho D_T}{T} \right)_{x=i-1/2} \frac{T_{x=i} - T_{x=i-1}}{t=n, t=n, t=n+1/2, t=n}$$

(IV-114)

The second spatial derivative evaluated at $\psi = i$ and $t = n + 1/2$ is the average of the second derivatives evaluated at $t = n + 1/2$ and $\psi = i - 1/2$ and $i + 1/2$. The coefficients are evaluated at $t = n + 1/2$ and $\psi = i + 1/2$ and $i - 1/2$. This requires values of the dependent variables at these points either by extrapolation or use of previously determined values.

The extrapolation of the dependent variables from known conditions to the half node conditions can be accomplished by expansion in a Taylor series about the known conditions. The dependent variables at the half nodes can be represented by equations of the following form

$$T_{i+1/2}^{n+1/2} = T_{i,n}^{n+1/2} + \frac{\partial T}{\partial t} \bigg|_{i} \frac{\Delta t}{2} + \frac{\partial T}{\partial x} \bigg|_{i} \frac{\Delta x}{2} + \frac{\partial T}{\partial x} \bigg|_{i} \frac{\Delta x}{n}$$

(IV-115)

In the original Douglas procedure $\frac{\partial T}{\partial t} \bigg|_{i} \frac{\Delta t}{n}$ is substituted for in terms of the original difference equations and the terms are collected in the
tridiagonal matrix form. It is not possible to follow a similar procedure with the space derivative because it does not appear directly in the differential equation. The spatial derivative can be evaluated as

$$ \frac{\partial Y_i}{\partial \psi} \bigg|_n \frac{Y_{i+1,n} - Y_{i-1,n}}{\Delta \psi} $$

(IV-116)

Then both the time and spatial extrapolations to the half nodes are second order correct and involve only known values of the dependent variables. A corresponding Taylor expansion can be performed in the backwards direction so that the dependent variables can be evaluated at the \(-1/2\) nodes.

The multicomponent diffusion coefficients have been retained until now. They will be replaced by the trace diffusion coefficient of specie \(i\) in a diluent. This approximation is justified for most flame conditions and follows from Curtiss and Hirschfelder (1949). The introduction of the trace diffusion coefficients changes the sign and allows the diffusion velocity of specie \(i\) to be written in terms of the mass fraction of \(i\). The difference equation for the flux of specie \(i\) due to molecular diffusion is written as

$$ \frac{\partial}{\partial \psi} \left( \rho \frac{m_i}{m} \sum_j D_{ij} \frac{\partial Y_j}{\partial \psi} \right) \bigg|_n - \frac{1}{2\Delta \psi^2} \left( \rho \frac{m_i}{m} \sum_j D_{ij} \right)_{n+1/2} \left( Y_{i+1} - Y_i \right) n+1/2 \quad n+1 \quad n+1 \\
- \left( \rho \frac{m_i}{m} \sum_j D_{ij} \right)_{n-1/2} \left( Y_i - Y_{i-1} \right) n+1/2 \quad n+1 \quad n+1 \\
- \left( \rho \frac{m_i}{m} \sum_j D_{ij} \right)_{n-1/2} \left( Y_i - Y_{i-1} \right) n+1/2 \quad n \quad n $$

(IV-117)

where the average molecular weight has been removed from the differencing process and is evaluated at the same conditions as the coefficients.

This is justified on two grounds. First, the transient solution is not
of interest and all parameters will change slowly as the steady state solution is approached. Second, the average molecular weight is a slowly changing function in almost all flame systems. Most flame systems have one component about 10 times the concentration of the fuel so even for large molecular weight changes on fuel combustion the average molecular weight of the system changes little. In fuel systems without one component in excess, such as $\text{H}_2-\text{O}_2$, the molecular weight change can be appreciable but the average molecular weight still changes slowly because only slow molecule changing reactions can change the average molecular weight of the system.

The transient term is simply evaluated as

$$\left. \frac{\partial Y}{\partial t} \right|_i = \frac{Y_i - Y_i}{n+1/2} = \frac{n+1}{\Delta t} \frac{n}{n+1}$$

(IV-116a)

which is second order correct about the half time node.

If the source term is to be evaluated at the half time node and the difference equations are to remain linear then the source term must be linearized. Douglas (1958) introduced an explicit extrapolation of the dependent variables to the half time node as an appropriate method of linearizing the source term for the implicit Crank-Nicholson procedure. It was shown in section IV-3.2 that linearization of the source term in the species balance equations does not introduce any step size restriction.

Instead of substituting the original difference equation into the equation for the extrapolated dependent variable it is easier in this study to evaluate all the dependent variables at the extrapolated positions and then to evaluate the source terms and the coefficients from them. The extrapolation formula for the half time position is
\[ Y_{i}^{n+1} = Y_{i}^{n} + \frac{\Delta t}{2} \frac{3Y_{i}^{n} - Y_{i}^{n-1}}{\Delta t} \]  

The difference equations for each species along with the differenced boundary conditions can now be written in tridiagonal matrix form.

This formulation results in

\[
\begin{bmatrix}
  a(1,1) & a(1,2) & 0 & \ldots & 0 \\
  a(2,1) & a(2,2) & a(2,3) & \ldots & 0 \\
  \vdots & \vdots & \ddots & \ddots & \vdots \\
  0 & \vdots & \ddots & \ddots & \ddots \\
  0 & \ldots & 0 & a(n,n+1) & a(n,n) \\
\end{bmatrix}
\begin{bmatrix}
  Y_{s}^{n+1} \\
  Y_{1}^{n+1} \\
  \vdots \\
  \vdots \\
  Y_{n}^{n+1} \\
\end{bmatrix}
= \begin{bmatrix}
  b_{1} \\
  0 \\
  \vdots \\
  \vdots \\
  b_{n} \\
\end{bmatrix}
\]

where the coefficients of the first two rows and the last two are different from the rest of the coefficients and the coefficient of the first row can be different for different species. The difference equations have been written for a grid spacing with the first point one half unit off the boundary to avoid oscillation, see Von Rosenberg (1969) p. 25 and Douglas (1961).

The coefficients for the second row have the same form as the rest of the coefficients except when \( Y_{0} \) is replaced by \( Y_{n} \) which cancels the two in the denominator for the difference terms of the form \( \frac{1}{2\Delta \psi^{2}} \left[ Y_{i} - Y_{i-1} \right] \).

The general form of the \( a(i,j) \) coefficients is

\[
a(i,i-1) = + \left( \rho^{2} \frac{m_{i}}{2\Delta \psi^{2}} \right) \frac{i-1/2}{n+1/2} \\
a(i,i) = - \frac{1}{\Delta t} - \left( \rho^{2} \frac{m_{i}}{2\Delta \psi^{2}} \right) \frac{i+1/2}{n+1/2} - \left( \rho^{2} \frac{m_{i}}{2\Delta \psi^{2}} \right) \frac{i-1/2}{n+1/2}
\]

(iv-119)  

(iv-120)
\[ a(i,i+1) = (\rho \frac{m}{2m_{i}^{i}} i \frac{\Delta x}{m_{i}^{i}} i+1/2 \times n+1/2 \] (IV-121)

\[ a_{i} = \frac{w_{i}}{\rho} i + \frac{Y_{i}^{i}}{\Delta t} + \frac{1}{2\Delta x} [ (\rho \frac{m}{2} \frac{\Delta x}{m_{i}^{i}} i \frac{\Delta x}{m_{i}^{i}} i+1/2 \times n+1/2 \frac{Y_{i+1}^{i} - Y_{i}^{i}}{n+1/2 n n} \]

\[ - (\rho \frac{m}{2} \frac{\Delta x}{m_{i}^{i}} i \frac{\Delta x}{m_{i}^{i}} i-1/2 \times (Y_{i}^{i} - Y_{i-1}^{i}) + (\rho \frac{m}{2} \frac{\Delta x}{m_{i}^{i}} i+1/2 \times n+1/2 \frac{Y_{i+1}^{i} - Y_{i}^{i}}{n+1/2 n n} \]

\[ - (\rho \frac{m}{2} \frac{\Delta x}{m_{i}^{i}} i-1/2 \times (T_{i}^{i} - T_{i-1}^{i}) + (\rho \frac{m}{2} \frac{\Delta x}{m_{i}^{i}} i+1/2 \times n+1/2 \frac{T_{i+1}^{i} - T_{i}^{i}}{n+1/2 n n} \]

\[ - (\rho \frac{m}{2} \frac{\Delta x}{m_{i}^{i}} i-1/2 \times (T_{i}^{i} - T_{i-1}^{i}) \]

(IV-122)

for the second row where \( i = 2 \), \( a(2,3) \) is the same and the other coefficients are

\[ a(2,1) = + (\rho \frac{m}{2} \frac{\Delta x}{m_{i}^{i}} i-1/2 \times n+1/2 \]

\[ a(2,2) = - \frac{1}{\Delta t} - (\rho \frac{m}{2} \frac{\Delta x}{m_{i}^{i}} i+1/2 \times n+1/2 \]

and

\[ b_{2} = \frac{w_{i}}{\rho} i + \frac{Y_{i}^{i}}{\Delta t} + \frac{1}{2\Delta x} [ (\rho \frac{m}{2} \frac{\Delta x}{m_{i}^{i}} i \frac{\Delta x}{m_{i}^{i}} i+1/2 \times n+1/2 \frac{Y_{i+1}^{i} - Y_{i}^{i}}{n+1/2 n n} \]

\[ - (\rho \frac{m}{2} \frac{\Delta x}{m_{i}^{i}} i \frac{\Delta x}{m_{i}^{i}} i-1/2 \times (Y_{i}^{i} - Y_{s}^{i}) + (\rho \frac{m}{2} \frac{\Delta x}{m_{i}^{i}} i+1/2 \times n+1/2 \frac{T_{i+1}^{i} - T_{i}^{i}}{n+1/2 n n} \]

\[ - (\rho \frac{m}{2} \frac{\Delta x}{m_{i}^{i}} i-1/2 \times (T_{i}^{i} - T_{s}^{i}) + (\rho \frac{m}{2} \frac{\Delta x}{m_{i}^{i}} i+1/2 \times n+1/2 \frac{T_{i+1}^{i} - T_{i}^{i}}{n+1/2 n n} \]

\[ - (\rho \frac{m}{2} \frac{\Delta x}{m_{i}^{i}} i-1/2 \times (T_{i}^{i} - T_{s}^{i}) \]
\[
\frac{D_T}{(\rho - \frac{T}{T})_{i-1/2}} \left( \left( \frac{m_i}{m} \right)_{i-1/2} \right) \frac{n+1/2}{\Delta \psi} (T_i - T_s)_{n \ \ n} \tag{IV-125}
\]

The coefficients in the last row are equal to

\[
a(n,n-1) = + \frac{\left( \rho - \frac{T}{T} \right)_{i-1/2}}{2\Delta \psi} \tag{IV-119}
\]

\[
a(n,n) = - \frac{1}{\Delta t} - \frac{\left( \rho - \frac{T}{T} \right)_{i-1/2}}{2\Delta \psi^2} \tag{IV-126}
\]

and

\[
b_n = \left( \frac{w_i}{\rho} \right)_{i} + \frac{n}{\Delta t} + \frac{1}{2\Delta \psi^2} \left[ - \left( \rho - \frac{T}{T} \right)_{i-1/2} \left( Y_i - Y_{i-1} \right) \right] \tag{IV-127}
\]

\[
- \left( \rho - \frac{T}{T} \right)_{i-1/2} (T_i - T_{i-1}) - \left( \rho - \frac{T}{T} \right)_{i-1/2} \left( T_i - T_{i-1} \right)
\]

The value of the first row coefficients depends on the specie involved. The values are for H

\[
a(1,1) = (+V_0'Y_0'\gamma_{82'})_s - \rho \nu + \left( \rho ^2 \frac{m_{H}}{m} \frac{\partial}{\partial \psi} \right) \frac{(Y_H'\gamma_{80} + Y_0'\gamma_{82} - 1)_s}{\Delta \psi} \tag{IV-128}
\]

\[
\frac{\left( \rho ^2 \frac{m_{H}}{m} \frac{\partial}{\partial \psi} \right) Y_{80}}{\Delta \psi} \frac{n+1/2}{Y_H - Y_H} + \frac{D_T}{\rho - \frac{T}{T}} \frac{\gamma_{80}}{\Delta \psi} \tag{IV-129}
\]

\[
a(1,2) = -[\rho ^2 \frac{m_{H}}{m} \frac{\partial}{\partial \psi} \frac{(Y_H'\gamma_{80} + Y_0'\gamma_{82} - 1)_s}{\Delta \psi}] \tag{IV-129}
\]

and
\[ b_1 = -\left( \frac{D_{TH}}{T} \frac{\partial T}{\partial \psi} \right) (Y_{82} Y_0 - 1)_{s} - \rho^2 \frac{m_H}{m} \frac{\partial}{\partial \psi} \left( \frac{Y_{82} Y_0 - 1}{\Delta \psi} \right)_{s} \frac{(Y_H - Y_{H_1})}{s_{n+1/2}} \]

For \( H_2 \)

\[ a(l,1) = (-\rho v - \rho^2 \frac{m_H H_2}{m} \Delta \psi\frac{\partial}{\partial \psi})_{s_{n+1/2}} \]

\[ a(l,2) = \left( \rho^2 \frac{m_H H_2}{m} \Delta \psi \frac{\partial}{\partial \psi} \right)_{s_{n+1/2}} \]

and

\[ b_1 = \left[ \left( \frac{D_{TH}}{T} \frac{\partial T}{\partial \psi} + Y_{80} Y_{82} Y_{H} \right)_{s} - \rho^2 \frac{m_H}{m} \frac{\partial}{\partial \psi} \left( \frac{Y_0 - Y_0}{\Delta \psi} \right)_{s} \frac{(Y_H - Y_{H_2})}{s_{n+1/2}} \right] \]

For \( O \)

\[ a(l,1) = \left( (-\rho v + \frac{1}{Y_0} Y_{81} \gamma_{81} + \gamma_{H_8} \gamma_{82}) \right) \rho^2 \frac{m_O}{m} \frac{\partial}{\partial \psi} \left( \frac{Y_0 - Y_0}{\Delta \psi} \right)_{s} \frac{D_{TH}}{T} \frac{\partial T}{\partial \psi} \]

\[ + \gamma_{H_8} \gamma_{82} \rho^2 \frac{m_O}{m} \frac{\partial}{\partial \psi} \left( \frac{Y_0 - Y_0}{\Delta \psi} \right)_{s} \frac{Y_{81} \gamma_{82}}{s_{n+1/2}} \]

\[ a(l,2) = -((-\rho v_{81} + \gamma_{H_8} \gamma_{82} - 1) \rho^2 \frac{m_O}{m} \frac{\partial}{\partial \psi})_{s_{n+1/2}} \]

\[ b_1 = -((-\rho v_{H_8} \gamma_{82} - 1) \rho \frac{m_O}{m} \frac{\partial}{\partial \psi} \left( \frac{Y_0 - Y_0}{\Delta \psi} \right)_{s} \frac{D_{TH}}{T} \frac{\partial T}{\partial \psi} + \rho^2 \frac{m_O}{m} \frac{\partial}{\partial \psi} \left( \frac{Y_0 - Y_0}{\Delta \psi} \right)_{s} \frac{(Y_H - Y_{H_2})}{s_{n+1/2}} \]

For \( O_2 \)

\[ a(l,1) = (-\rho v - \rho^2 \frac{m_O}{m} \Delta \psi \frac{\partial}{\partial \psi} \frac{O_2}{s_{n+1/2}}) \]

\[ a(l,2) = \left( \rho^2 \frac{m_O}{m} \frac{\partial}{\partial \psi} \frac{O_2}{s_{n+1/2}} \right) \]
\[
\begin{aligned}
D_{T_{01}} & \quad \frac{b_1}{T_0} = \left( \frac{\rho}{T} \frac{\partial T}{\partial \psi} - \gamma_{81} V_0^2 V_0^{\rho} + \rho \frac{m_{O_2}}{m \Delta \psi} \right) \left( \frac{Y_{O_2}^l - Y_{O_2}^n}{s} \right) + \rho \nu Y_{O_2}^n \\
\text{For OH} & \quad a_{1,1} = (-\rho \nu - \rho^2 \frac{m_{OH}}{m \Delta \psi} s) \\
& \quad a_{1,2} = (\rho^2 \frac{m_{OH} \sigma_H}{m \Delta \psi} s) \\
& \quad b_{1} = (\rho \frac{H}{T} \frac{\partial T}{\partial \psi} - \gamma_{82} \gamma \gamma_{0} \rho \gamma - \gamma_{82} \gamma \gamma_{0} \gamma) \left( \frac{Y_{OH}^l - Y_{OH}^n}{s} \right)
\end{aligned}
\] (IV-139)

The coefficients of the first row for all other reactant species will be

\[
\begin{aligned}
a_{1,1}^i & = (-\rho \nu - \rho^2 \frac{m_i}{m \Delta \psi} s) \\
a_{1,2}^i & = (\rho^2 \frac{m_i \sigma_i}{m \Delta \psi} s) \\
b_{1}^i & = (\rho \nu Y_{i0}^l + \rho \frac{i}{T} \frac{\partial T}{\partial \psi} + \rho^2 \frac{m_i}{m \Delta \psi} \left( \frac{Y_{i}^l - Y_{i}^n}{s} \right)) \\
& \quad \left( \frac{Y_{i}^l - Y_{i}^n}{s} \right)
\end{aligned}
\] (IV-143) (IV-144) (IV-145)

and non-reacting species will have the same coefficients except

\[
\begin{aligned}
b_{1}^i & = (\rho \frac{i}{T} \frac{\partial T}{\partial \psi} + \rho^2 \frac{m_i}{m \Delta \psi} \left( \frac{Y_{i}^l - Y_{i}^n}{s} \right))
\end{aligned}
\] (IV-146)

### IV-3.2.2 The Energy Difference Equation

The energy equation is differenced in the same manner as the specie equations. The heat capacities are expressed as mean values.
and the non-linear part of the thermal diffusive heat flux is retained in the coefficient. The Crank-Nicholson difference of the accumulation term is

\[ \sum (\rho C_p T_i \frac{\partial Y_i}{\partial \psi} - C_p \rho \frac{\partial T}{\partial \psi} - (\rho C_p)_{i-1/2} \frac{(T_{i+1} - T_i)}{n+1/2} \frac{n}{n+1/2}) \]

The heat flux by conduction difference is

\[ \frac{\partial}{\partial \psi} \lambda \frac{\partial T}{\partial \psi} = \frac{\rho}{2\Delta \psi} \left[ (\rho C_p)_{i+1/2} \frac{(T_{i+1} - T_i)}{n+1/2} + (\lambda \rho)_{i-1/2} \frac{(T_{i} - T_{i-1})}{n+1/2} \right] \]

The heat flux by molecular diffusion difference equation is

\[ \sum (\rho C_p T_i \frac{\partial Y_i}{\partial \psi} - C_p \rho \frac{\partial T}{\partial \psi} - \rho m_i D_{ij} \frac{\partial n_i}{\partial \psi} \frac{1}{m_i} \frac{\partial T}{\partial \psi} = \sum \rho m_i \frac{\partial^2 Y_i}{\partial \psi^2} \frac{\partial T}{\partial \psi} \]

The difference equation for heat flux by thermal diffusion is

\[ \sum (\rho C_p T_i \frac{\partial T}{\partial \psi} - C_p \rho \frac{\partial T}{\partial \psi} = \sum \rho C_p \frac{D_{T}}{\partial \psi} \frac{\partial T}{\partial \psi} \]

Substituting the boundary conditions and grouping terms yields a tridiagonal matrix of the form (IV-118) where the coefficients are

\[ a(1,1) = \frac{(\rho C_p)_{i-1/2}}{\Delta t} + \frac{\rho_{i-1/2}}{2\Delta \psi} \frac{(\lambda \rho)_{i+1/2}}{n+1/2} + \frac{\rho_{i-1/2}}{\Delta \psi} \frac{(\lambda \rho)_{i-1/2}}{n+1/2} \]
\[
\begin{align*}
\left(\sum_i C_{p_i} \rho \frac{m_i}{m} \mathcal{O}_i \frac{\partial \psi_i}{\partial \psi}\right)_{i} + \left(\sum_i C_{p_i} \rho \frac{D_{T_i}}{T} \frac{\partial T_i}{\partial \psi}\right)_{i} & = \left(\sum_i C_{p_i} \rho \frac{D_{T_i}}{T} \frac{\partial T_i}{\partial \psi}\right)_{i} n + 1 / 2 \\
\rho_i & = \frac{\Delta x}{n + 1 / 2} (\lambda \rho)_{i+1/2} - \left(\sum_i C_{p_i} \rho \frac{D_{T_i}}{T} \frac{\partial T_i}{\partial \psi}\right)_{i} n + 1 / 2 \\
\lambda \rho & = \frac{\Delta x}{n + 1 / 2} (\lambda \rho)_{i-1/2} + \left(\sum_i C_{p_i} \rho \frac{D_{T_i}}{T} \frac{\partial T_i}{\partial \psi}\right)_{i} n + 1 / 2 \\
\left(\sum_i C_{p_i} \rho \frac{m_i}{m} \mathcal{O}_i \frac{\partial \psi_i}{\partial \psi}\right)_{i} + \frac{1}{2\Delta x} \left(\frac{T_1}{n} \frac{\Delta \psi}{\Delta x} - \frac{T_2}{n+1/2} \frac{\Delta \psi}{\Delta x} \right) - \left(\sum_i C_{p_i} \rho \frac{D_{T_i}}{T} \frac{\partial T_i}{\partial \psi}\right)_{i} n + 1 / 2 \\
b(l) & = \frac{\Delta x}{n+1/2} (\lambda \rho)_{i-1/2} \left(T_2 - T_1\right) + \left(\sum_i C_{p_i} \rho \frac{D_{T_i}}{T} \frac{\partial T_i}{\partial \psi}\right)_{i} n + 1 / 2 \\
\frac{1}{2\Delta x} \left(\frac{T_1}{n} \frac{\Delta \psi}{\Delta x} - \frac{T_2}{n+1/2} \frac{\Delta \psi}{\Delta x} \right) & = \frac{1}{\Delta x} \left(\frac{T_1}{n} \frac{\Delta \psi}{\Delta x} - \frac{T_2}{n+1/2} \frac{\Delta \psi}{\Delta x} \right) + \left(\sum_i C_{p_i} \rho \frac{m_i}{m} \mathcal{O}_i \frac{\partial \psi_i}{\partial \psi}\right)_{i} \frac{\Delta \psi}{\Delta x} + \left(\sum_i C_{p_i} \rho \frac{D_{T_i}}{T} \frac{\partial T_i}{\partial \psi}\right)_{i} \frac{\Delta \psi}{\Delta x} \\
\left(\sum_i C_{p_i} \rho \frac{D_{T_i}}{T} \frac{\partial T_i}{\partial \psi}\right)_{i} n + 1 / 2 & = \frac{1}{\Delta x} \left(\frac{T_1}{n} \frac{\Delta \psi}{\Delta x} - \frac{T_2}{n+1/2} \frac{\Delta \psi}{\Delta x} \right) + \left(\sum_i C_{p_i} \rho \frac{D_{T_i}}{T} \frac{\partial T_i}{\partial \psi}\right)_{i} \frac{\Delta \psi}{\Delta x} \\
\left(\sum_i C_{p_i} \rho \frac{D_{T_i}}{T} \frac{\partial T_i}{\partial \psi}\right)_{i} & = \frac{1}{\Delta x} \left(\frac{T_1}{n} \frac{\Delta \psi}{\Delta x} - \frac{T_2}{n+1/2} \frac{\Delta \psi}{\Delta x} \right) + \left(\sum_i C_{p_i} \rho \frac{D_{T_i}}{T} \frac{\partial T_i}{\partial \psi}\right)_{i} \frac{\Delta \psi}{\Delta x} \\
\left(\sum_i C_{p_i} \rho \frac{D_{T_i}}{T} \frac{\partial T_i}{\partial \psi}\right)_{i} & = \frac{1}{\Delta x} \left(\frac{T_1}{n} \frac{\Delta \psi}{\Delta x} - \frac{T_2}{n+1/2} \frac{\Delta \psi}{\Delta x} \right) + \left(\sum_i C_{p_i} \rho \frac{D_{T_i}}{T} \frac{\partial T_i}{\partial \psi}\right)_{i} \frac{\Delta \psi}{\Delta x} \\
The general term has the form
\end{align*}
\]
\[ a(i,i-1) = - \frac{\rho_i}{n+1/2} \frac{\lambda \rho}{2\Delta \psi} \frac{\partial}{\partial t} \frac{\partial}{\partial \psi} \frac{\gamma_i}{n+1/2} + (\Sigma_i \frac{\partial}{\partial t} \rho \frac{\partial}{\partial \psi})_i \]

\[ + (\Sigma_i \frac{D_T}{T} \rho \frac{\partial^2}{\partial \psi^2})_i \]

\[ a(i,i) = \frac{n+1/2}{2\Delta \psi} \left( \frac{(\lambda \rho)_{i+1/2}}{n+1/2} + \frac{(\lambda \rho)_{i-1/2}}{n+1/2} \right) + \frac{n+1/2}{\Delta t} \]

\[ a(i,i+1) = - \frac{\rho_i}{n+1/2} \frac{\lambda \rho}{2\Delta \psi} \frac{\partial}{\partial t} \frac{\partial}{\partial \psi} \frac{\gamma_i}{n+1} \]

\[ + (\Sigma_i \frac{\partial}{\partial t} \rho \frac{\partial}{\partial \psi})_i \frac{D_T}{T} \frac{\partial^2}{\partial \psi^2} \frac{\gamma_i}{i+1/2} \frac{\delta \psi}{i+1/2} \]

\[ - \frac{\delta \psi}{2\Delta \psi} \]

and

\[ b_i = \Sigma_i h_i \delta \psi^{298} \omega_i + \Sigma_i \frac{\partial}{\partial t} \left( T-298 \right) \omega_i - \frac{n+1/2}{\Delta t} \frac{\gamma_i}{T_i} \frac{T_i}{n} \]

\[ \rho_i \]

\[ - \frac{n+1/2}{2\Delta \psi} \frac{(\lambda \rho)_{i+1/2}}{n+1/2} \left( T_{i+1} - T_i \right) + \frac{n+1/2}{n+1/2} \frac{(\lambda \rho)_{i-1/2}}{2\Delta \psi} \left( T_i - T_{i-1} \right) \]

\[ - (\Sigma_i \frac{\partial}{\partial t} \rho \frac{\partial}{\partial \psi})_i \frac{\partial^2}{\partial \psi} \left( T_{i+1} - T_{i-1} \right) \]

\[ (\Sigma_i \frac{\partial}{\partial t} \rho \frac{\partial}{\partial \psi})_i \frac{D_T}{T} \frac{\partial^2}{\partial \psi^2} \frac{\gamma_i}{n+1/n} \]

\[ - \frac{\delta \psi}{2\Delta \psi} \frac{n+1/2}{n+1/2} \left( T_{i+1} - T_{i-1} \right) \]

and the last row coefficients are
\[ a(n,n-1) = -\frac{\rho_n}{n+1/2} \left( \lambda \rho \right)_{n-1/2} \frac{2\Delta \psi}{n+1/2} \] 
\[ + \left( \Sigma_i C_P \rho \right)_{n} \left( \begin{array}{c} m_i \\ \frac{\partial Y_i}{\partial \psi} \end{array} \right)_{n} \frac{\Delta \psi}{n+1/2} \] 
\[ + \frac{D_{T_i}}{T \frac{\partial T}{\partial \psi}}_{n} \] 
\[ + \frac{(rC_P)_n}{n+1/2} \frac{\rho_n}{\Delta t} + \frac{n+1/2}{2\Delta \psi^2} \left( \lambda \rho \right)_{n-1/2} \frac{2\Delta \psi}{n+1/2} \] 
\[ - \left( \Sigma_i C_P \rho \right)_{n} \left( \ra - \delta \right) \frac{\partial Y_i}{\partial \psi}_{n} \] 
\[ + \frac{D_{T_i}}{T \frac{\partial T}{\partial \psi}}_{n} \frac{\Delta \psi}{n+1/2} \] 
\[ (IV-156) \]

\[ a(n,n) = \frac{(rC_P)_n}{n+1/2} \frac{\rho_n}{\Delta t} + \frac{n+1/2}{2\Delta \psi^2} \left( \lambda \rho \right)_{n-1/2} \frac{2\Delta \psi}{n+1/2} \] 
\[ - \left( \Sigma_i C_P \rho \right)_{n} \left( \ra - \delta \right) \frac{\partial Y_i}{\partial \psi}_{n} \] 
\[ + \frac{D_{T_i}}{T \frac{\partial T}{\partial \psi}}_{n} \frac{\Delta \psi}{n+1/2} \] 
\[ (IV-157) \]

and

\[ b_n = -\frac{(rC_P)_n}{n+1/2} \frac{T_{n,n}}{\Delta t} + \frac{n+1/2}{2\Delta \psi^2} \left( \lambda \rho \right)_{n-1/2} \frac{2\Delta \psi}{n+1/2} \frac{T_n - T_{n-1}}{n \ \ \ \ n} \] 
\[ - \left( \Sigma_i C_P \rho \right)_{n} \left( \ra - \delta \right) \frac{\partial Y_i}{\partial \psi}_{n} \frac{T_n - T_{n-1}}{n \ \ \ \ n} \] 
\[ + \frac{D_{T_i}}{T \frac{\partial T}{\partial \psi}}_{n} \frac{\Delta \psi}{n+1/2} \frac{T_n - T_{n-1}}{n \ \ \ \ n} \] 
\[ (IV-158) \]

where \( x = n \) replaces the index \( i \) and represents the last grid point.
IV-3.3 Solution of the Differenced Flame Equations

The differenced flame equations are now in the form of linear algebraic equations. There is one equation for each grid point for each original differential equation. The algebraic equations for each differential equation form a tridiagonal matrix. Instead of \( k \) specie equations and one energy equation the problem consists of \( m \times (n \text{number of grid points}) \times (k+1) \) algebraic equations grouped in \( k+1 \) tridiagonal matrices. These matrices are coupled both through temperature and compositions.

The Thomas Algorithm is a fast standard method for solving tridiagonal matrices. This method is well known and will not be further discussed. See von Rosenberg (1969), p. 113.

The way the difference equations have been written, with the source term evaluated either at the old time or at an explicitly extrapolated new time, the coupling of the difference equations appears only in the constant term. Consequently, each tridiagonal matrix can be solved in turn and the coefficients for the next matrix to be solved can be up-dated. Iteration could be performed at each time step but is usually unnecessary when the transient solution is not of interest.

Von Rosenberg (1962) has used this method for a simple problem. Spalding and Stephenson (1971) have used a similar solution technique. They found that successive up-dating of coefficients allowed a larger time step than evaluating the coefficients at the beginning of a time step. They also found that composition variations and not temperature variations were the major cause of instability. The stability of the solution was also dependent on the order of dependent variable calculation. Temperature is best calculated last and the
most important species is best calculated first. In the $\text{H}_2$-$\text{Br}$ flame
the kinetic scheme is most sensitive to $\text{Br}$ so the order of calculation
for this flame is $\text{Br}$, $\text{H}$, $\text{HBr}$, $\text{H}_2$, $\text{Br}_2$. In general it is desirable to
calculate the active radicals first and the stable product specie last.

IV-4 Summary of the Flame Equations

The completely general flame equations were written and simplified.
General experience with flat flame burners has shown that flame regions
are essentially one dimensional near the reaction zone. A number of
terms can be completely eliminated from the flame equations based on
order of magnitude analysis. These are bulk viscosity, viscous terms,
pressure driven diffusion, external force driven diffusion, temperature
driven diffusional energy flux (Dufour effect), and kinetic energy.
A second set of terms which were studied but appear to have minor
effects are both thermal and chemiluminescent radiation. The momentum
equation has been eliminated because of the small pressure change
through the flame although the buoyant term may have a minor effect
on the flame velocity for low pressure flames.

After reviewing methods of solution of the flame equations it
was decided to write the equations in the form of second order partial
differential equations. The von Mises' coordinates were introduced
into the flame equations which eliminated the convective terms and
automatically gives desirable grid scaling.

The hot boundary conditions were specified in the usual manner
as zero dependent variable gradients. The cold boundary conditions
were specified as a material balance at the burner surface and the
burner surface temperature. The material balance at the burner
surface included radical recombination reactions.
The differential equations were differenced using the Crank-Nicholson method. Coefficients and source terms in the specie balance equations were evaluated at explicitly extrapolated positions and times. No linearization was used in the energy equation because it would have introduced step size limitations. The resulting differencing equations are easy to solve tridiagonal matrices.
V. EQUIPMENT AND PROCEDURE

The equipment to be described has been developed for use in several coal research projects in M.I.T.'s Fuels Research Laboratory. The equipment was designed to cover experimental conditions of interest for pulverized coal flames. The equipment also covers the operating range of some gasifier units. Pulverized coal flames have maximum temperatures up to 2200⁰K, particle heating rates up to 10⁵ K/sec, and residence times of interest from several milliseconds to hundreds of seconds. Gasifier units are much more variable than combustion units. Gasifiers can have conditions ranging from temperatures of less than 1000⁰K, heating rates of several ⁰K/sec, and residence times of hours to conditions very close to those encountered in a pulverized coal flame.

The equipment can simulate the extremely rapid heating expected in the pulverized coal flame; for example, data has been taken on coal devolatilization, in a dispersed phase, with time resolution of about 0.5 milliseconds, heating rate of about 2 x 10⁵ K/sec, and a maximum temperature of 2100⁰K. Experimental conditions of gasifiers are of secondary interest and have not been matched nearly so well. Data have been gathered on coal devolatilization in the dispersed phase at temperatures as low as 1000⁰K, with heating rates on the order of 10⁴ K/sec, and maximum residence time of one second. Devolatilization of coal in fixed beds has covered a wider range. Fixed bed results have been obtained for devolatilization of
coal for temperatures as low as 700°K, with heating times on the order of several degrees kelvin per minute, and maximum residence times of up to eight hours.

The equipment has been used in a number of co-operative coal studies. The description of the flow furnace, free fall furnace, and crucible experiments that follow were written by Kobayashi (1976), and are reproduced here with only slight modifications.

V-1.0 Flow Furnace

Flow reactors have been used widely by various researchers. Gray and Kimber (1967) applied such a system to coal studies at temperatures up to 2800°K. One of the main advantages of flow furnaces is the similarity to actual systems. By controlling both gas and wall temperatures, a wide range of simulation is possible, and the results may be readily applicable to real systems. A typical flow furnace system includes a temperature controlled furnace, a high temperature gas supply device, a coal feeder and a sampling probe. The relative complexity of the system and material problems at high temperatures are major detriments of such an apparatus.

For the present study, a laminar flow furnace was chosen for its versatility. Similar systems were developed by BCURA researchers (Field, 1970 and Badzioch and Hawksley, 1972), but some important improvements were made in system designs and characterizations. These improvements include a partially fluidized vibrating feeder, a water quenched collector with
a bronze filter and particle velocity measurements by a laser doppler anemometer. In their systems char particles were quenched by thermal conduction from water cooled collector walls and then separated by cyclone separators. Conduction quenching was found to be unsatisfactory in this study. Good recovery of particles was not achieved because of the adhesion of char particles to the collector wall. Thus they had to use ash as a tracer to determine weight loss. It should be noted, however, that in the present study, ash tracer results differed by more than 5% from directly determined weight losses for measurements above 1300°K. Part of the discrepancy is attributable to particle loss in our system, but the major discrepancy is caused by chemical changes in the ash at high temperatures. The chemical changes in the ash have been independently confirmed in experiments where particle collection is not a problem. In our system this problem was solved by collecting char particles with a bronze filter at the mouth of the collector. Water was directly injected at the mouth of the collector, and this quenched the coal particles rapidly.

V-1.1 Laminar Flow Experiment

A schematic of the laminar flow furnace system is shown in Figure V-1. The system is built around a modified ASTRO model 1000A graphite furnace (ASTRO Industries, Inc., Santa Barbara, California). A 3.5 in. I.D., 12 in. long graphite resistance heating element is used to control furnace temperatures. A 4 in. I.D. graphite radiation shield and packed
graphite powder provide thermal insulation. The outer shell is about 11 inches in diameter and water-cooled for easy access. The furnace is equipped with a programed automatic temperature control which allows temperature changes to be made at desired rates. This feature is especially important when ceramic muffle tubes are used, since they are susceptible to thermal shock. The temperature is controlled through a tungsten-rhenium thermocouple which is located just outside the heating element in the center of the furnace. The maximum operating temperature of the furnace is about 3000°K with a graphite muffle tube. Three pairs of observation ports are located along the axis of the furnace at intervals of 1.5 inches. The ports have quartz windows which supply an observation area of 0.5 in. in diameter. Optical instruments such as a radiation pyrometer or a laser doppler anemometer were used through these windows. Coal particles are injected into the center of the 2 in. I.D. graphite muffle tube through a 0.047 in. I.D., 3/16 in. O.D. water-cooled stainless steel injector. A 5/8 in. O.D graphite tube is used as a heat insulator to minimize the heat loss to the water-cooled injector. Preheated gas is introduced horizontal to the axis of the furnace and straightened through a 1 inch thick graphite honeycomb. The honeycomb hole is 0.067 in. in diameter and the distance between holes is 0.083 inches. The lower surface of the honeycomb is 0.5 in. above the center of the first observation port. Six 2-3/8 in. disks are placed 1 inch apart above the honeycomb to prevent radiant heat loss. The coal particles are heated as the
carrier gas mixes with the preheated main gas flow. The char is collected in a water-cooled bronze filter after being quenched by water jets. The rest of the gas is cooled by an exchanger and exhausted. Since the muffle tube is constructed from graphite, atmospheric air must be excluded at all times. Two ball valves provide a convenient method for quickly closing the passages through which the collector is removed or for shutting off the plasma gun. The graphite muffle tube and the honeycomb could be replaced by an alumina muffle tube and an alumina honeycomb for experiments in oxidizing atmospheres. With the alumina muffle tube, however, sudden introduction of preheated gas by starting the plasma gun might cause severe thermal shock.

V-1.2 Coal Feeder

The coal feeder employs a mechanical vibrator and partial fluidization of coal particles. The combined system results in relatively uniform feed rates. The main body is made of polished plexiglas which allows observation of the coal level and feed rate. The I.D. of the plexiglas section is 0.5 inches and the length 3 inches; about 5 gm. of coal can be charged. The feed rate is controlled by the needle valve opening, the vibrator strength and the carrier gas flow rate. The carrier gas is introduced through the hollow needle valve and injected radially through four equally spaced, 0.010 inch holes at the tip of the needle valve. The gas fluidizes the coal particles locally, thus preventing packing and clogging in the narrow
region. An external electric vibrator oscillates the entire feeder assembly. The exit of the feeder is connected to a 0.065 in O.D. and 0.047 in. I.D. stainless steel tubing which vertically enters the furnace. The vertical arrangement of the feeder-injector line allows the use of a fine tube with a very small amount of carrier gas flow (as small as 5 cc/min). Less carrier gas allows more rapid heating of the injected particles. Feed rates between 0.01 gm/min and 1.0 gm/min can be obtained with reasonable uniformity. In normal operations about 0.15 gm/min was used.

V-1.3 Particle Collector

The collector consists of three concentric copper tubes. The external cooling water passes through two of the passages and the third is used to withdraw the quenched gases. Eight 1/8 in. O.D. copper tubes pass through the second water passage to carry the quenching water to be directly injected. Heat transfer analysis showed that cooling by conduction to the water-cooled wall is insufficient to achieve char quenching because of the relatively large hot gas flow rate (up to 11/sec) and the necessarily large collector diameter. This problem was solved by directly injecting quenching water at the mouth of the collector through twelve holes drilled in the flared upper section of the sintered bronze filter. (The filters were manufactured specially by Thermet Inc., Gloucester, Mass.). The porous bronze filter allows some of the quenching water to pass through the whole area of the upper section of
the filter, preventing coal particles from adhering and being exposed to intense radiation from the furnace wall. The bronze filter is 0.740 in. O.D. at the open end, 0.4 in. O.D. and 4 in. long at the straight section, and the wall thickness is 0.060 inches. The average size of bronze is about 15 micron, and coal particles larger than 5 micron are retained in the filter.

V-1.4 Gas Preheater

An AVCO plasma gun model PG 040 is attached to the furnace to preheat the main gas stream. The plasma gun has a water-cooled tungsten cathode and an annular water-cooled copper anode. An AIRCO model 1500-C7 welding rectifier supplies D.C. power to the gun. The maximum power input to the plasma gun is 40 Kw. The plasma heats the gas with a 30 percent thermal efficiency. The temperature of the preheated gas is controlled by changing the power input and the gas flow rate. Argon, helium, nitrogen or hydrogen can be used as working gases. A graphite muffle tube restricts the working gas, therefore only inert gases can be used.

V-1.5 Suction System

A steam ejector supplies sufficient suction to withdraw directly injected quenching water and the quenched argon gas. Water is separated from the gas by a gravitational separation vessel. The quenched gas is dried through a packed bed of calcium sulfate and metered by a Fischer & Porter flowmeter.
Experimental Procedure

The furnace is heated to a desired temperature using the automatic temperature controller. Three tungsten-rhenium thermocouples, which were introduced through the observation ports, are used to monitor the temperature inside the muffle tube. After steady-state is reached, the main gas in introduced and the plasma gun is started. The temperature of the main gas is controlled to the same temperature as the furnace wall temperature. This is done by matching the thermocouple readings before and after the introduction of the main gas. The main gas flow rate is controlled by a Fischer & Porter flowmeter to give desired main gas velocities. The pressure of the furnace is maintained at about 2 inches of water.

A pre-dried bronze filter is weighed and placed in the collector. Suction rates varied between 1/3 to 1/2 of the main gas flow rates depending on the furnace temperatures. The flow rate of the quenching water jets was maintained at 0.7 1/min for most runs. After a desired suction rate and a water flow rate are obtained, the collector is raised into the furnace and positioned at a prescribed distance from the coal particle injector. About 0.05 to 0.5 gm of coal is weighed and charged into the feeder. Then, a carrier gas flow rate and a needle valve opening are set and the vibrator is turned on. The coal level in the feeder is continuously monitored and the end of the feeding is visually judged. As char particles accumulate in the bronze filter, a cake builds up. In order to maintain the same suction rate, the valve opening
of the suction line has to be increased to compensate for the increased pressure drop across the filter. The maximum pressure drop allowed is about 20 in. Hg. Upon completion of the coal particle injection, the collector is removed from the furnace and replaced with a new bronze filter. The collector is raised again to a different location and the next run is started. Normally about ten runs are repeated at the same experimental conditions with different collector locations. A summary of operating conditions is shown in Table V-1. After all runs are finished, the filters are dried at 110° C for three hours in a nitrogen atmosphere. The filters are then cooled in a desiccator and weighed as soon as the room temperature is reached. Some of the char samples are analyzed for ash content or sent to Galbraith Laboratories Inc., Knoxville, Tennessee, for the ultimate analysis. Weight loss of coal is determined by the difference of the weights between the coal fed and the collected char.

V-2.0 Free Fall Experiment with Bronze Collector

In order to obtain longer reaction times, coal particles were allowed to fall under the influence of gravity through a preheated furnace. The schematic of the system is similar to the flow furnace shown in Figure V-1. The main component of the system is an ASTRO model 100A graphite furnace. The same temperature control system, which is used for the laminar flow furnace, controls the furnace wall temperature. A 24 in. long, 3 in. O.D., 2½ in. I.D. alumina muffle tube shields the
pore diameter of about 5 micron. The gas exits through a \( \frac{1}{4} \) in. pipe fitting under the center of the bronze disk.

V-2.1 Experimental Procedure

The furnace is heated to a desired temperature at a heating rate between 250\(^\circ\)C/hr and 350\(^\circ\)C/hr, using the temperature programmer. After a steady-state is reached, a pre-weighed bronze filter is placed on the bottom flange. Then the furnace is alternatively evacuated and filled with argon several times to eliminate atmospheric air. About 1 gram of coal is weighed and charged in the feeder. The suction rate is controlled so that the furnace pressure is maintained at atmospheric pressure for fixed main gas and carrier gas flows. The vibrator is started and coal is fed in about 10 minutes, giving a feed rate of 0.1 gm/min. After all the particles are fed, the bronze disk is removed and quickly weighed to avoid adsorption of moisture. The collected char is transferred to a sample bottle for analyses, such as ash content, elemental composition and particle size distribution.

V-2.2 Free Fall Experiment with Alumina Collector

The object of this experiment is to obtain the asymptotic weight loss values at high heating rates and very long reaction times. The furnace is the same as used in the free fall expe-
graphite heating element from the reaction zone. A 15 in.
long, 2½ in. O.D., 2 in. I.D. alumina tube supports an alumina
honeycomb flow straightener. The honeycomb, made by E. I. du
pont de Nemours, has a nominal pore diameter of 1/16 inch.
The maximum temperatures of the alumina tubes and honeycomb
are 2100°K and 1900°K respectively. A 9 in. long, 3½ in. I.D.
cooling section is attached to the bottom of the furnace. The
coal feeder and the water-cooled injector are the same as the
ones used in the laminar flow system, except the diameters of
the tubes. The water-cooled injector has a 0.250 in O.D. and
a 0.101 I.D. Small amounts of main gas (about 0.05 l/sec) are
introduced from the top of the furnace. The gas is heated by
conduction from the muffle tube wall and honeycomb. The honey-
comb induces uniform velocity and temperature profiles in the
radial direction. The temperatures along the axis of the fur-
nace were measured by a chromel-alumel thermocouple up to 1500°K
and by a platinum-rhodium or an iridium-rhodium thermocouple
above 1500°K. Since the main gas Reynolds number is small,
the flow is practically fully developed for the entire region.
Therefore the temperature of the main gas is considered to be
close to the wall temperature of the muffle tube. Coal parti-
cles are introduced into the center line of the main flow through
the water-cooled injector. Carrier gas flow rates between
2 cc/min and 25 cc/min were used. Char particles are collected
in a 3 in. diameter, 1/8 in. thick sintered bronze disk at the
bottom of the cooling section. The bronze disks were manufac-
tured by Thermet Inc., Gloucester, Mass. They have an average
riment with the bronze filters. A 40 mm O.D., 165 mm long cylindrical alumina crucible (Coors CN-170) is supported by a 1 7/8 in. O.D., 1/8 in. thick alumina disk, which is attached to a 1/2 in. O.D., 3/8 in. I.D. alumina tube. A thermocouple is placed between the support disk and the bottom of the collector to monitor the temperature during the experiment. The crucible temperature is recorded continuously on a chart recorder. The collector is raised or lowered by a motor-driven linear actuator at a constant speed. This is to protect the ceramic material from thermal shock caused by a sudden temperature change. At 1830°K it takes about 20 minutes to position or remove the alumina collector.

V-2.3 Experimental Procedure

After a desired temperature of the furnace is attained, a pre-weighed alumina collector is raised to the hot zone of the furnace by the linear actuator. The furnace is continuously purged by argon to prevent air leaks. The temperature at the bottom of the collector is recorded and when a steady-state is reached, about 1 gram of coal is fed in approximately 10 minutes. Main gas flow rates between 0 and 0.05 l/sec and carrier gas flow rates between 2 cc/min and 24 cc/min were used. After all the particles are fed, the collector is kept for 10 minutes at the same position in order to assure sufficient reaction time for the particles fed last. The collector is then lowered into the cooling section and transferred to a desiccator. About half of the char sample and the material
left in the crucible are analyzed for ash content.

V-3.0 Crucible Experiment

The object of the crucible experiments is to determine weight loss under slow heating conditions and extremely long residence times. Instead of feeding and collecting coal particles, as in the case of free fall and laminar flow experiments, about 1 gram of coal is weighed and placed in a 15 ml alumina crucible (Coors CH-16), then the crucible is raised into the hot zone of the furnace using the linear actuator discussed above. The temperature between the crucible and the support disk is recorded by a thermocouple during the whole cycle of heating and cooling. Heating rates between 0.5°C/sec and 5.0°C/sec can be obtained. It should be noted that this experiment is close to the ASTM proximate analysis for the determination of volatile matter, where one gram of coal is placed in a 15 ml platinum crucible and lowered in a furnace heated to 950°C and held for seven minutes.

V-3.1 Experimental Procedure

The procedure is the same as that of the free fall experiment with alumina collector, except no coal is fed.

V-4.0 Oxidation Experiments

The purpose of the oxidation experiments is to investigate the distribution of oxidation products from coal under
different burning conditions. The operating conditions of most interest are flame temperature and fuel equivalence ratio. The distribution of the nitrogeouse products in the gas phase and the condensed phase are of particular interest for the evaluation of the contribution of fuel nitrogen to noxious nitrogen products.

Oxidation experiments were done in the free fall furnace described in section V-2. Either air or helium-oxygen mixtures, simulating air, were used as the oxidizing atmosphere. This main gas flow was typically on the order of 3000 cc/min. A small amount of additional oxidizing gas, about 30 cc/min, was used to carry the coal into the furnace. These conditions resulted in a small flame stabilized on the injector nozzle. The flame length depended somewhat on operating conditions, but was typically about two inches long. Large amounts of soot and unburned coal were visible leaving the flame under fuel rich flame conditions, but only ash was recovered under lean conditions. The furnace wall temperature is controlled in the manner previously described. The wall temperature was confirmed with an optical pyrometer and thermocouple traverses. The flame temperature was measured with an optical pyrometer and is considered accurate to about 50^0 K. The flame temperature will increase as the wall temperature is increased, but the flame temperature will increase more slowly than the wall temperature because the flame temperature is primarily determined by the heat release of the flame and not the wall conditions.
Nitric oxide concentrations were measured with a chemiluminescence NO meter from a slip stream of the total gas flow out of the furnace. The meter response to NO\textsubscript{x} was recorded on a strip chart recorder and integrated over the time. This technique allowed the fraction of the nitrogen in the coal that was converted to nitrogen oxides to be determined. Any nitrogen dioxide present was converted to nitric oxide by a molydenum converter prior to nitric oxide detection. The chemiluminescence meter was calibrated at the operating conditions used during actual sampling by using nitrogen gas as a zero gas and a certified 290 ppm nitrogen oxides in helium calibration gas supplied by Matheson gas company. The concentration of the calibration gas was confirmed by independent Saltzman analysis for total nitrogen oxides. The accuracy of nitrogen oxides concentrations determined with the chemiluminescence meter, in the range of nitrogen oxides from the furnace (100-200 ppm), was about 5-10%.

Quenched char and condensable material were collected at the bottom of the furnace on a porous sintered bronze disk. The recovered material was weighed to determine the percent of the material burned and some samples were sent to Galbraith Laboratories Inc., Knoxville, Tennessee for nitrogen analysis by the Kjeldahl procedure.

V-5 ASTM Proximate Equipment

A drying oven, a cylindrical furnace and a brick-insulated furnace were used to determine moisture, volatile matter and
ash contents. ASTM standards (D3173-73, D3174-73 and D3175-73, 1972) were followed wherever possible. Some modifications were made, however, to accommodate smaller samples sizes and different experimental equipment. A Hoskin cylindrical furnace (Model 303, 5.0 amps) is the main part of the system to determine volatile matter. The furnace is capable of a maximum temperature of 1100°C at full load. The heated cylindrical tube is 1.38 in. in diameter and 13 in. long. The equipment has a cooling section 15 in. long and 1.5 in. I.D. in order to provide adequate cooling for the devolatilized samples in an inert atmosphere. This prevents oxidation of the hot samples. The whole assembly is sealed with a high temperature alumina cement. The furnace is continuously purged with nitrogen when determining proximate volatile matter. A chromel-alumel thermocouple is centered in the heating zone 5.0 inches from the bottom. A porcelain crucible (5 ml capacity) containing the samples to be analyzed is suspended in the hot zone of the furnace about 0.2 inches above the tip of the thermocouple. A reasonably steady hot zone (± 20°C) is maintained 4.3 inches to 8.6 inches from the bottom.

Volatile matter determined by this system were compared with the the results of two independent laboratories (Galbraith Laboratories Inc., Knoxville, Tennessee, and M.I.T. Central Analytical Facility) which followed the ASTM specifications. Agreements within 0.5 percent of the weights of original coals were obtained. The agreement justifies the present system.

Ash content was determined in a magnesium brick furnace.
The inside dimensions of the furnace are a base 8.5 in. by 4 in. and a height of 9 in. This furnace is large enough to accommodate the cylindrical alumina collector used in the free-fall experiment. Four silicon carbide heating elements (Norton XL 3/8 in. O.D. by 13 in. long) supply necessary heat to the furnace. Glazed porcelain crucibles were used to hold the samples. It was confirmed that the use of different crucible sizes did not affect ash content. ASTM standard procedures were possible with the exception of the size of the crucibles and samples.
VI. COAL CHARACTERIZATION

Coals differ widely depending on geological age, geographical location, geological conditions. Major differences may be found in coal composition even between different positions in a particular coal seam. Classifications developed to differentiate between different coals have been based on rank, physical appearance, elemental analysis and functional group analysis.

Rank is a gross measure of properties such as heat of combustion, carbon content, agglomerating and agglutining tendencies of coals with definitions differing between countries. The classification accepted in the U.S.A. is summarized in Table VI-1.

Different petrographic constituents in coal have different optical properties and form a basis for a classification based on reflectivity (Tschamler and de Ruiter, 1963). In order of increasing reflectances, the major constituents are exinite, vitrinite, micronite and fusinite.

Because of ease of utilization, rank, sometimes supplemented by elemental analysis, has been the classification adopted by industry for providing a measure of those properties that determine the end use of coal. Research workers have been seeking a more fundamental measure of coal behaviour and limited success has been achieved using petrographic analysis. Functional form analysis provides a more fundamental measure of coal structure but its use is qualified by the difficulty of the measurements, which usually require solvation of the coal with possible
TABLE VI-1

ASTM COAL RANK

ASTM - D388-19 (1973)

<table>
<thead>
<tr>
<th>Percent Fixed Carbon on Dry Mineral Matter Free Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;98 Meta-Anthracite</td>
</tr>
<tr>
<td>92-98 Anthracite</td>
</tr>
<tr>
<td>86-92 Semi-Anthracite</td>
</tr>
</tbody>
</table>

Non-Agglomerating

Agglomerating

<table>
<thead>
<tr>
<th>Percent F.C.</th>
<th>Non-Agglomerating</th>
</tr>
</thead>
<tbody>
<tr>
<td>78-86 Low Volatile Bituminous</td>
<td></td>
</tr>
<tr>
<td>69-78 Medium Volatile Bituminous</td>
<td></td>
</tr>
<tr>
<td>&lt;65 High Volatile or Subbituminous</td>
<td></td>
</tr>
</tbody>
</table>

High Volatile or Subbituminous

<table>
<thead>
<tr>
<th>Heating Value on Moist Mineral Matter Free Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;14K H-V-A-Bituminous</td>
</tr>
<tr>
<td>13-14K H-V-B-Bituminous</td>
</tr>
<tr>
<td>10.5-13K H-V-C-Bituminous</td>
</tr>
</tbody>
</table>

Either Non-
Agglomerating or
Non Weathering

Weathering and
Agglomerating

<table>
<thead>
<tr>
<th>Heating Value (BTU/lb)</th>
<th>Weathering and Agglomerating</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.5-11.5K Subbituminous A</td>
<td></td>
</tr>
<tr>
<td>9.5-10.5K Subbituminous B</td>
<td></td>
</tr>
<tr>
<td>8.3-9.5K Subbituminous C</td>
<td></td>
</tr>
<tr>
<td>6.3-8.3K Lignite A</td>
<td></td>
</tr>
<tr>
<td>&lt;6.3K Lignite B</td>
<td></td>
</tr>
</tbody>
</table>
modification of the coal structure.

It is the long-range objective of fundamental coal studies to correlate the behaviour of coals with a classification scheme, preferably simple. For the current study, a lignite and a bituminous coal, two widely different coals, have been selected. The characterization of these, incomplete because of time and financial constraints, is given below.

VI-1.0 Montana Lignite

The Montana lignite was chosen as representative of a low rank, low sulfur, non-caking western coal which could be strip mined. These coals are likely to find future use as raw material for gasifiers and possibly as fuel for local power generation. The reserves of lignites in the United States represent approximately $6 \times 10^4$ quadrillion BTUs or 28.8% of the ultimate United States Coal reserves.

VI-1.1 Visual Appearance of Montana Lignite

Scanning electron micrographs of the Montana lignite used in these studies are shown in figure VI-1. The lignite has been ground and classified to nominally 38-43 microns. The low magnification micrograph shows many small particles have escaped mechanical size classification and a few large, irregularly shaped particles are also present in the supposed narrowly-sized fraction. The micrographs at higher magnification show the particle surface is relatively smooth, has few visible macro-pores, and has ash particles on the order of several microns
RAW MONTANA LIGNITE, 38-45µm

FIGURE VI-1. Scanning electron micrograph of raw Montana lignite-A.
physically held on the surface.

The photomicrographs of polished sections under oil immersion are shown in figure VI-2. The micrographs show that the coal particles are not uniform in internal macropore area or in reflectance. Four different levels of reflectance have been identified in the polished section slides. Most particles appeared to be composed of only one petrographic element although occasionally one particle will contain as many as three different elements.

The top micrograph in figure VI-2 shows three particles of different reflectances. The whitish particle on the right side of the micrograph is tentatively identified as micronite; the highly reflective fusanite particles are very rare in lignites and are not evident in the samples; the dull, barely visible particle just to the left of the micronite particle has been identified as exinite; and the particle below and to the left of the exinite particle has been identified as vitrinite. The top micrograph shows some macropore structure in the vitrinite and exinite, but most of the macropore structure is in the medium reflective micronite. The macropores appear either in micronite in the form of circular voids as large as ten microns in diameter or as dendritic like structures with stem diameters on the order of several microns. Fewer pores are visible in vitrinite and exinite; these pores are either irregular shaped voids on the order of 5-10 microns in diameter, or relatively straight fissures, about one micron in diameter.
FIGURE VI-2. Photomicrograph of polished raw lignite-A.
VI-1.2 Size Distribution

The Montana lignite was received as $\frac{1}{8}$ inch particles. These particles were ground in a ball mill and separated through roto-taped Tyler screens. Most of this study was conducted with the 38-43 micron size range, although some data was taken using the 74-88 micron size range. These two size ranges were chosen as being representative of coal fed to a pulverized coal flame.

The electron micrograph in figure VI-1 showed that the closely sized fraction had a number of undersized particles and a few oversized particles, shown more quantitatively by the particle size distribution in figures VI-3 and VI-4. The cumulative mass distribution was fitted with the Rossin-Rammler (1939) distribution function, as for example in figure VI-3. Scanning electron micrographs of lignite particles were counted on a Zeiss particle counter and Rosin-Rammler parameters were developed using a least square fit of the particle frequency. The mean particle diameter derived from the Rosin-Rammler distribution was 52.3 microns. The Rosin-Rammler derived curve is compared in figure VI-4 with the original data. The original data gave a mean particle size distribution of 47.6 microns and a standard deviation of 15.2 microns. The fit of the data is considered satisfactory, in spite of the differences in calculated and measured frequency at large particle diameters, because the size interval is small and relatively few oversized particles are present.
Figure VI-3. Rosin-Rammler cumulative size distribution of lignite particles.

Rosin-Rammler distribution
Raw lignite

798 particles

b = 1.33 x 10^6
s = 3.42
x = 52.3
FIGURE VI-4. Lignite particle size frequency distribution.
VI-1.3 Surface Area

Numerous measurements of surface areas of raw coal and processed coals have been reported. Spencer and Bond (1966), however, have questioned the use of adsorption isotherms to derive absolute surface areas of microporous solids. Van Krevelen (1961) showed that the areas determined by conventional adsorption methods at liquid nitrogen temperatures are two orders of magnitude lower than values derived from adsorption at room temperature or values derived from methanol heat of wetting data. The diffusion process appears to have an activation energy of about 4 kcal/g-mole. The activated diffusion process accounts for the low values of surface area obtained at low temperature, because the adsorbate cannot penetrate completely into the microstructure of coal in a reasonable period of time at low temperatures.

Marsh (1965) has reviewed the various methods of determining surface area and concluded that adsorption of CO\textsubscript{2} near room temperature gives the most reasonable values for surface areas of coal and cokes. Typical surface areas for coals with less than 85% carbon (dmmf) are in the range of 200 m\textsuperscript{2}/g. Adsorption of inert gases at 77\textdegree K gives values on the order of 2 m\textsuperscript{2}/g. Adsorption of krypton at 77\textdegree K for the lignite used in this study gave a surface area of 2 m\textsuperscript{2}/g when analyzed using the Dubinin-Polanyi equation and 1.2 m\textsuperscript{2}/g when analyzed using the BET equation. These values are not representative of the total surface area but are considered to be representative of that fraction.
of the surface area contained in pores with diameters greater than about 12 Å. (See Van Krevelen, Marsh, Gan, et al., 1972, and Tingey and Morrey, 1973.)

Surface areas from CO₂ adsorption at room temperature are not yet available for the coals used in this study. The surface area is expected to be reasonably close to the surface area of 183 m²/g measured by Nsakala et al (1975) for a North Dakota lignite with a daf carbon content of 71%. This value is slightly lower but in reasonable agreement with the surface areas found by Gan et al (1972) of 225-308 m²/g for North American lignites containing between 63 and 72% carbon. Swann et al. report a value the CO₂ adsorption area of Australian Yallourn brown coal of 290 m²/g comparable to that of American lignites.

The integrated particle size distribution curve yields a superficial surface area of 0.11 m²/g. This value is 20 times smaller than the krypton adsorption area and 2000 times smaller than the normal CO₂ areas for lignites.

VI-1.4 Proximate Analysis

Proximate analysis - moisture, volatile matter and ash content - were performed at three independent laboratories with similar results. The proximate analysis are reported in table VI-2 along with other information for the two coals used in this study. The volatile matter was approximately 36.2%, the equilibrium moisture content was close to 13.6%, and the ash was 7.8% on an as received basis. The lignite was treated as a sparkling coal.
### TABLE VI-2

**COAL CHARACTERIZATIONS**

<table>
<thead>
<tr>
<th>COAL</th>
<th>MINE</th>
<th>BTU/lb MOIST MM FREE*</th>
<th>PROXIMATE ANALYSIS A.R. Wt. %</th>
<th>ULTIMATE ANALYSIS A.R. Wt. %</th>
<th>SULFUR FORMS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>H₂O</td>
<td>VM</td>
<td>ASH</td>
</tr>
<tr>
<td>PITTSBURGH SEAM #8 hVA-b</td>
<td>IRELAND</td>
<td>14,377</td>
<td>2.2</td>
<td>40.7</td>
<td>10.8</td>
</tr>
<tr>
<td>MONTANA LIGNITE-A</td>
<td>SAVAGE</td>
<td>8,809</td>
<td>13.6</td>
<td>36.2</td>
<td>7.8</td>
</tr>
</tbody>
</table>

* HIGHER HEATING VALUES WERE CALCULATED ON THE BASIS OF EQUILIBRIUM MOISTURE WITH MINERAL MATTER, AS DETERMINED BY PADIA (1976) FROM LOW TEMPERATURE ASHING, REMOVED. THE MINE MOUTH MOISTURE CONTENT OF THE BITUMINOUS COAL WILL BE CLOSE TO ITS EQUILIBRIUM MOISTURE CONTENT SO THE HEATING VALUE WILL REMAIN UNCHANGED. LIGNITE FROM THE SAVAGE MINE HAS BEEN FOUND BY PAULSON ET AL. (1972) TO CONTAIN 28.2% MOISTURE; THE HEATING VALUE CALCULATED ON THIS BASIS WOULD BE 7346 BTU/lb.
VI-1.5 Heat of Combustion

Rank classification of coal, below 69% daf carbon content, is based on the heating value and the agglomerating and aggluti-
ting properties of the coal. The heating value is the high
heating value of the coal (water as a liquid) on moist mineral
free basis. The mineral matter is usually calculated based on
the ash and sulfur content of the coal by empirical equations,
most frequently the Parr formula, but is best obtained by use
of low-temperature ashing.

The heat of combustion was measured on a dry sample of the
Montana lignite and corrected to a moist mineral free basis
using the mineral matter determined by low temperature ashing
and either the equilibrium moisture content or the moisture
content found by Paulson et al (1972), for samples from the
same mine. The heating values are in reasonable agreement with
heating values previously calculated using the Dulong formula.
The measured heating value is reported in Table VI-1 as 8809
BTU/lb with equilibrium moisture content and 7346 BTU/lb with
mine moisture; the latter value classifies the coal used in this
study as lignite-A.

VI-1.6 Elemental Analysis

Ultimate analysis of the coals used in this study were
performed at the Galbraith Laboratories, Inc., Knoxville,
Tennessee and are reported in Table VI-2 on an as received
basis and in Table VI-3 on several common bases. Sulfur form
## TABLE VI-3

**LIGNITE**

CHARACTERIZATION OF MONTANA LIGNITE
FROM THE SAVAGE MINE IN RICHLAND COUNTY,
GROUND AND CLASSIFIED TO 38-45µ

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>ULTIMATE AIR</th>
<th>ULTIMATE DRY</th>
<th>ULTIMATE daf</th>
<th>ULTIMATE dmf*</th>
<th>ULTIMATE C-H-O BASIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>13.60</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>54.90</td>
<td>63.54</td>
<td>69.88</td>
<td>73.30</td>
<td>71.30</td>
</tr>
<tr>
<td>H</td>
<td>4.96</td>
<td>5.74</td>
<td>6.31</td>
<td>6.62</td>
<td>6.44</td>
</tr>
<tr>
<td>N</td>
<td>0.72</td>
<td>0.83</td>
<td>0.92</td>
<td>1.23</td>
<td>-</td>
</tr>
<tr>
<td>Pyritic S</td>
<td>0.11</td>
<td>0.13</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.18</td>
<td>0.21</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ORGANIC S</td>
<td>0.55</td>
<td>0.64</td>
<td>0.73</td>
<td>0.73</td>
<td>-</td>
</tr>
<tr>
<td>TOTAL S</td>
<td>0.84</td>
<td>0.98</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ASH</td>
<td>7.84</td>
<td>9.07</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O(DIFF.)</td>
<td>17.14</td>
<td>19.84</td>
<td>22.16</td>
<td>18.12</td>
<td>22.26</td>
</tr>
</tbody>
</table>

* MINERAL MATTER FOUND FROM LOW TEMPERATURE ASHING BY PADIA (1976) TO BE 11.50% (WET BASIS)
analysis is also reported in Table VI-2.

The Montana lignite contained 73.3% carbon on a dry mineral matter free basis, 0.83% nitrogen and 0.98% sulfur on a dry basis. Approximately 65% of the sulfur is organic sulfur. Oxygen was determined by difference so is not considered very accurate. Oxygen is determined by subtracting ash and all other elements from 100%. This procedure can lead to rather substantial errors in the oxygen concentration because mineral matter changes weight when sulfides and carbonates react during ashing. The procedure gives 22% too high an oxygen concentration for the Montana lignite.

VI-1.7 Ash Analysis

The mineral elements of ash (Table VI-4) were determined by atomic absorption of the metallic elements, reported as if the elements are in their natural oxidation state.

The principal component of mineral matter in coals is common clays such as SiO₂ and Al₂O₃. The ash from a Montana lignite contained 27% silica and 16% alumina. The ash also had high concentrations of calcium (28% as CaO), magnesium (9% as MgO), and a surprisingly large amount of sulfur (13.5% as SO₃). Iron and phosphors are the only other significant elements; Fe₂O₃ accounts for 3.4% of the ash and P₂O₅ accounts for 1%. Titanium, potassium, and sodium are the remaining major elements in the lignite ash.
### TABLE VI-4

**ASH CHARACTERIZATION**

<table>
<thead>
<tr>
<th>Wt.% on ignited basis</th>
<th>Montana Lignite-A</th>
<th>Pittsburgh Seam #8 High Volatile Bituminous-A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash</td>
<td>7.84</td>
<td>10.55</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1.02</td>
<td>0.30</td>
</tr>
<tr>
<td>SiO₂</td>
<td>26.80</td>
<td>37.52</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.41</td>
<td>29.34</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>16.41</td>
<td>19.15</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.50</td>
<td>0.57</td>
</tr>
<tr>
<td>CaO</td>
<td>28.44</td>
<td>4.65</td>
</tr>
<tr>
<td>MgO</td>
<td>9.02</td>
<td>0.73</td>
</tr>
<tr>
<td>SO₃</td>
<td>13.45</td>
<td>4.10</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.35</td>
<td>1.29</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.27</td>
<td>0.38</td>
</tr>
</tbody>
</table>

VI-1.8 Functional Group Analysis

No functional group analysis has, as yet, been performed on the coals used in this study, nor has a functional group analysis of the lignite used in this study been found in the literature. Tingey and Morrey have compiled average functional group analysis for various rank coals from literature values. Values for the functional group composition for a lignite of 70.6% carbon will be used for comparison purposes until direct measurements become available.

Tingey and Morrey's functional group distribution is shown in Table VI-5. A lignite can be expected to have an average ring size of about 2-4, 27% of the carbon will be aliphatic carbon and 65% of the hydrogen will be attached to aliphatic carbons. Most of the carbon (51.7%) in such small ring systems is peripheral carbon. The aliphatic hydrogen is mostly attached to aliphatic carbon that is attached either to α or β position to an aromatic ring; hydroxyl hydrogen accounts for only 4.6% of the hydrogen.

Oxygen concentration and distribution are not included in the functional group summary presented by Tingey and Morrey. Oxygen concentrations can be estimated by difference, after allowance for a concentration of nitrogen and sulfur of about 2%. The oxygen concentration obtained by difference is 23%, which is a high but reasonable value for an American lignite. Hydroxyl oxygen may then account for a third of the oxygen present with most of the remaining oxygen present as carbonyl oxygen. These results are consistent with generalized analysis reported by Dryden (1963).
TABLE VI-5

FUNCTIONAL GROUP ANALYSIS OF A LIGNITE

From Tingey and Morrey (1973)
and Dryden (1963)

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Hydrogen Distribution % of total H</th>
<th>Carbon Distribution % of total C</th>
<th>Oxygen Distribution % of total O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total daf</td>
<td>4.74</td>
<td>70.6</td>
<td>-22.</td>
</tr>
<tr>
<td>Average Ring Sizes</td>
<td>-</td>
<td>2-4</td>
<td>-</td>
</tr>
<tr>
<td>Aromatic</td>
<td>30.7</td>
<td>73.2</td>
<td>-</td>
</tr>
<tr>
<td>Monoring</td>
<td>16.4</td>
<td>13.2</td>
<td>-</td>
</tr>
<tr>
<td>Condensed Ring</td>
<td>14.3</td>
<td>11.5</td>
<td>-</td>
</tr>
<tr>
<td>Peripheral C</td>
<td>-</td>
<td>51.7</td>
<td>-</td>
</tr>
<tr>
<td>Interior C</td>
<td>-</td>
<td>21.5</td>
<td>-</td>
</tr>
<tr>
<td>Aliphatic</td>
<td>64.7</td>
<td>26.8</td>
<td>-</td>
</tr>
<tr>
<td>Methylene Bridges</td>
<td>14.0</td>
<td>16.9</td>
<td>-</td>
</tr>
<tr>
<td>$\alpha \text{CH}_x$</td>
<td>25.7</td>
<td>17.6</td>
<td>-</td>
</tr>
<tr>
<td>$\beta \text{CH}_x$</td>
<td>23.7</td>
<td>9.2</td>
<td>-</td>
</tr>
<tr>
<td>Hydroxyl</td>
<td>4.6</td>
<td>3.7</td>
<td>-36.</td>
</tr>
<tr>
<td>Carbonyl</td>
<td>-</td>
<td>-</td>
<td>-45.</td>
</tr>
<tr>
<td>Carboxyl</td>
<td>-</td>
<td>-</td>
<td>-19.</td>
</tr>
</tbody>
</table>
VI-2.0 Pittsburgh Seam #8 Bituminous Coal

The Pittsburgh bituminous coal was chosen as a coal representative of a deep mined, high sulfur, caking eastern coal. This coal is highly swelling and caking and is representative of coals that might be used in coking operations or in direct fired utility boilers. United States reserves of bituminous coal represent about 46% of total coal reserves or approximately 9.6 x 10⁶ quadrillion BTUs.

VI-2.1 Visual Appearance of Pittsburgh Bituminous Coal

The bituminous coal was ground and classified in the same manner as the lignite. Scanning electron micrographs of the classified bituminous coal are shown in figure VI-5. The electron micrograph at low magnification shows, as for lignite, irregular shaped particles and poor classification. There are more fines present in the bituminous coal than in the lignite, and this is thought to be because the bituminous coal has much lower equilibrium moisture content and exhibits more pronounced static attraction. The bituminous coal, when viewed under higher magnification, appears to have a hard, smooth surface with some visible fracture patterns. The lignite had very few macropores but the bituminous coal appears to be almost entirely free of such large external openings. A few micron-size ash particles were observed clinging to the bituminous coal particle surface.

Polished surfaces of bituminous coal, shown in figure VI-4 viewed under cedar oil exhibit similar petrographic elements to those observed earlier for lignite. The predominance of
RAW PITTSBURGH SEAM #8 BITUMINOUS COAL
38-45\(\mu\)m

FIGURE VI-5. Scanning electron micrograph of raw Pittsburgh seam #8 hvA bituminous coal.
FIGURE VI-6. Photomicrograph of polished raw Pittsburgh seam #8 hvA bituminous coal.
a low reflecting element, most likely vitrinite, and two elements that reflect more light are seen in the top micrograph. The larger and darker of the two highly reflecting elements appears similar to the element identified as micronite in the lignite; the smaller highly reflective element appears to be a rare fusanite element. The macropore structure of the micronite elements appears to be less pronounced than was found for the lignite, but the lower reflective elements in bituminous coal appear to have greater macropore structure than the lignite. As in the lignite, most particles are petrographically pure, although several petrographic forms are occasionally observed; for example, three different reflectivities are evident in one particle in the bottom micrograph.

VI-2.2 Particle Size Distribution

Mass particle size distributions, calculated in the same manner as for the lignite, gave a poorer fit of the data for bituminous coal than for lignite, even though more than three times as many particles were counted. The fit of cumulative particle mass by the Rosin-Rammler distribution function is shown in figure VI-7. The mass average particle size determined from the cumulative distribution is 64.9 microns, while average particle diameter determined from the raw data is 57.5 microns and the standard deviation is 22.2 microns. The average particle size determined from both methods is larger than the maximum screen size of 43 microns. A 43 micron opening could allow a particle with a maximum dimension in at least one direction
FIGURE VI-7. Rosin-Rammler accumulative size distribution of bituminous coal particles.
of about 60 microns to pass. Narrow particles with two dimensions less than the maximum size opening could pass through the screen with a very large size in one dimension. Electron micrographs were checked and a few odd shaped particles appeared in the pictures. A few large particles can skew a mass average distribution to much higher mass average particle sizes. Another possibility that cannot be completely eliminated, but which could account for the large particles present in the classified sample is rents or enlarged holes in the screens. The original data and the derived Rosin-Rammler distribution curve are shown in figure VI-8. The agreement is considered satisfactory with the reservations previously mentioned in the section on lignite distribution.

VI-2.3 Surface Area

Surface areas, determined using krypton adsorption, are as in the case of lignite significantly below the true surface area, representing only pores with restrictions greater than about 12 Å. Calculations of the surface area from krypton adsorption data at 77.0 K using the Dubinin-Polanyi equation gave 2.1 m²/g, the BET equation gave 1.25 m²/g. Gan et al (1972) measured the CO₂ adsorption area for a Pittsburgh seam bituminous coal with 82.4% carbon (dmmf) and found a surface area of 141 m²/g. This value is consistent with the value of about 150 m²/g obtained from neon adsorption at 298.0 K for a coal with 83% C (Dryden, 1963).
RAW BITUMINOUS
FREQUENCY DISTRIBUTION

\( \bar{x} = 57.5 \)
\( \sigma = 22.2 \)
\( s = 2.54 \)
\( b = 2.49 \times 10^{-5} \)
2574 Particles

FIGURE VI-8. Bituminous particle size frequency distribution.
VI-2.4 Proximate Analysis

Proximate analyses for the bituminous coal of this study is reported on an as received basis in Table VI-2. The Pittsburgh seam #8 bituminous coal has a low equilibrium moisture content of about 2.2%. This value is taken to be representative of mine samples.

VI-2.5 Heat of Combustion

The heat of combustion of the Pittsburgh Seam #8 bituminous coal, determined in the same way as that of lignite, is 14,377 BTU/lb on a moist mineral matter free basis. This value is consistent with other values reported for Pittsburgh seam coals and classifies this coal as a high volatile A bituminous coal.

VI-2.6 Elemental Analysis

Elemental analysis of the bituminous coal and sulfur form analysis are presented in Table VI-2 on an as received basis, and in Table VI-6 on other commonly used bases. The bituminous coal has 1.04% nitrogen and a high sulfur content of 4.55% on an as received basis. The major portion of the sulfur is pyritic (2.29%) but the organic sulfur is much higher (1.58%) than that of ordinary plant materials. The carbon content is 82.27% on a dry mineral matter free basis.

VI-2.7 Ash Analysis

The ash composition of the two coals are compared in Table VI-4. The bituminous coal has a higher ash content than lignite,
TABLE VI-6

BITUMINOUS COAL

CHARACTERIZATION OF PITTSBURGH SEAM #8

BITUMINOUS COAL FROM THE IRELAND MINE

GROUND AND CLASSIFIED TO 38-45μ

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>ULTIMATE A.R.</th>
<th>ULTIMATE DRY</th>
<th>ULTIMATE daf</th>
<th>ULTIMATE dmf*</th>
<th>ULTIMATE C-H-O BASIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>2.20</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>67.90</td>
<td>69.46</td>
<td>77.80</td>
<td>82.27</td>
<td>83.31</td>
</tr>
<tr>
<td>H</td>
<td>4.91</td>
<td>5.01</td>
<td>5.62</td>
<td>5.95</td>
<td>6.01</td>
</tr>
<tr>
<td>N</td>
<td>1.04</td>
<td>1.06</td>
<td>1.19</td>
<td>1.26</td>
<td>-</td>
</tr>
<tr>
<td>Pyritic S</td>
<td>2.29</td>
<td>2.35</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.68</td>
<td>0.65</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Organic S</td>
<td>1.58</td>
<td>1.52</td>
<td>1.81</td>
<td>1.91</td>
<td>-</td>
</tr>
<tr>
<td>Total S</td>
<td>4.55</td>
<td>4.53</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ASH</td>
<td>10.52</td>
<td>10.76</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O(DIFF.)</td>
<td>8.88</td>
<td>9.19</td>
<td>13.58</td>
<td>8.61</td>
<td>10.87</td>
</tr>
</tbody>
</table>

* Mineral matter found from low temperature ashing by Padia (1976) to be 15.27% (wet basis).
about 10.5 weight percent versus about 7.8 percent. A very
large portion of the bituminous coal's ash is composed of iron
compounds, mostly present as pyrites (Padia, 1976). The high
pyrites content of the mineral matter accounts for the major
portion of the sulfur content of the bituminous coal. Iron,
calculated as ferric oxide accounts for 30% by weight of the
ash compared with 38% for silica and 19% for alumina. Calcium,
residual sulfur trioxide and potassium are the only other con-
stituents of consequence in bituminous ash.

VI-2.8 Functional Group Analysis

Functional group analysis has not as yet been performed
on the bituminous coal sample of this study. A partial func-
tional group analysis has been reported in the literature on a
vitrain concentrated sample of a Pittsburgh Seam bituminous
coal. Heredy and Fugassi (1966) investigated a benzene extract
for hydrogen distribution by proton NMR for a vitrain concen-
trate from the same mine (Ireland) as the bituminous coal used
in this study. Their results showed that 16.3% of the hydrogen
was substituted on condensed aromatic rings, 14.7% of the hydro-
gen was attached to either monocyclic aromatic rings or pheno-
lic oxygen; 69% of the hydrogen was attached to aliphatic car-
bons, 29.6% to α carbons and 39.4% to β carbons. These figures
agree only fairly with the figures reported in Table VI-7 and
have not been considered in constructing Table VI-7 since the
benzene extract accounted for only about 10% of the total coal.
TABLE VI-7

FUNCTIONAL GROUP ANALYSIS OF
A HIGH VOLATILE BITUMINOUS COAL

From Tingey and Morrey, (1973)
and Dryden, (1963)

<table>
<thead>
<tr>
<th></th>
<th>Hydrogen Distribution</th>
<th>Carbon Distribution</th>
<th>Oxygen Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% of total H</td>
<td>% of total C</td>
<td>% of total O</td>
</tr>
<tr>
<td>Total daf</td>
<td>5.57</td>
<td>82.4</td>
<td>~9.</td>
</tr>
<tr>
<td>Average Ring Size</td>
<td>-</td>
<td>5-8</td>
<td>-</td>
</tr>
<tr>
<td>Aromatic</td>
<td>19.6</td>
<td>70.5</td>
<td>-</td>
</tr>
<tr>
<td>Monoring</td>
<td>11.2</td>
<td>52.9</td>
<td>-</td>
</tr>
<tr>
<td>Condensed Ring</td>
<td>8.4</td>
<td>6.8</td>
<td>-</td>
</tr>
<tr>
<td>Peripheral C</td>
<td>-</td>
<td>37.1</td>
<td>-</td>
</tr>
<tr>
<td>Interior C</td>
<td>-</td>
<td>33.4</td>
<td>-</td>
</tr>
<tr>
<td>Aliphatic</td>
<td>75.7</td>
<td>29.5</td>
<td>-</td>
</tr>
<tr>
<td>Methylene Bridges</td>
<td>5.3</td>
<td>6.4</td>
<td>-</td>
</tr>
<tr>
<td>$\alpha$ CH$_X^-$</td>
<td>36.0</td>
<td>15.4</td>
<td>-</td>
</tr>
<tr>
<td>$\beta$ CH$_X^+$</td>
<td>37.8</td>
<td>14.1</td>
<td>-</td>
</tr>
<tr>
<td>Hydroxyl</td>
<td>4.7</td>
<td>3.8</td>
<td>45.</td>
</tr>
<tr>
<td>Carbonyl</td>
<td>-</td>
<td>-</td>
<td>55.</td>
</tr>
<tr>
<td>Carboxyl</td>
<td>-</td>
<td>-</td>
<td>0.</td>
</tr>
</tbody>
</table>
Retcofsky and Friedel (1970) have also investigated functional group distribution of a vitrain rich sample of the coal from a Pittsburgh seam bituminous coal. Their findings are consistent with the results of Tingey and Morrey reported in Table VI-7. Retcofsky and Friedel studied high resolution proton NMR of pyridine and carbon disulfide coal extracts. The pyridine extract contained 21.4% of the coal and had an elemental analysis close to that of the whole coal; the carbon disulfide extract contained only 2.5% of the coal and had significantly higher carbon and hydrogen contents and lower oxygen content than the original coal. Aromatic carbon accounted for 73% of the carbon in the pyridine extract, 35% of the hydrogen was aromatic, the α aliphatic hydrogen accounted for 26% and β+ hydrogen accounted for 36% of the total hydrogen. Hydroxyl hydrogen accounted for only 3% of the total hydrogen. The values derived from the carbon disulfide extract were similar although a higher percentage of aliphatic compounds seem to be present in the carbon disulfide extract.

The average ring size of a high volatile bituminous coal with 83% carbon content may be 5-8; the distribution of the carbon may be about 70% aromatic, 30% aliphatic, with only 6% of the carbon in methylene bridges; the distribution of the hydrogen may be 20% aromatic, 75% aliphatic and about 5% in the phenolic OH; the oxygen may be split equally between hydroxyl and carbonyl oxygen with negligible amounts in carboxyl and ether groups.
VI-3 Physical Properties of Coal

Estimates of some of the physical properties of coal have been used in this study. These values are not very accurate and have been used only for crude calculations. The values of interest are specific gravity, thermal conductivity, and specific heat. The interpretation of these values for a substance such as coal that is very heterogenous and changes both chemically and physically when mildly heated is questionable. Even when no changes occur in the coal the values are uncertain because the values strongly depend on coal rank, mineral matter content and moisture content.

Average values of the physical properties needed have been taken from McCabe and Boley (1945), Badzioch et al (1964) and Kirov (1965). Specific gravity is usually between 1.3 and 1.35 for coals. Specific gravity will increase roughly 0.01 unit for a percent increase in ash content. Thermal conductivity of raw coals below 400°C varies from $5 \times 10^{-4}$ to $8 \times 10^{-4}$ cal/g-cm-sec-K. Above about 300-400°C, where carbonization reactions begin, the thermal conductivity rises rapidly until at 900°C (the maximum temperature in Badzioch et al's study) it has a value of about $60 \times 10^{-4}$ cal/g-cm-sec-K. This high value in all probability represents conductive heat transfer augmented by radiative transfer through pores and convective transfer by volatile products flowing through cracks and pores. The latter two effects are difficult to separate from the former experimentally. The thermal conductivity of the particle is needed for purposes of calculating the rate of temperature rise in the
particle. Since the resistance to heat transfer by conduction within the particle is negligible relative to the external resistance, uncertainty in the value of the thermal conductivity is of little significance.

Measurements of specific heat will also be effected by the heterogenous nature of coal and by the physical and chemical changes coal goes through as it is heated. The specific heat of raw coal increases with increasing volatile matter and increasing moisture content and decreases with increasing ash content. The specific heat of raw coals with less than 10% volatile matter (d.a.f.) will be between 0.2 and 0.25 cal/g-K, while coals with volatile matter (d.a.f.) between 10 and 50% will have specific heats between 0.25 and 0.35 cal/g-K. Coals with volatile matter in the range of 40% (d.a.f.) will have specific heats around 0.3 cal/g-K.

Char residuals (based on weight of raw coal) could have a maximum specific heat of 0.42 cal/g-K at 320°C for a char from a coal with 50% d.a.f. volatile matter. The specific heat of chars produced from coals with volatile matter (d.a.f.) greater than 30% have a specific heat maximum in the region of rapid devolatilization. The specific heat then decreases towards an asymptotic value at temperatures above 1100°C. The position of the specific heat maximum is displaced towards higher temperatures as the volatile matter of the coal decreases. Chars produced from coals with d.a.f. volatile matter in the range of 30-40% would be expected to have a specific heat value of about 0.33 cal/g-K based on the weight of the raw coal.
VII. COAL RESULTS

This section will report the results obtained on evolution and oxidation of nitrogen contained in coal using the equipment and procedures described in section V. The results described include nitrogen loss from coal held in crucibles, nitrogen loss from coal rapidly heated in the dispersed phase, and conversion of coal and char nitrogen to nitric oxide when burned in a small coal flame.

VII-1. The Coal Flame

Coal supplies slightly over half of the fossil fuel burned to generate electric power. Its use can be expected to increase as the other fossil fuels become less abundant and more costly. Most of the coal burned for power generation is burned in pulverized coal flames in large units (hundreds of megawatts electrical capacity). Combustion of coal yields higher emissions of sulfur dioxide, particulate matter, and nitrogen oxides than other fuels. The data reported in this section were taken in an effort to understand some of the complex aspects of the oxidation and reduction of the nitrogen contained in the coal with the ultimate goal of investigating strategies for control of the fuel nitrogen contribution to total nitrogen oxide emissions.

A schematic of a pulverized coal flame is shown in Figure VII-1. Coal is ground to less than 200 micron particles, most particles are less than 100 microns, and fed through the
FIGURE VII-1 Schematic of a single coal particle burning in a pulverized coal flame.
primary injection nozzle. A fraction of the total air (usually 15-20% of the stoichiometric air requirements) is used to carry the coal into the flame region. A large 500 mw utility boiler typically feeds about 200 tons/hr coal and 3300 tons/hr air. If four burners are used, each burner will be fed 50 tons/hr coal and about 50 tons/hr air through the primary nozzle. The remaining air is preheated and fed through swirl vanes surrounding the primary nozzle.

The coal particles exit the nozzle in a slightly fuel rich atmosphere. The reducing nature of this atmosphere is increased further by recirculation of partially combusted gases from the flame region. The coal particles are heated, possibly as high as 2200°C, by the hot recirculating gases in about one millisecond. The coal particle rapidly loses volatile matter over the next tens of milliseconds. This volatile matter, depending on the velocity and uniformity of ejection, can exclude oxygen from the particle surface and burn as a diffusion flame surrounding the particle. The volatile matter may not be able to form an effective oxygen shield in all cases, and the particle will simultaneously undergo gas phase volatile matter burning and heterogeneous solid phase combustion. Burning of the volatile matter is usually complete in about 100 milliseconds.

Volatile burning will leave a char residue, even if the solid has been burning simultaneously with the volatile matter. The char will be heterogeneously oxidized in about 300 milliseconds. Most gas phase constituents will approach
equilibrium concentration as the combustion products exit. Nitrogen oxides, however, will not approach equilibrium concentration, even in a long residence time reactor such as a large utility boiler. Gas phase equilibrium takes on the order of several seconds at the high temperatures existing in coal fired boilers.

Experiments that might be used to isolate the different regions of coal combustion are listed at the bottom of Figure VII-1. Volatile matter removal can be investigated by devolutilizing coal under conditions of reduced oxygen concentration which suppress ignition of the particle. Devolatilization of coal particles under inert atmospheres will be reported in this section. Coal oxidation under the conditions when the coal particle is surrounded by a diffusion flame of the volatile matter can be investigated by burning the coal particle in a dilute phase so that particles have little interaction with each other. Only overall oxidation experiments where the coal particles burned as small diffusion flames will be reported in this section. Char oxidation kinetics can be investigated by manufacturing the char in an atmosphere where the coal particles will not ignite and then reinjecting the coal particles into an oxidizing atmosphere where the particles will burn heterogeneously as individual particles. Some results from char oxidation will be reported in this section. The gas phase reactions of the products produced from coal devolatilization and partial combustion, descriptions of which are needed to complete the picture of the oxidation of the
nitrogen content in coal, are best studied in simplified systems such as flat flame burners, and do not constitute part of the present study.

**VII-2.0 Devolatilization Results**

Coal was devolatilized under three different modes of operation in this study. The first mode is devolatilization of crucible held samples. This procedure is described in section V-3. The second mode is the free fall mode which is described in sections V-2. The third mode is the laminar flow mode which is described in section V-1.

**VII-2.1 Devolatilization Results from Crucible Experiments**

The purpose of the crucible experiments is to investigate the effect of temperature on the behavior of coal devolatilization in inert atmospheres at long residence times. The nature of the experiments precluded the attainment of the rapid heating conditions typically found in pulverized coal flames. Heating rates were typically on the order of several degrees Kelvin per second. The data reported here are for times at which the coal weights had reached their asymptotic values.

**VII-2.1.1 Pittsburgh Seam #8 hvA-Bituminous Coal**

Figure VII-2 shows the retention of various elements in the coal and ultimate weight loss for crucible held coal as the temperature increases from 600 to 2200°K. The chars were
FIGURE VII-2  Crucible devolatilization of Pittsburgh Seam #8 hv A-bituminous
analyzed after times considered to represent asymptotic weight loss and are represented on a dry basis. The weight loss for temperatures above about 1200°K is asymptotic at about 40%, below 1200°K the weight loss drops. The weight loss observed after 12 hours at 600°K is only about 10%. Carbon loss levels off at 1200°K, when the weight loss is about 30%. Hydrogen is initially removed more slowly than oxygen but after both oxygen and hydrogen contents of the char have dropped to about 40% of their original values the rate of fractional loss of hydrogen and oxygen loss become approximately equal. Oxygen, hydrogen, and nitrogen are completely removed from the char at high temperatures, under the conditions of asymptotic weight loss. Nitrogen is much more stable in the char than either hydrogen or oxygen.

VII-2.1.2 Montana Lignite-A

Element loss from the lignite samples held in crucibles is shown in Figure VII-3. The retention trends of the various elements are very similar to the trends observed for similar experiments using the bituminous coal. The proximate analysis volatile matter, dark symbols, agrees well with the ultimate weight loss obtained by slowly heating coal samples. Carbon loss and total weight loss increase only slightly above the proximate analysis temperature of 1223°K. The asymptotic carbon loss was about 20% although the carbon loss appeared to increase slightly as the devolatilization temperature increased above 1700°K. The char showed no additional weight
FIGURE VII-3 Crucible devolatilization of Montana lignite-A.
loss above about $1600^\circ$K. The asymptotic weight loss was 44% which is only slightly greater than the proximate volatile matter of 41%. Little weight loss of carbon occurs at low temperatures.

Oxygen, hydrogen, and nitrogen are completely removed at high temperatures. Hydrogen and oxygen loss as the percent of the element originally present are very nearly the same. Initially there is approximately five times as much hydrogen present as oxygen on a mole basis. Hydrogen and oxygen contents are reduced to low values at temperatures in the range of $1600^\circ$K and are both reduced to zero above $1800^\circ$K.

Nitrogen is, again, the most refractory of the elements that are completely removed from coal. The lignite coal used in this study has approximately 28% of the original nitrogen removed under proximate analysis conditions. This value agrees well with the amount of nitrogen removed under the crucible tests of this study.

**VII-2.2 Devolatilization of Dispersed Coal Particles**

Experiments were conducted on devolatilization of coal falling freely through an inert gas surrounded by hot walls. The purpose of this set of experiments was to obtain devolatilization data for coal that is rapidly heated ($\sim 10^4^0$K/sec) in a dispersed phase for relatively long residence times, on the order of one second. A slight modification of this experiment was used to gather data on rapidly heated coal devolatilization at longer residence times by dropping the
coal into a crucible where further devolatilization of the char, occurs on a sample held at the maximum temperature of the experiment.

**VII-2.2.1 Pittsburgh Seam #8 Bituminous Coal**

Data gathered on element loss from the bituminous coal under a variety of experimental conditions, including free fall conditions, is shown in Figure VII-4. The free fall data has a residence time of approximately one second and the free fall into a crucible data has residence times varying from $3 \times 10^4$ to $6 \times 10^5$ seconds. The laminar flow experiments gave devolatilization residence time from several milliseconds to a maximum of about 300 milliseconds. The long residence time data is replotted from the crucible experiments discussed in section VII-2.1.1.

The retention of the various elements are plotted in Figure VII-4 versus time in milliseconds with furnace temperature as a parameter. A log time scale is used so that the data can be represented on one plot. The retention of each element (weight percent of the original element retained after devolatilization) is plotted with a common time axis to facilitate comparisons of the stability of the different elements in the coal matrix. The solid lines extended past one second represent retention of the element for coal that has been dropped through the furnace, caught in a crucible, and held at furnace temperature for the time indicated. The dotted lines connecting two points represent the change in retention with additional
PERCENT OF ELEMENT RETAINED IN CHAR
PITTSBURG SEAM #8 BITUMINOUS COAL

FIGURE VII-4  Element loss with devolatilization of a
Pittsburgh Seam #8 hvA-bituminous coal.
devolatilization when the char produced at the shorter residence time is reinjected into the furnace and held at the same temperature for additional time.

An asymptotic carbon retention of 75% was approached at 300 milliseconds for 1260°K, of 65% at 100 milliseconds for 1510°K, and of 60% at 50 milliseconds for 1740°K. Although the total weight loss appeared to attain an asymptotic value of 52% dry at 1940°K and 32 milliseconds and 57% dry at 2100°K and 21 milliseconds, the carbon loss does not appear to be complete. This implies that further slow carbon loss might be obtained at longer residence times at these high temperatures. The carbon retention was about 50% at 32 milliseconds and 1940°K and about 40% at 21 milliseconds and 2100°K. Kobayashi (1976) presents a more complete discussion of the same data and analysis of the char and figures on weight loss are included in Appendix IV.

Hydrogen is relatively easy to remove from coal during pyrolysis. Below 1260°K, hydrogen loss is relatively rapid until about 50% of the hydrogen has been removed, the remaining hydrogen is removed much more slowly. However, hydrogen can be almost completely removed at 1260°K for residence times on the order of ten minutes. At high temperatures the complete removal of hydrogen is rapid, 21 milliseconds at 2100°K. Large quantities of hydrogen are still retained in the char after pyrolysis at 740°K for 22 hours. Slow evolution of hydrogen probably continues for even longer periods at 740°K, unless further evolution of hydrogen is constrained
by thermodynamics.

Nitrogen is the most difficult element to ultimately remove from the coal matrix after carbon. At low temperatures, around 700°K, nitrogen loss is very small, at 1260°K nitrogen loss is also small but can be seen to continue at a slow rate by the two square points joined by dotted lines. Nitrogen removal is complete at temperatures above 1500°K at long, but reasonable residence times, as indicated by the data around five minutes residence times. Nitrogen removal by pyrolysis and oxidation is the major concern of this thesis and will be discussed in more detail from an expanded plot of nitrogen removal.

Sulfur is not as difficult to remove from coal as carbon and nitrogen, but is more difficult to remove than hydrogen and oxygen. The data indicates that at temperatures below about 1900°K sulfur removal is slow once 50% of the sulfur has been removed. The amount of sulfur easily removed from coal is apparently temperature dependent. The asymptotic retention of sulfur in the char at 1260°K is about 70% but at 1510 and 1740°K is about 40%. Sulfur was almost completely removed at 2100°K and 21 milliseconds.

Oxygen appears to be slightly easier to remove than hydrogen at higher temperatures but somewhat more difficult to remove at lower temperatures. All the oxygen can be removed at 1260°K and ten minutes residence time or at times less than 7 milliseconds at temperatures of 2100°K and less than 15 milliseconds at 1940°K. Slow evolution of oxygen at 1260°K
is evident from the decrease in oxygen concentration between the two points connected by a dotted line.

VII-2.2.2 Montana Lignite

Data on the element retention of devolatilized lignite (shown in Figure VII-5) used in this study versus residence time at different furnace temperatures is similar to the results for the bituminous coal just presented. The release of hydrogen appears to be more rapid under certain conditions for lignite than bituminous coal; all the other elements showed a similar behavior for bituminous coal and lignite. The curves for element retention are, in general, similar in shape and magnitude to the retention curves developed for bituminous coal.

Carbon loss appears to become asymptotic for all temperatures at about 100 milliseconds. The asymptotic carbon retentions are: 75-80% at 1260°K, 65% at 1510°K, 55-60% at 1740°K, ~50% at 1940, and ~40% at 2100°K. Little additional carbon appears to be removed under conditions of low temperature and long residence times.

Hydrogen loss is complete at either moderate temperatures and long residence times or high temperatures and short residence times. For example, hydrogen was completely removed from char devolatilized at 1750°K for five minutes or at 2100°K for 30 milliseconds. Hydrogen is more easily removed from lignite than from bituminous coal at temperatures below 1510°K; above this temperature the rate of hydrogen removal from the two coals appears to be approximately equal.
FIGURE VII-5. Element loss with devolatilization of a Montana lignite-A.
Nitrogen, as for bituminous coal, is the element most resistant to ultimate devolatilization after carbon. The rates of nitrogen removal from bituminous coal are slightly faster than from lignite at all temperatures. The difference is, however, not great. The nitrogen removal from both coals will be discussed in more detail later.

The percent removal, from the two coals, of sulfur show similar behavior, with the exception of the greater sulfur removal at 1260°K from the bituminous coal. As for bituminous coal, sulfur removal is relatively slow. Indications are that sulfur can be completely removed at high temperatures but cannot be effectively removed at low temperatures. Asymptotic retention of sulfur at temperatures below 1510°K is approximately 50%.

Percentage oxygen removal from lignite is approximately equal to the removal for bituminous coal at temperatures below 1510°K, but oxygen removal from bituminous coal is considerably faster at temperatures above 1940°K. Oxygen can be completely removed within reasonable times from lignite char at all temperatures above 1260°K.

VII-2.2.3 Nitrogen Pyrolysis from Lignite and Bituminous Coal

The nitrogen retention data from Figures VII-4 and 5 for the fast flow and free fall experiments is replotted in Figure VII-6 with expanded scales. The retention for the bituminous coal shows two discrepancies for nitrogen retention at 1260°K. One point at 1260°K shows less retention than the
FIGURE VII-6 Retention of nitrogen in devolatilized lignite and bituminous coal chars.
well established retention curve at 1510^0\text{K} and a second point shows less weight loss than a similar free fall point at 1000^0\text{K}. Both these points are thought to be erroneous and should be rechecked.

There are two features of the retention curves for lignite that also should be noted. One datum point has higher retention than a smooth curve through the rest of the data would indicate. This point was obtained in an attempt to increase the residence time of the fast flow furnace past the residence times that the furnace yielded when operated in the normal mode. The plasma gun could not be used to heat the large quantity of gas used to carry the particle at the low flow rate required; it is, therefore, likely that this point had a significantly lower temperature than the rest of the data at 1510^0\text{K}. Two data points taken at a temperature of 1740^0\text{K} and short residence times show approximately the same small nitrogen loss. The nitrogen content of the original coal has been checked many times but, the nitrogen content determined by the Dumas method gave consistently lower results than the nitrogen content determined by the Kjeldahal method. This can only be caused by incomplete reduction of nitrogen oxides generated during the burning of coal in the Dumas method. The Dumas method gave nitrogen results about 20% lower than the Kjeldahl method for lignite, digestion of the nitrogen compounds from bituminous coal is known to be more difficult (Jodidi (1910) and Shacklock and Drakeley (1927) so the nitrogen content of the bituminous coal was measured using a 24 hour Kjeldahl digestion. Use
of the nitrogen contents determined by the Dumas method gave inconsistent results for nitrogen in the early stages of devolatilization, therefore the higher Kjeldahl results for nitrogen content of the original coal have been used. Even when the Kjeldahl results are accepted there is a residual uncertainty in the nitrogen measurements. This uncertainty could indicate that the two points showing nitrogen retention of approximately 97% actually represent conditions where no nitrogen evolution occurs; this explanation agrees with the hypothesis on nitrogen devolatilization to be presented in the discussion section.

Figure VII-6 shows more clearly that nitrogen is a very refractory element in coal. At the most extreme conditions of the experiments presented here, no more than 70% of the nitrogen has been removed. Additionally nearly all the nitrogen is retained in the char for an induction period that depends on temperature. Bituminous coal has an induction period of about 100 milliseconds at $1260^\circ K$, 60 at $1510^\circ K$, $\sim 20$ at $1740^\circ K$, 12 at $1940^\circ K$, and near zero at $2100^\circ K$. The induction times for lignite are; 100 milliseconds at $1260^\circ K$, 30 at $1510^\circ K$, 20 at $1740^\circ K$, 10 at $1940^\circ K$, and 2 at $2100^\circ K$. The induction times for lignite and bituminous coal appear to be consistent considering that some extrapolations were necessary.

The nitrogen retention for lignite at $1510^\circ K$ levels off at 67% and about 100 milliseconds. The shape of the curve appears different when compared with the rest of the data, however the asymptotic value at one second is very well
FIGURE VII-7  Conversion of coal nitrogen as a function of fuel equivalence ratio in a 1500°K furnace.
for the two coals and the limited number of particle sizes studied. There is some indication that the burnout of bituminous coal may be more difficult than the burnout of lignite.

As expected, the char burnout is near 100% at lean conditions but residual char remains as the fuel equivalence ratio approaches stoichiometric and burnout continues to decrease until an asymptotic value of about 70% at a fuel equivalence ratio of 1.5 is obtained. Nitrogen retained in the char follows a curve complimentary to the burnout curve. When char burnout is complete there is obviously no nitrogen retained in the char; however, when char oxidation is incomplete nitrogen is retained in the residual char. Nitrogen retained in the char reaches an asymptotic value of 45% at fuel equivalence ratios above 1.75.

The conversion of fuel nitrogen to nitrogen oxides approaches 60% at very lean fuel equivalence ratios but decreases as fuel equivalence ratio increases. At a fuel equivalent ratio of 0.7 the conversion of fuel nitrogen to nitrogen oxides is about 30%, at 1.2 about 15% and above 2 the conversion is asymptotic at about 5%.

Similar conversion of lignite in a 1750°K furnace is shown in Figure VII-8. Several differences are apparent between the oxidation of coals at 1500°K and at 1750°K: (1) burnout at the higher temperature is complete even at a fuel equivalent ratio of 1.5 and even at very rich conditions the burnout is still 95%; (2) the conversion efficiency of fuel nitrogen to nitrogen oxides is marginally lower, about 5 absolute percent.
The conversion of fuel nitrogen to nitrogen oxides was about 60% at very lean fuel equivalence ratios, 22% at 0.7, 10% at 1.2, and reaches an asymptotic conversion efficiency of about 1% for fuel equivalence ratios above 2.

VII-3.2 Oxidation of Lignite Char

Lignite coal was devolatilized at 1500°C for one second and then oxidized in a 1500°C furnace supplied with varying amounts of oxidizer. Char produced in this manner has about 47% (d.a.f.) weight loss and 0.67% nitrogen. The results are shown in Figure VII-9 and show similar trends, but with some differences, to oxidation of the raw coal. Asymptotic burnout was not apparent for oxidation of char as it was for oxidation of coal at the highest fuel equivalence ratio of 2.6. This may result because the char has already been devolatilized at 1500°C and has very little volatile matter left to lose but for the case of raw coal about 50 percent of the initial weight may be lost by pyrolysis in addition to any oxidation that occurs.

The nitrogen retained in the char is higher than found for raw coals but, there is more char remaining at a given condition. The fractional retention of the nitrogen in the char is expected to increase as the fuel equivalence ratio is increased, with a consequent increase in the amount of residual char.

The conversion of coal nitrogen to nitrogen oxides follows a trend similar to the one observed for oxidation of raw coals.
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The conversion of coal nitrogen to nitrogen oxides follows a trend similar to the one observed for oxidation of raw coals.
FIGURE VII-8  Conversion of coal nitrogen as a function of fuel equivalence ratio in a 1750°K furnace.
FIGURE VII-9  Conversion of nitrogen vs fuel equivalence ratio in a 1500°K furnace for a lignite char previously devolatilized at 1500°K for 1 second.
One striking difference between the conversion of coal nitrogen from chars and from coals is the conversion for chars is significantly lower. The char conversion at a fuel equivalence ratio of 0.7 is 12 percent compared to 29% for the coal, the char has approximately 7% of the nitrogen retained in the residual char while the coal has about 4% of the nitrogen retained. At a fuel equivalence ratio of about 1.2, the conversion of the nitrogen in the char reaches an asymptotic value of about 4% but about 50% of the nitrogen is retained in the solid residual, whereas at the same conditions, the conversion of the nitrogen in the raw coal is about 15% and the nitrogen retained in the char from the coal is about 36%.

The residual unburned material from char oxidation is greater than from coal oxidation at similar conditions and the nitrogen retention of the residual from the char is correspondingly higher; however, even under conditions where no residual is left for either char or coal oxidation the conversion efficiency of the char is significantly lower than that for the raw coal.
VIII. DISCUSSION OF RESULTS

This section will discuss the results on devolatilization and oxidation of coal nitrogen presented in section VII. Stress will be placed on the fundamental interpretation of the results, although the lack of definite knowledge of many aspects of coal structure and behavior will preclude fundamental, quantitative conclusions. In the absence of enough information to formulate a reliable fundamental model for coal nitrogen devolatilization and oxidation, an empirical model will be presented. Additionally, practical implications of the results of this thesis to control of industrial burners will be discussed. Other discussions of this work have appeared elsewhere, see Pohl and Sarofim (1975), Pohl and Sarofim (1976), Kobayashi (1976), and Kobayashi, et al. (1976).

VIII-1. Discussion of Crucible Results

At the start of this project, no data existed in the open literature on devolatilization of nitrogen from coal at conditions applicable to pulverized coal flames. A relatively large body of data was available on nitrogen behavior in coal subjected to coking conditions. Coal coking takes place at low temperatures, 950°C, slow heating rates, 0°C/min, and in packed beds. When control of conversion of coal nitrogen to nitric oxide in pulverized coal flames became of interest, the data available on nitrogen behavior at coking conditions was extrapolated to the conditions of pulverized coal flames.
and used to construct speculative models. Extrapolation of the coking data have lead to misinterpretation of coal nitrogen behavior in pulverized coal flames. However, valuable information about the chemical structure and mechanism of nitrogen pyrolysis can be obtained from the differences in nitrogen behavior between the conditions applicable to coking and those applicable to pulverized coal flames.

VIII-1.1 Previous Work on Coal Nitrogen Distribution at Coking Conditions

Recovery of coke by-products became of interest in the late nineteenth century. This interest generated complete data on compound distribution for coal pyrolyzed in coking ovens. Three nitrogen compounds were of commercial interest (ammonia, hydrogen cyanide, and nitrogen based heterocyclic compounds) so relative complete information is available of the distribution of coal nitrogen to these three products under coking conditions.

v. Künle (1928) measured the retention of nitrogen from a Saxony bituminous coal under simulated coking conditions. His data is shown in Figure VIII-1 and indicates a nearly linear decrease in nitrogen retention with temperature increase. Extrapolation of the data of v. Künle indicates that nitrogen could be completely removed at a carbonizing temperature of about 1200°C. Data to be shown later shows that, while the central portion of a curve, such as the one shown in Figure VIII-1, can be approximated as linear, that the initial and
FIGURE VIII-1 Retention of nitrogen in char versus coking temperature.
final nitrogen loss with increasing temperature are not as rapid as the center portion of the curve would predict.

The United States Bureau of Mines has measured and tabulated a large mass of data on compound distribution of various United States coals under coking conditions. Most of the data for coking coal is summarized by Fielder and Davis (1934) although some information on product distribution from the lower rank coals appeared later, for instance, data on subbituminous coals was reported by Davis and Parry (1939). The Bureau of Mines data along with data reported by Kiner (1945) and Hill (1945) and an empirical correlation derived from work by Lowry (1942) have been presented by Pohl and Sarofim (1975) and is reproduced in Figure VIII-2.

The data are plotted as percent of coal nitrogen that remains with the char, is volatilized and collected as ammonia, nitrogen, hydrogen cyanide, heterocyclic nitrogen compounds, and nitrogen that is recovered with the tar. Some preliminary data (shown as half-filled symbols) from this study are also shown in Figure VIII-2. The bars indicate the range of nitrogen distribution to the various products of commercial coking operations. The solid lines indicate average nitrogen distribution for a wide variety of coking coals, the shaded areas indicate the range of the nitrogen distribution data.

At temperatures below about 600° C most of the nitrogen is retained in the char. The small amount of nitrogen devolatilized is divided between molecular nitrogen and tar nitrogen in the ratio of about two to one. At the highest temperature of
DISTRIBUTION OF N IN COAL PYROLYSIS PRODUCTS

DATA:
Fielder & Davis (1934)
Kirner (1945)
Hill (1945)
Lowry et al. (1942)
Empirical Fit to Fielder & Davis (1934), Avg Properties

- Open Symbols, Coking t~Hrs
- Half Shaded Symbols
- Free Fall t~1 Sec
- Crucible t~4 MIN
- Crucible t~10 MIN

o Lignite
- Bituminous
- Commercial
- Coking
- Operations

% N Retained in Char
% N Evolved as NH3
% N Evolved as N2
% N Retained in Tar
% N Evolved as HCN and (CN)2
% N Retained in Heterocyclic Form

T °C

FIGURE VIII-2 Distribution of coal nitrogen in coke products.
previous work, 1200°C, 30 percent of the nitrogen was still retained in the char. The devolatilized nitrogen at 1200°C goes to the following products; approximately 25% to ammonia, 45% to molecular nitrogen, 5% to tar, 2% to hydrogen cyanide, and less than 1% is recovered as heterocyclic nitrogen.

The points of interest in Figure VIII-2 are: molecular nitrogen accounts for an increasingly large fraction of the devolatilized nitrogen as the temperature increases, ammonia appears to have a peak yield at around 1000°C and accounts for most of the nitrogen that does not appear as molecular nitrogen, the nitrogen retained in the tar appears relatively constant, less than 5%, up to 1200°C, hydrogen cyanide yield increases with temperature but never accounts for more than 2% of the nitrogen, heterocyclic nitrogen yield is less than 1.5% and is probably close to 0.5% at coking temperatures. It will be shown later that ammonia concentrations are expected to be much lower and hydrogen cyanide concentrations much higher at pulverized coal flame conditions than at coking conditions.

Lowry, et al. (1942) has successfully, empirically correlated the averages of all dependent variables from coking operations using only the proximate analysis as a characterization of the coals and either two to three parameters. The correlation gives very little deviation from the average values but large deviations may exist for any one experiment. The probable error was quoted, by H. C. Porter in the discussion of the paper, as 18-20%, so 50% of the data points would have
larger errors. These errors make the correlation clearly unacceptable for many purposes. The errors could result from scatter in the experimental data, although it is unlikely that data scatter for the types of tests conducted could approach the magnitude of the claimed scatter. It is more likely that the proximate analysis is not an adequate characterization of coal, even for coking operations. The success of the Lowry correlation is based on average properties but its failure to adequately describe individual points with acceptable accuracy is the crucial concern about empirical models proposed to describe coal operations. Namely, the parameters needed to correlate coal behavior are not well known and the effect of experimental conditions are difficult to separate from the behavior of the coal.

More recently, Bronshtein, et al. (1970) has reported the effect of heating rate and temperature on the nitrogen distribution during coking of a Kuznec bituminous coal. The data are shown in three plots in Figure VIII-3. The heating rate was varied from 1°C/min to 15°C/min and the temperature ranged from 300 to 900°C; these conditions all fall within the range of heating rates and temperatures used to coke coal. The data are plotted as percent volatile matter or percent nitrogen yield in either the char or as molecular nitrogen versus temperature. Solid lines connect points of constant heating rate and dotted lines connect points of constant temperature. Direct comparison of the independent effects of heating rate and maximum temperature are somewhat difficult
FIGURE VIII-3  Effect of temperature and heating rate on nitrogen distribution between coke products.
because coal heated at slow heating rates has considerably longer residence times than coals heated at higher rates.

The volatile matter at the slowest heating rate has an asymptotic volatile content of 42.5% at a total residence time of 15 hours, but if the heating rate is increased to 7°C/min the maximum volatile attained, not yet asymptotic, is 45% after a total residence time of 2 hours. Higher heating rates have lower residence times and lower maximum yields, but there is no indication that the volatile matter evolution has ceased at the higher heating rates. The volatile matter released at a heating rate of 3°C/min appears to approach an asymptotic value of about 41% volatile, but the residence time is only 5 hours at this point compared to 15 hours at the slower heating rate, and slow volatile evolution would be expected to continue until the volatile matter was at least as large as that obtained with slower heating.

The yield of molecular nitrogen increases with temperature as the other coking data showed. The highest yield of nitrogen is obtained at the slowest heating rate, which is also the longest residence time. Nitrogen yield at faster heating rates increases much more rapidly than the yield at the slower heating rates, but an increase in total nitrogen yield with an increase in heating rate is observed only when the heating rate is increased from 7°C/min to 10°C/min.

Nitrogen retention in the char follows a pattern that is the reverse of the molecular nitrogen yield, except an equivalent amount of nitrogen is retained in the char at
heating rates of 1 and 3°C/min. Nitrogen evolution is much faster with higher heating rates but usually the increase of nitrogen evolution rate does not offset the effect of increased residence time. At 900°C only 30% of the nitrogen is retained in the char after 15 hours at a heating rate of 1°C/min or after 5 hours at a heating rate of 3°C/min. This data implies that all the nitrogen can be removed from the char even at low temperatures if one is patient enough.

Additional data from Bronshtein, et al. (1970) is shown in Figure VIII-4. This figure attempts to show the effect of heating rate on the distribution of nitrogen products. The yields represent integration of the product over the time of heating. It is impossible to separate the effects of heating time and heating rate on this figure. If for practical considerations the maximum heating times are considered to represent asymptotic yields (this is obviously not strictly true, see Figure VIII-3) then a guess of the effect of heating rate can be hazarded. It appears that heating rate, in the range of 1-15°C/min, has little effect on the amount of nitrogen that appears as ammonia and heterocyclic nitrogen compounds, increases the nitrogen retained in the char, obviously an effect of heating time, and decreases the yield of molecular nitrogen. Gas phase equilibrium, to be presented later, predicts that molecular nitrogen is the favored nitrogen product at all temperatures, so the increase in molecular nitrogen with increased heating time, in addition to indicating greater nitrogen loss from the char, might indicate that formation of molecular
FIGURE VIII-4  The effect of heating rate on coke product nitrogen distribution.
nitrogen is kinetically constrained.

VIII-1.2 Crucible Results from This Work

Crucible results in this study extended the maximum temperature of available data from about 1500°K to 2200°K. The nitrogen retention in the char and weight loss (dry basis) are shown versus maximum temperature in Figure VIII-5. The nitrogen retention and weight loss are reported at the times at which weight loss approached an asymptotic value. Under conditions of asymptotic weight loss the chars may still undergo slow nitrogen loss.

The data in Figure VIII-5 agree reasonably with the coking data presented in Figures VIII-1.3. The low temperature portion of the nitrogen retention curve for lignite shows little nitrogen loss at temperatures below 750°K; for bituminous coal, 5% of the nitrogen is lost at the same temperature, even though the dry weight losses are about equal. In general the nitrogen loss from the bituminous coal under coking conditions seems to be slightly greater than from the lignite. This slight difference might be explained by some small amount of the coal nitrogen being bonded in exinite resinous bodies that can distill without significant thermal degradation.

The retention of nitrogen in lignite and bituminous coal char is proportional to temperature between 80 and 20% retention in agreement with other data. The first and last portion of the nitrogen removal appears to be slower. The slow removal of nitrogen from coals implies that nitrogen is contained
in coal in a relatively stable form, probably predominately in heterocyclic nitrogen compounds.

Some of the data at $1223^\circ$K are results from ASTM Proximate Analysis test and some are data taken under conditions similar to the ASTM test but not exactly the same. The nitrogen retention under ASTM Proximate Analysis conditions is 72% for the lignite and 63% for the bituminous coal. There appears to be little difference between nitrogen retention for either coal between actual and simulated ASTM Proximate Analysis tests. There was no obvious correlation between ASTM nitrogen retention and the nitrogen retention of chars in pulverized flames.

The nitrogen loss from both coals is complete at high temperatures as extrapolation of the other coking data would indicate. Very little nitrogen (less than 10%) is retained in the char at temperatures above $1750^\circ$K. Nitrogen is completely removed for both coals at a temperature of $2200^\circ$K, even though the weight loss is only 44% dry, and char has retained about 70-75% of the original carbon. The carbon retained in the crucible experiments is much higher than the carbon retained under simulated pulverized coal flame conditions. The conclusion is that under slow heating in packed beds carbon can form complexes that are stable to at least $2200^\circ$K but that nitrogen compounds may form higher molecular weight complexes but these complexes are not stable at pulverized coal flame conditions.

The total weight loss at $2200^\circ$K is only marginally greater than the ASTM volatile matter, 44% compared to 42% dry. The
ASTM volatile levels indicated by the dashed lines are well established by repeated tests from different laboratories. The weight loss shown at 1223°C, the ASTM temperature, was slightly lower for both lignite and bituminous coal but the difference is not thought to be significant.

VIII-1.3 Models Based on Coking Type Data

Sterling and Wendt (1972) predicted, based on limited coking data, that 80% of the coal nitrogen would remain with the char in a pulverized coal flame. As will be shown later, this prediction has little meaning because it was based on temperatures significantly lower and residence times much longer than exist in pulverized coal flames. An asymptotic limit on nitrogen removal such as Sterling and Wendt imply can only result from a thermodynamic constraint, which should be temperature dependent. Data presented in section VII clearly shows that little nitrogen will be retained in the char at the high temperatures of pulverized coal flames and that the nitrogen retained in the char under simulated pulverized coal flame conditions is kinetically controlled.

Fine, et al. (1974) speculated, based on coking data from v. Künle (1928) and Kirner (1945), that most of the coal nitrogen would be volatilized at pulverized flame conditions and rapid devolatilization of nitrogen would lead to lower overall conversion of coal nitrogen to nitric oxide. This finding was based on their data which showed fuel nitrogen conversion in diffusion flames was much lower than conversions
in premixed flames. The same comments apply to this study as the argument on Sternling and Wendt (1972), even though the two studies reached opposite conclusions based on the same type of data.

Pohl and Sarofim (1975), who had some preliminary results of this study available to them, concluded that at pulverized coal flame conditions: (1) fuel nitrogen devolatilization is kinetically controlled, (2) a significant fraction of nitrogen will be retained in the char after devolatilization.

Vogt and Laurendeau (1976) reviewed the evidence available in the open literature (the review did not include Pohl and Sarofim (1975)) and reached the following conclusions: (1) volatile burning appears responsible for nitric oxide emission from pulverized coal flames, (2) pyrolysis of coal nitrogen can be divided into three regions; (i) pyrolysis of amines and low molecular weight heterocyclic nitrogen compounds at temperatures less than 1200°K, (ii) pyrolysis of high molecular pyridine based polymers that were formed by condensation reactions in coal pores during pyrolysis, (iii) pyrolysis of nitriles and heterocyclic nitrogen compounds that are firmly imbedded in the char matrix.

While nitrogen distribution in products from coking of coal supplies valuable information about the chemical nature of the nitrogen compounds in coal and how they behave under rather limited conditions, extrapolation of coking data to pulverized coal flames is, at best, hazardous and probably completely unjustified.
VIII-2.0 Discussion of Pyrolysis Results

In a pulverized coal flame, depicted schematically in Figure VIII-1, particles enter the furnace, are heated in a relatively rich atmosphere where some volatile matter is lost, and are finally heterogeneously oxidized. Development of control strategies for nitric oxide will depend on the fraction of coal nitrogen converted and the mechanism of conversion in the various regions of coal burning. This section will discuss the nature of nitrogen pyrolysis from the coal in the devolatilization region.

The rate of nitrogen evolution in the devolatilization region will be shown to be kinetically controlled for the conditions typical of pulverized coal flames. Because the nitrogen evolution is kinetically controlled, the split of nitrogen between the char and the volatiles can be altered to reduce total nitric oxide emissions by changes in operating variables of the pulverized coal flame. The conditions that effect the split of coal nitrogen between the char and the volatiles are temperature and time of devolatilization.

Data on nitrogen loss during devolatilization at pulverized coal flame conditions is very scarce. A correlation between nitrogen loss data of this study and total weight loss data is present and shows that total weight loss data can be used to expand nitrogen loss data to coals where only total weight loss data exists. Indirect evidence of the nature of the nitrogen compounds in coals is drawn from the nitrogen loss versus total weight loss curve, results of nitrogen loss
at long heating times, and other more direct literature evidence.

The usual first order empirical rate constant for nitrogen evolution is presented and its severe limitations are discussed. Criteria for developing a fundamental kinetic model for nitrogen removal from coal are presented and some qualitative interpretations are made about the nature of nitrogen pyrolysis from coal based on the form of the fundamental kinetic model.

VIII-2.1 Division of Coal Nitrogen Between the Char and Volatile Matter

Effective means of reducing the contribution of thermal nitric oxide have been developed but methods for nitric oxide reduction based on temperature control seemed to have little effect on the contribution of fuel nitrogen to nitric oxide. Pershing, et al. (1973) and Pershing and Wendt (1976a and 1976b) have shown that fuel nitrogen accounts for about 80% of the nitric oxide emissions from pulverized coal flames. Empirically developed control techniques reported by Crawford, et al. (1975), Selker (1975), Heap, et al. (1973), and Armento and Sage (1973) have demonstrated about a 50% reduction in total nitric oxide emission from pulverized coal flames. No information was available, however, on the contribution of the nitrogen contained in the char and volatiles to total nitric oxide emission or how the coal nitrogen might be
distributed until this study. Information from this study on the contribution of nitrogen contained in the volatile matter and the char to total emissions will be presented by Pohl and Sarofim (1976). Pershing and Wendt (1976b) will also present some limited results on the behavior of coal nitrogen oxidized from chars.

This section will discuss the results of devolatilization of nitrogen from coals under inert conditions with emphasis on the factors controlling the extent of coal nitrogen devolatilization. Reference to Figures VII-1 and Chedaille and Hemsath (1968) indicates that devolatilization in a pulverized coal flame will be completed within 100 milliseconds and the maximum gas temperature during devolatilization for bituminous type coals will be about 2000\(^{0}\)K. Actual local temperatures could be several hundred degrees higher. Figure VIII-6 shows that at the times and temperatures characteristic of a pulverized coal flame large changes in the fraction of nitrogen retained in the char can be achieved by slightly altering flame conditions. This is an important point because effective control of nitrogen oxide emissions will depend on whether the nitrogen is oxidized with the volatile matter or with the char.

VIII-2.2 Nitrogen Devolatilization in a Pulverized Coal Flame

All of the pyrolysis data of this study were taken on coal devolutilized in an inert atmosphere. In a pulverized coal flame, coal devolatilization occurs in a rich but not
oxygen free atmosphere. The pyrolysis data of this study was taken in an inert atmosphere because the inert atmosphere allowed the effects of thermal decomposition to be clearly separated from the effects of oxidation. It is realized that thermal and oxidative pyrolysis and burning may not be entirely independent but devolatilization of coal in an inert atmosphere provides clear evidence on thermal pyrolysis which can be supplemented later with additional data on the effect of small quantities of oxygen on the devolatilization process.

In an actual pulverized coal flame the coal particle is injected through the primary nozzle where the surrounding atmosphere is rich overall, but initially gas phase lean, because insufficient air for complete combustion of the coal is added in the primary nozzle. The richness of the gas atmosphere is increased by devolatilization and recirculation of rich combustion products. Chedaille and Hemsath (1968) have reported gas phase oxygen concentrations in pulverized coal flames burning Gras coal from Grande-Bretagne, France with 23% volatile matter and a Flambant coal from Pays-Bas, France with 36.6% volatile matter. Gas phase oxygen concentrations obviously are close to 21% near the nozzle where little volatile matter has evolved or product mixing has taken place, but the oxygen concentration drops to very small values in 30-40 milliseconds. Oxygen concentrations for burning maigie coals that contained only 8% and 12% volatile matter had high oxygen concentrations for longer times than the more volatile coals.
VIII-2.2.1 Empirical Correlation of Nitrogen Pyrolysis From Coal.

Empirical models can be developed that adequately represent pyrolysis data. Little physical significance can be ascribed to, nor can the models usually be extended beyond the range of coals studied, the experimental conditions and the type of equipment used. These conditions, of course severely limit the usefulness of empirical models, nonetheless some processes are so poorly understood that it is fruitless to try to develop physically realistic models. In the cases where fundamental models are difficult to develop, model tests and empirical relations have fulfilled useful engineering functions. Coal pyrolysis, in the past, has been considered too complicated to model except empirically. The new information developed on the chemical and physical structure of coal allows some physically realistic models of complex coal processes to be proposed. The empirical interpretation of coal nitrogen pyrolysis will be presented in this section and a more fundamental interpretation will be presented later.

Pyrolysis is usually interpreted as a rate phenomena which depends on remaining material to the first power and has an Arrhenius temperature dependence. Later discussions will demonstrate that, while this model is useful as an empirical relation, it has little physical significance.

The usual first order treatment of nitrogen pyrolysis from coal, except that the rate is restricted to the first 10% of nitrogen loss, is compared with fundamental first
FIGURE VIII-6 Comparison of rate of nitrogen removal from coal with pyrolysis of model nitrogen compounds and fundamental rate constants.
order rate constants in Figure VIII-1. The rate constants were taken from a compilation by Benson and O'Neal (1970) and represents reliable experimental values which have been heavily weighted by absolute rate theory considerations. Also shown on the plot is some pyrolysis data taken on nitrogen compounds that might be considered to represent the form of fossil fuel nitrogen. The nitrogen compound pyrolysis data was taken from Hurd and Simon (1962) and Axworthy (1975).

The pseudo-first order rate constant derived from the initial slopes of the data presented in Figure VIII-6 yields a pseudo-first rate constant of

$$k_N = 9.3 \times 10^3 \exp(-22,700/RT) \sec^{-1} \quad (VIII-1)$$

for the Montana lignite-A and Pittsburgh Seam #8 hv-A bituminous coals studied here. It is apparent that the rate constant derived in this study does not resemble elementary first order reaction rate constants. Rate constants derived from pyrolysis of model nitrogen compounds are reasonably in agreement with the rate constants derived for nitrogen removal from the coals of this study but are in poor agreement with fundamental first order rate constants.

Kobayashi (1976) has derived rate constants from the same data in a parallel study and found an overall weight loss constant for both coals of about

$$k_N = 6.6 \times 10^4 \exp(-25,000/RT) \sec^{-1} \quad (VIII-2)$$
The rate constants derived for loss of hydrogen, carbon, and oxygen were also very similar to the constants for nitrogen loss and overall weight loss. Kobayashi has tabulated previously derived coal pyrolysis rate constants and found the constants, within a range of scatter, to be consistent with each other and to be consistent with rate constants derived similarly in this study. The rate constants do not agree with the theoretical values that would be predicted if the kinetic models used to interpret the data were physically realistic. The conclusion to be drawn is that first order kinetic models can explain individual sets of data, provided enough parameters are used, but can not predict consistent rate constants for coal pyrolysis.

Rate constants derived for pyrolysis of polymers have values similar to rate constants derived in a similar manner for coal pyrolysis. Van Krevelen, et al. (1951), Chermin and Van Krevelen (1951), Yellow (1964), Jüntgen and Van Heek (1967), and Jüntgen and Van Heek (1970) have used polymer compounds as models for coal pyrolysis and find similarities between the rate constants derived for pyrolysis of coal and polymers. The rate parameters reported in Van Krevelen et al. (1951) and Yellow (1964) are wrong but these values have been corrected by Jüntgen and Van Heek (1970).

Rate constants derived from pyrolysis results usually more closely resemble constants derived from pyrolysis of coal and model compounds than elementary rate constants. The
rates of reactions derived from polymer pyrolysis are typically in the range of 1.0 to 0.001 for temperatures of between 500 and 800\(^\circ\)K. Different authors have used different rate parameters to reproduce this rate but almost none of the rate parameters used resemble values expected for elementary first order reactions based on absolute rate theory or reliable rate measurements of elementary reactions.

Madorsky (1951 and 1953) found the activation energy of polystyrene pyrolysis to be about 58 kcal/g mole and a preexponential factor, based on a first order reaction, to be \(6 \times 10^{17}\) sec\(^{-1}\). The preexponential factor is considered to be too high by a factor of about one hundred. Lowering the preexponential factor and raising the exponential factor to compensate would result in rate parameters more near those expected, but changing the rate constant can not give representative rates of overall pyrolysis if the mechanism of pyrolysis is improperly understood. Chermin and Van Krevelen (1957) have tabulated the measured energies of activation for pyrolysis of many different polymers: these values ranged from 48-76 kcal/g mole. These activation energies appear to be slightly too low to accurately represent a simple first order fission reaction and would be more realistic values for concerted first order fission reactions or more likely the activation energies are representative of a complex reaction mechanism.

Rate parameters derived for pyrolysis of simple model compounds, also do appear to represent any simple first order
fission process. Depp, et al. (1956) has used model compounds that involved aliphatic linkages between aromatic structures to qualitatively explain some aspects of coal pyrolysis. Virk, et al. (1974) has used pyrolysis data gathered on aromatic ring structures to speculate on the nature of hydorgasification of coal.

Depp, et al. (1956) measured coke products from pyrolysis of model compounds with aliphatic linkages between aromatic units varying from one to four carbon atoms. Depp found similarities between the coking behavior of the model compounds used and bituminous coal. He postulated a relatively complex kinetic model to account for easy rupture of the aliphatic bridges and the products measured. Depp did not derive rate constants, as would have been difficult, from his relatively complex model.

Virk, et al. (1974) tabulated the existing data on pyrolysis of unsubstituted aromatic ring compounds and claimed the rate of pyrolysis of these compounds could be correlated by the delocalization energy of the parent compound. Review of the original rate data used by Virk and extension to other compounds or use of other estimates of stabilizing energy do not support Virk's conclusions.

First order decomposition reactions should be partially related to the delocalization energy but the correlation would be expected to be crude, at best, since other factors can greatly effect the energy of reaction other than the stabilization energy. Additionally if the mechanism is complex,
as will be postulated later the delocalization energy would not be expected to correlate very well with a pseudo-first order pyrolysis rate constant as Virk, et al. claim.

Rate of pyrolysis of simple compounds other than nitrogen compounds are not plotted on Figure VIII-1 but constants derived from pyrolysis of simple compounds do not agree any better with expected rate constants that do values similarly derived for pyrolysis of coals and polymers. The available data on unsubstituted aromatic compound pyrolysis is presented in Virk, et al. (1974). Rate constants derived from Kinney and DelBel (1954) should be considered to have a large uncertainty and only the values obtained from pyrolysis experiments when no coke was present should be considered. This limits the data to one temperature, 1000°C. The first order rate constants derived in this manner decrease with residence time. Average values of the first order rate constants, for the residence times investigated, were 0.039, 0.045, 0.016, 0.002, and 0.026 sec⁻¹ for benzene, naphthene, anthracene, chrysene, and pyrene respectively. The lowest rate obtained was 5 x 10⁻⁴ sec⁻¹ for chrysene with a residence time of 41 seconds. The derived rate cluster around the fundamental rate constant for removal of a substituent on an aromatic ring. The data on aromatic compound pyrolysis are only marginally below the coal, other model compound, and polymer data. But because of the paucity and unreliability of the data no firm conclusions can be drawn although it would seem unlikely that pyrolysis of these compounds would
be simpler than pyrolysis of the other compounds discussed, especially when all the compounds form chars.

VIII-2.2.2 Empirical Correlation Between Nitrogen Loss and Total Weight Loss

A correlation between pyrolysis of nitrogen from the coals of this study with total volatile loss will be presented. This correlation will allow the meager data on nitrogen pyrolysis from coals subjected to pulverized coal flame conditions to be reasonably extended to coals where applicable total weight loss data exists. Total weight loss data for coals in pulverized coal flames is restricted, but the data on weight loss is more extensive and easier to obtain than nitrogen pyrolysis data under the same conditions.

The rate of nitrogen loss during pyrolysis is not independent of the loss of other elements during pyrolysis because C, H, O, N, and part of the S are bonded together in intricate chemical structures. Kobayashi (1976) has demonstrated the similarity between individual element removal rates and the rate total weight loss. His results are presented in Appendix V. Gray, et al. (1975) has produced empirical correlations between the extents of various element loss during hydrogasification of coal. Figure VIII-2 presents the correlation between nitrogen loss and total weight loss for the conditions of this study.

Figure VIII-2 shows nitrogen retention versus d.a.f. weight loss for the two coals of this study subjected to
FIGURE VIII-7  Correlation between nitrogen loss and total weight loss during pyrolysis of coal.
pyrolysis in flow experiments (open points), free fall into crucible (half-open points), and crucible results (solid points). The correlation between nitrogen loss and total weight loss is good for both coals when only the laminar flow data is considered. The data for pyrolysis of the coals in crucibles shows much higher rate of nitrogen loss than carbon loss.

In the long residence time crucible experiments reported in section VIII-1 it was demonstrated that the total weight loss reached an asymptotic value only slightly higher than would be predicted by the ASTM Proximate Matter Test, but that elements other than carbon were completely removed. This can be explained because carbon is the only element that can form a highly condensed substance that is stable at pulverized coal flame temperatures. Nitrogen does not have sufficient bonding electrons to participate in high order condensation reactions with carbon. Nitrogen must, therefore, be present only on the periphery of the char structure where it can be removed under the conditions of a pulverized coal flame.

Gray, et al. (1975) observed similar behavior in his experiments on hydrogasification of coal. Under conditions similar to those used in this work Gray found that nitrogen loss and carbon loss were related linearly with a slope of 1.8. However, when coal was pyrolyzed in his "hot rod" reactor which will give heating and environmental conditions more nearly like those encountered in the crucible experiments of this experiment, nitrogen loss was no longer linearly
related to carbon loss. Nitrogen loss was more rapid than carbon loss and nitrogen could be completely removed with removal of as little as 30% of the carbon.

Nitrogen loss does not commence with carbon loss but is delayed until approximately 10-20% of the carbon is lost. This could be because some of the carbon is contained in alphatic structures that are easy to remove compared to destruction of aromatic structures, while most of the nitrogen is probably held in heterocyclic ring structures.

Nitrogen is removed from coal more rapidly than total weight loss occurs, after the initial delay in nitrogen removal, as is evidence from the slope of the curves; the ratio of nitrogen loss versus weight loss is 1.25 for the lignite and 1.5 for the bituminous coal. These values can be compared with the values found by Gray et al. (1975) for nitrogen versus carbon loss in hydrogasification since carbon loss accounts for approximately 70-80% of the total weight loss for the experiments of this study.

Nitrogen loss from different coals at pulverized coal flame conditions in an inert atmosphere can then be crudely estimated, probably within 10 to 20 percent, from total weight loss data by use of the shape and nature of Figure VIII-2. No nitrogen loss should be assumed until approximately 15% of the total weight has been lost, then nitrogen loss can be estimated as approximately 1.25-1.5 times the total weight loss until approximately 60% d.a.f. weight loss has occurred.
Extrapolation of this relationship beyond 60% weight loss is uncertain and would predict that, for pyrolysis of coals under inert pulverized coal flame conditions, complete nitrogen loss will occur at 80-90% total weight loss.

The limited number of studies of coal pyrolysis applicable to pulverized coal flames is presented below. It is hoped that the total weight loss data generated in these studies can be used to supplement the data on nitrogen loss presented in this study.

The only information available in the open literature on the behavior of coal nitrogen in pulverized coal flames is data on the overall conversion of fuel nitrogen contained in coals to nitric oxide and a preliminary report of this work by Pohl and Sarofim (1975). Coates, et al. (1974) did make gas analysis of nitrogen in the products of coal pyrolysis under simulated pulverized coal flame conditions, but the nitrogen analysis typically showed several times as much nitrogen in the sample as was contained in the coal. These anomalous results are probably caused by atmospheric nitrogen leaks and the results are not reliable.

Eddinger, et al. (1966) studied the pyrolysis of an Elkol sub-bituminous B coal from Wyoming that had a carbon content of 70.7% and a volatile content of 35.5%. Their experimental conditions were: heating rate-2500°C/sec, residence time-8-40 milliseconds, and furnace temperature-1000-1500°C. The results showed 5-16% soot production and 60-65% ultimate weight loss when soot was included as volatile matter.
Kimber and Gray (1967a) reported devolatilization of CRC 902 and 802 coals heated at rates of $10^{50}$ K/sec to temperatures between 780 and 2000°C for residence times of 12-100 milliseconds. The maximum weight loss achieved in this set of experiments was 70% d.a.f.

Kimber and Gray (1967b) also studied a NCB 902 coal that had 35-37% volatile matter. They achieved 72% d.a.f. maximum weight loss. The range of experimental conditions was: furnace temperature 1050°K - 2200°K, heating rates of $10^5$- $10^6$ K/sec, and residence times of 15-110 milliseconds.

Stickler, et al. (1974) found 40% weight loss from a Pittsburgh Seam coal with 39% volatile matter and 79% carbon when the coal was pyrolyzed at 1750°K for 60 milliseconds.

Coates, et al. (1974) studied a hVB coal from carbon county, Utah with 70% carbon content and 34% volatile matter. A maximum weight loss of 64% was found when the pyrolysis conditions ranged from 1058-1453°K and times of 10-260 milliseconds. Ash tracer calculations, reported above, indicated about a 10% higher weight loss than Coates, et al. reported.

Ubbayakar, et al. (1976) have pyrolyzed a Pittsburgh Seam bituminous coal with 39% volatile matter and 82% d.a.f. carbon and found up to 68% d.a.f. weight loss. Their range of experimental conditions were: heating rate, $10^{50}$ K/sec, residence times, 7-70 milliseconds, and temperatures, 1800-2250°K. They found on the order of 20% soot of which 10-20%
is formed in the char pores and the remaining 80-90% of the soot is formed in the gas phase.

In a study parallel to this study, Kobayashi (1976) and Kobayashi, et al. (1976) studied pyrolysis of the two coals reported here under the same pyrolysis conditions. The coals were a Pittsburgh Seam #8 hvA bituminous coal with 82% carbon (dmmf) and 36% volatile matter. The conditions of the experiments varied from temperatures of 1000-2100°K, heating rates of $2 \times 10^4$-$5 \times 10^5$ K/sec, and residence times of 3-1000 milliseconds. The bituminous coal had a maximum weight loss of 65% or 72% d.a.f. if the weight loss was corrected for soot formation, and the lignite had a maximum weight loss of 65% d.a.f. No soot formation was observed during pyrolysis of the lignite.

VIII-2.2.3 Prospects for Development of a Coal Nitrogen Pyrolysis Model

Since the amount of nitrogen devolatilized from coal under different conditions may have a large effect on control strategies, it is desirable to develop a predictive model for nitrogen pyrolysis from coal that will be applicable to conditions in a pulverized coal flame. Preliminary efforts to develop such a model will be discussed below.

Pyrolysis refers to loss of a specified material, or more frequently weight, of a sample that was originally of some starting material. It is obvious that almost all pyrolysis, regardless of the starting material, involves an entire
spectrum of reactions of different orders including but not limited to parallel, consecutive, and competitive reactions. Most pyrolysis is interpreted as occurring in a single reaction which is first order in material remaining to be reacted. The material yet to be reacted is sometimes defined as the material left to be removed. It is not surprising that interpretation of pyrolysis data by first order kinetic laws yields rate parameters that do not resemble rate constants for elementary reactions: the results of such models are difficult to extend to coals and equipment other than the ones studied.

It is extremely difficult to derive meaningful rate parameters for a substance as complicated as coal. Pyrolysis of polymers and model compounds retain many of the difficulties involved in interpretation of coal pyrolysis data, but are simpler because the starting material is known and is of a limited structure. Information obtained on polymer and model compound pyrolysis will be used as an aid to understanding the pyrolysis of nitrogen compounds from coal.

Previous workers in coal pyrolysis have been ingenious in devising qualitative models to fit very complex pyrolysis data. Most of the modeling efforts on coal pyrolysis have been directed towards understanding the coking of coal since, until recently, the chemical structure of coal was not thought to greatly effect the burning of coal. The previous models of coal pyrolysis have been reviewed by Dryden (1959), Van Krevelen (1961), Dryden (1963), Jones (1964), Yellow (1965,
and Kobayashi (1976). Until very recently, Cheong, et al. (1975), pyrolysis reaction models, whether parallel, consecutive or competitive, included only first order reactions.

It is unfortunate that first order reactions probably do not completely control the rate of pyrolysis because rate constant estimation techniques for first order reactions are reasonably well established—Robinson and Holbrook (1972), Benson (1968), Benson and O'Neal (1970)—and Westman and Delury (1956) and Rodinguin and Rodinguina (1964) have shown that analytic solutions can be developed for very complex first order kinetic schemes by use of the Laplace-Carson transform. Pyrolysis reactions appear to involve many second order reactions and possibly to have mass transfer constraints.

The study of coal pyrolysis has not advanced as rapidly as the aligned field of polymer pyrolysis, partly because coal pyrolysis is more complex but also because most coal investigators have been entrenched in the use of first order kinetic models. The first order kinetic models when supplemented by an appropriate number of empirical parameters, can result in excellent empirical fits of a given set of weight loss data for a particular coal pyrolyzed under specified conditions in a particular apparatus. The ability of each investigator to select his own parameters and to develop models to describe his particular experiment has given the first order model false legitimacy. Even when chemical details of coal pyrolysis began to be investigated the first order
interpretation dominated coal pyrolysis hypotheses. If the
traditional approach to explaining the behavior of coal during
pyrolysis was universally applicable, even in a restricted
sense, individual investigators would not still be postulating
their own models with empirically developed parameters.

A great deal of the information generated in the study
of polymer and complex compound pyrolysis is applicable to
interpretation of coal pyrolysis data. The information from
these fields will be presented below and will form the basis
of a pyrolysis model to be proposed on this study. The
points to be made are (i) rate constants derived from first
order models vary with the extent of reaction (ii) no single
rate order interpretation yields satisfactory results through
the entire course of reaction (iii) bimolecular reactions are
prominent in pyrolysis (iv) condensations reactions can
produce stable residues (v) the amount of residue produced
depends on many complex factors.

VIII-2.2.3.1 Variation of Pyrolysis Rate Constants

Polymer degradation clearly shows that the rate of
pyrolysis depends very strongly on the material present and
the extent of reaction. Madorsky (1952) has long advocated
that in complex pyrolysis of polymers, only the initial rate
of reaction is meaningful since it is the only rate where the
reactants are certainly known.

Madorsky (1953) has shown that the direction of change
of the rate of reaction with extent of reaction can vary
widely with small changes in structure of the polymer. For instance, Madorsky found that poly-meta-methylstyrene showed a peak rate of pyrolysis when 25% of the material had been devolatilized, that the rate of pyrolysis of poly-alpha-deutrostyrene continually increased with extent of devolatilization, and the rate of pyrolysis of hydrogenated poly-styrene decreased continually with extent of reaction. There are chemical reasons for these seemingly anomalous behaviors, but the point to be made is the rate of reaction in pyrolysis depends on the initial material and the extent of reaction, i.e., pyrolysis reactions are complex.

The complex nature of pyrolysis reactions leads to two corollaries to the change in pyrolysis rate with extent of reaction. Madorsky (1952 and 1953) has shown that the apparent order of reaction also changes with extent of reaction for some polymers. The apparent order of pyrolysis varied between zero and one. Since interpretation of pyrolysis reactions by first order rate models indicates that both the order and rate of pyrolysis depend on the extent of reaction and, as will be shown below, the rate also depends on the previous history of the material to be pyrolyzed, interpretation of pyrolysis data by fitting constants to the integral of the rate of reaction, at best discards valuable kinetic information and most probably makes parameters developed by the integral approach meaningless in any context outside the original experiment. Carroll and Manche (1965) have stated the applicability of the integral interpretation of pyrolysis
data as follows: "...the integral method when applied to nonisothermal kinetics is inadequate to deal with complex reactions. I see no reason to restrict this statement to nonisothermal data.

**VIII-2.2.3.2 Bimolecular and Free Radical Pyrolysis Reactions**

The free-radical chain pyrolytic decomposition of relatively simple molecules and polymers is well established and there is good evidence that a similar mechanism is responsible for coal decomposition. Szwarc (1950) identified quinone type structure as a product of p-xylene pyrolysis which lead him to postulate that biradicals were stabilized by resonance similar to that known to stabilize quinone. Biradicals are thought to be important species in the pyrolysis of many compounds. See Benson and O'Neal (1970). Blades, et al. (1954) further established the radical nature of aromatic compound pyrolysis by studying toluene pyrolysis. The benzyl radical was postulated as the stable radical in the Blades sequences of reactions. Hurd, et al. (1962a), (1962b) and Hurd and Macon (1962) have postulated detailed mechanisms for pyrolysis of a number of single aromatic ring compounds. As expected, except for the initiation step, pyrolysis of these aromatic compounds occurs entirely through free radical mechanisms and many of the intermediates are multiple free radicals that are resonance stabilized.

It has, also, long been recognized that polymer pyrolysis
proceeds by a free radical mechanism. Madorsky (1953) showed that some polymers decompose by random chain sission followed by free radical abstraction of hydrogen atoms from adjacent sites. Wall et al. (1955) has investigated polymer pyrolysis using the simplified classical polymer mechanism of (i) initiation (ii) propagation (iii) intermolecular and intramolecular transfer and (iv) chain termination by disproportionation. This set of reactions involves many radical reactions some of which are bimolecular. Martin (1964) has stressed the complex radical nature of polymer pyrolysis with emphasis on the pyrolysis of cellulose. Ehlers, et al. (1969) has proposed a free radical mechanism involving bimolecular reactions to explain the products produced during pyrolysis of polyphenylenes.

VIII-2.2.3.3 Application of Polymer and Model Compound Information to Coal Pyrolysis

There is little doubt that many of the same structures contained in the polymers and model pyrolysis experiments discussed exist in coal. These structures in coal may be more complicated and the physical structure of the coal may increase further the complexity of coal pyrolysis, but the units of the structures are expected to behave in a manner similar to that found for polymers and simpler compounds. Much of the work on the chemical nature of pyrolysis has concentrated on finding polymers of known structure that
behave similarly to coal when subjected to the same pyrolysis conditions. Much of this work has been summarized by Van Krevelen (1961). The approach was to pyrolysis the coal and the model compounds nonisothermally, use the integral technique to develop first order parameters to fit some preconceived model, to compare the parameters derived for coal and model compound pyrolysis, and to draw conclusions about the regions in which different chemical reactions occur. This technique has given some valuable information about the nature of coal pyrolysis but the information has not yet been able to develop a physically realistic model of coal pyrolysis.

VIII-2.2.3.4 Condensation and Char Formation in Pyrolysis

The petroleum industry has been interested in condensation reaction leading to the formation of aromatic compounds which can be used as chemical intermediates or as a means of increasing the octane number of gasoline. Three mechanisms have been proposed for condensation of linear hydrocarbons into aromatic rings: (i) Groll (1933) has postulated that aromatic condensation takes place by acetylenic condensation (ii) Hauge and Wheeler (1929) have postulated that butadiene is the active intermediate in aromatic ring building (iii) Errede and Cassidy (1959) have shown that under certain conditions condensation takes place by phenyl radical addition. In the general case all three mechanisms can occur, although one mechanism may be favored under certain conditions.
Many investigators have identified relatively complex fused ring structures when simple hydrocarbons are pyrolyzed. Large aromatic ring systems are expected to lead to stable molecules that produce char.

Groll found that propylene gives the largest aromatic yield of any gaseous hydrocarbon; this led him to postulate that demethanization of propylene yields the acetylene diradical. Three acetylene diradicals were proposed to condense to form benzene without formation of a four carbon intermediate. Larger fused ring systems could be built up by condensation of acetylene diradicals to form vinyl benzenes which form fused ring structures on dehydrogenation. Observation of arenes and polycyclic aromatic compounds supported this mechanism.

Weizman, et al. (1951a,b,c) found a number of large polynuclear aromatic compounds in the products of cracked petroleum feed stocks. The results indicated that the aromatic compounds were produced by condensation of butadiene with another olefin. Complex polynuclear aromatic compounds were found, such as substituted pyrenes, fluorenes, and chysenes. Since butadiene was postulated as a necessary compound in building polynuclear rings, aromatic feeds must partially decompose before further condensating. This contention was partially supported by the limited condensation of aromatic feed stocks.

Kinney and Crowley (1954) found results similar to
Weizman, et al., for pyrolysis of C₂ and C₃ hydrocarbons. The prevailing condensation mechanism was, again, thought to be olefin butadiene condensation.

Hurd, et al. (1962a,b) found many condensed ring structures in the pyrolysis products of aromatic and hetero-aromatic ring compounds. He proposed Diels-Alder condensation to form large structures from propylene and butadiene diradicals. Hurd's mechanism also included condensation of phenyl radicals.

Kinney and DelBel (1954) postulated aromatic ring condensation, without ring destruction, possibly through condensation of biradical intermediates. Studies on pyrolysis of substituted aromatic compounds have indicated that production of fused ring compounds can occur without destruction of the aromatic ring. Szwarc (1950) found many crosslinked polymers and fused ring compounds in the pyrolysis products of disubstituted ring compounds. Blades, et al. (1954) identified bibenzyl and biphenyl compounds in the products of pyrolysis of toluene, and found anthracene as a product of bibenzyl pyrolysis.

A detailed study on the free radical condensation of benzyl type radicals was conducted by Errede and Cassidy (1959) under low pressure conditions that suppressed ring rupture. Substituted aromatic compounds such as p-xylene, toluene, diarylmethanes, bibenzyl, and o-xylene were pyrolysed under conditions favorable to production of anthracene. Pyrolysis of p-xylene produced about 3% condensed products.
of which about one-sixth were anthracene products. Toluene pyrolysis produced about 0.5% residue which was 70% bibenzyl, 20% diarylmethanes, and 10% anthracene. Yields of anthracene produced from pyrolysis of diarylmethanes ranged from 55% for p-tolyl-p-xylylmethane to 91% for o-benzyltoluene. Pyrolysis of bibenzyl produced an anthracene yield of 16%. The results were explained by condensation of two benzyl radicals followed by hydrogen elimination.

Additional studies have been performed on the formation of char during polymer pyrolysis. These studies, because of the complex nature of char formation have usually been limited to investigating factors that influence the quantity and nature of the char produced. The mechanism proposed to account for char formation in polymer pyrolysis are totally consistent with the mechanisms established for condensation of simpler compounds.

Madorsky (1953) found the distribution of molecular weights of the volatile and residual products in polystyrene pyrolysis depends on small structural changes in the original polymer; the molecular weight of the material condensed from the volatile matter was 300-700.

Wall et al. (1955) attributed the change in the nature of the volatile and residual products from polymer pyrolysis to the nature and extent of hydrogen atom transfer. Winslow, et al. (1955) claims most polymer degradation represents competition between chain scission, leading to volatile matter,
and chain condensation to form carbon-like residues. Evidence to support this contention came from x-ray scattering which showed that the chars were composed of loosely packed hexagonal carbon arrays with poorly developed crystal structure. Free radical measurement of the chars showed that free radicals decreased markedly at temperatures where hydrogen is lost from aromatic rings. Ring condensation and hydrogen removal left a highly condensed pure, rather amorphous carbon matrix.

Further support of the competition between chain scission and condensation has been supplied by Winslow and Matreyel (1956). They found that polystyrene could be completely pyrolyzed but that large amounts of char formed from the pyrolysis of polystyrene that had been co-polymerized with small amounts of polyvinylbenzenes. This indicated that the more highly substituted polyvinylbenzenes promoted condensation over ring scission. Condensation of the polymers that had been co-polymerized with polyvinylbenzene started at about 1-2% weight loss; this was evident from changes in the physical structure of the residue and release of methane, ethane, and small amounts of unsaturated gases. The evidence is consistent with radical fragments removing hydrogen from the polymer which cause the radical ring structure to condense. The chars formed from pyrolysis of these polymers showed x-ray patterns characteristic of dense carbon structures.

Ehlers, et al. (1969) postulated that the chars formed from pyrolysis of polyphenylenes were composed of highly
crosslinked essential nonaromatic polymers. He based this conclusion on the disappearance of the i.r. aromatic absorption of the pyrolyzed chars. However, few alternatives to highly condensed aromatic ring structures can satisfy the requirement of a pure carbon structure; additionally the aromatic absorption band loses intensity as aromatic structures become more highly condensed.

Two other factors which have been found empirically to effect the rate and nature of char formation are heating rate and the presence of carbon substances. Rapid heating to high pyrolysis temperatures generally produces much less char than slow heating to the same temperature. This has usually been explained as the competition between ring scission—a process that proceeds rapidly only at high temperatures—and condensation—a process that has a much smaller kinetic temperature dependence but is thermodynamically favored at low temperatures. Unfortunately, the evidence is complicated by the difficulty of rapidly heating coal in beds and because more of the volatile matter may be released at a faster rate at higher temperatures when the coal is rapidly heated. All of these effects may influence the amount of char formed.

Martin (1964) has given an extreme example of the effect of heating rate on char formation—rapidly heated cellulose leaves no residue but slowly heated cellulose produces a large quantity of residue. He attributed this difference to drastic molecular changes caused by competitive reactions
during heating.

Kinney and DelBel (1954) have pyrolyzed unsubsti
tuted aromatic hydrocarbons in the presence and absence of large quantities of coke. The presence of coke slightly increased char formation and the larger the amount of coke present the larger the increase in char production. The effect of coke on char formation is presumably to provide an adsorption site where the adsorbed molecules can either become part of the coke matrix or more likely, react with other fragments to form higher order condensed compounds.

The above discussion has shown (i) model compounds, polymers, and coal all can form stable residual char on pyrolysis (ii) both gas phase and solid phase condensation can occur when compounds are pyrolyzed and this condensation is radical in nature (iv) heating rate and chemical structure effect the amount and nature of the char formed during pyrolysis (v) the reactions leading to stable char production are competitive with the reactions leading to devolatilization.

VIII-2.2.3.5 The Chemical Nature of Coal Nitrogen

In order to apply the information available from pyrolysis of model compounds to the pyrolysis of coal, the nature of the structure of the coal must be reasonably known. There is extensive literature on the chemical structure which will not be discussed here, although some of the pertinent information is presented in section VI, coal characterization. The
information on the nature of the nitrogen compounds in the coal is, however, directly pertinent to this study and will be discussed below.

The source of the nitrogen content of coal is still somewhat of a mystery. Since the nitrogen content of original plant material is insufficient to account for the high level of nitrogen in coal, it has been proposed by Kirner (1945) that nitrogen accumulated in coal by preferential decomposition of the other organic materials, by Zubovic (1966) that nitrogen compounds are stabilized in metal chelates, and by Stephan, et al. (1966) that nitrogen addition occurred during anaerobic bacteria digestion. Carbon has been found by Koyama (1966) to be more stable to microbiological digestion than nitrogen, which is more stable than hydrogen. Addition of nitrogen by bacterial action during decomposition of the plant material provides an alternative, and more plausible, explanation for the nitrogen content of coals.

The form of the nitrogen in the coal has generally been considered to be heterocyclic from the time that Beet (1940) discovered a compound extracted from coal that appeared to be nicotinic acid. It is still unclear to what extent nitrogen is present in forms other than resonance stabilized ring structures. Amino acids have been identified by Swain (1966) and Zubovic (1966) surviving in paleozoic rock formations. The nitrogen in many of the surviving amino acids was heterocyclic. Some authors, Kirner (1943), Beet (1940), Deal,
et al. (1953) Montgomery and Holly (1957), Ramachandran, et al. (1959) Davies and Lawson (1966), Entel (1958) Hayatsu, et al. (1975), and King, et al. (1975), contend that coal nitrogen occurs mainly in heterocyclic rings with only small amounts of nitrogen contained in aliphatic groups. Zubovic (1966), Birkofer and Orywal (1968) Hauck (1975) and Lawson and Purdie (1966) have claimed that the large majority of nitrogen is aliphatic. This study and a large number of studies on the nature of nitrogen compounds in fossil fuels indicate that nitrogen in coal is contained mostly in heterocyclic rings.

Identification of original compounds in coal is very difficult because the original compounds are difficult to remove unaltered. The form of the nitrogen compounds present in all fossil fuels are generally assumed to be similar. This allows inferences to be drawn regarding the form of the nitrogen in coal from more extensive evidence of nitrogen compound forms in other fossil fuels; compound identification is much easier in petroleum products.

Amines and amides have been identified in coal or coal destruction products only after the fuel was subjected to rather extreme destruction conditions, such as high pyrolysis temperatures, strong mineral acid or alkaline leaching. There appears to be little evidence that single bonded carbon-nitrogen material can be recovered from fossil fuels without extensive fuel decomposition, and singly bonded nitrogen should be
easier to remove than heterocyclic nitrogen.

Hartung and Jeuell (1962) have recovered small quantities of nitrile nitrogen compounds from fossil fuels. Most of the nitrile compounds recovered are cyanocyclic compounds that contain benzene, substituted benzene, or rarely cyclohexane. Benzonitriles have been identified in pyrolysis products of heterocyclic nitrogen products.

Small quantities of pyrroles have been identified in fossil fuels by Hartung and Jeuell (1962) Hayatsu, *et al.* (1975), Birkofe and Orymal (1968), and Hauck (1975). The pyrroles are commonly substituted in positions that suggest that pyrrole formed the center of a more complex molecule. Recovery of benzo substituted pyrroles strongly suggests that the higher order nitrogen compound are composed of condensed rings.

Pyridines usually comprise the largest quantity and number of nitrogen compounds recovered from fossil fuels. See Deal (1953), Davies and Lawson (1966), Hayatsu, *et al.* (1975), Entel (1958), Montgomery and Holly (1957), and La Lau (1960).

The emphasis on recovery of pyridine compounds is partly because the basicity of the pyridine compound leads to easier isolation and indentification than pyrrole. Again, as is the case of pyrrole, substitution of the pyridine nucleus and recovery of large fused ring structures containing the pyridine nucleus implies that much of the nitrogen is contained
in fused ring structures.

This study supplied indirect evidence that the nitrogen compounds in coal are resistant to pyrolysis compared to other volatile elements in coal. A small fraction of the carbon content of the coal appears to be lost prior to any nitrogen loss. These results are consistent with the interpretation that most of the nitrogen is contained in a stable form in the coal. In view of other evidence, the stable form of nitrogen is likely to be mostly in heterocyclic form.

VIII-2.2.3.6 Pyrolysis Rate Constants at Constant Extent of Reaction

The information presented on the nature and mechanism of pyrolysis of model compounds and the structure of nitrogen compounds allows a simplified model of pyrolysis of nitrogen compounds from coal to be developed.

In view of the change in pyrolysis rate with extent of reaction a simple improvement on the empirical model might be obtained by developing rate parameters at different extents of reaction. This approach has been used by Carroll and Manche (1965) but implies that the rate of pyrolysis is a function only of the amount of pyrolysis that has taken place and not the previous temperature and time history of the particle. Evidence on the effect of heating rate on the nature and extent of char formation does not support that
pyrolysis is independent of the prior treatment of the coal. Nonetheless some improvement is obtained by developing an empirical rate constant at different extents of reaction; such a development is shown in Figure VIII-3.

Rate constant derived from the first 10% of reaction are

\[ k = 1.5 \times 10^5 \exp(-31,600/RT) \text{ sec}^{-1} \] (VIII-3)

for the bituminous coal and

\[ k = 1.5 \times 10^5 \exp(-28,600/RT) \text{ sec}^{-1} \] (VIII-4)

for lignite. The activation energies for the rate constants are seen to be marginally closer to those expected for elementary rate constants.

Pyrolysis of amines have been studied by Jolly (1934) and Smith and Sawyer (1976) and low temperature oxidation of amines has been reported by Jolly (1934), Cullis and Smith (1950) and Smith and Sawyer (1976). Pyridine pyrolysis has been reported by Ploquin (1947), Krumholz (1948), Hurd and Simon (1962), Linnell (1962), and Axworthy (1975); picoline pyrolysis by Roberts and Szwarc (1948) and Hurd and Simon (1962); pyrolysis of methylpyrazine by Hurd and Simon (1962); and pyrrole, benzonitrile, and quinoline pyrolysis by Axworthy (1975). Axworthy has also reported the effects of oxygen on the rate of pyrolysis of pyridine and benzonitrile.

Smith and Sawyer (1976) pyrolyzed methylamine at 1000-1167°K and Jolly (1934) pyrolyzed aliphatic amines at 600-800°K.
FIGURE VIII-8. Pseudo-first order Arrhenius parameters for coal pyrolysis at different extents of reaction.
Smith and Sawyer found ammonia to be the major product, while Jolly found ammonia to account for only 10-20% of the nitrogenous products.

Smith and Sawyer found only very small amounts of hydrogen cyanide but hydrogen cyanide accounted for from 70-80% of the nitrogen in the products from Jolly's experiments. Smith and Sawyer's nitrogen material balances are not credible (the nitrogen atom deficit was 80% of the original nitrogen in some cases). The nitrogen material balances of Jolly, on the other hand, accounted for 87% of the nitrogen added to the system.

Jolly's values for high hydrogen cyanide concentrations, which agree with results of Axworthy and this study, suggest that hydrogen cyanide is the primary product of nitrogen compound pyrolysis rather than ammonia, even though ammonia is the favored product of the pyrolysis of primary amines and ammonia is strongly thermodynamically favored over hydrogen cyanide at the low temperatures used by Jolly.

Smith and Sawyer found small amounts of molecular nitrogen present in the pyrolysis products from their experiments in amounts corresponding to approximately 1/4 of the ammonia present. Jolly showed that molecular nitrogen accounted for 5-10% of the nitrogenous products from his experiments and that nitrogen production is favored by higher temperatures.

Mechanisms for pyrolysis of amines have not been worked out in detail. Jolly and Smith and Sawyer imply that pyrolysis occurs through hydrogen removal to produce hydrogen cyanide.
Jolly postulates direct removal of hydrogen from the carbon atom and Smith and Sawyer postulated that an imine is formed prior to additional hydrogen and hydrogen cyanide formation. Jolly postulates that ammonia is formed through the addition of hydrogen to methylamine to yield methane and ammonia; this implies that hydrogen cyanide should be formed before ammonia.

The only nitrogen product of low temperature oxidation of amines identified by Jolly was nitrogen. Cullis and Smith found ammonia and nitrogen oxides to be the major amine oxidation products ($N_2$ was not measured) at $600^0K$ but more hydrogen cyanide than ammonia was recovered at temperatures above $650^0K$. Smith and Sawyer found only small quantities of hydrogen cyanide from pyrolysis of methylamine in flames at temperatures between 1320 and $1600^0K$. They found the major product to be nitrogen with smaller amounts of nitrogen equally distributed between nitrogen oxides and ammonia. Additionally, they found quantities of a solid substance tentatively identified as hexamethylenetetraamine. The nitrogen balances presented by Smith and Sawyer for the oxidation experiments were much better than those for the pyrolysis experiments. Smith and Sawyer's hydrogen cyanide measurements seem to be suspect.

Hurd and Simon (1962) reviewed the early work on pyridine pyrolysis and reported (i) Roth (1886) found hydrogen cyanide and bipyridine as products (ii) Meyer and Hoffman-Meyer (1921) found bipyridine as the main pyrolysis product (iii) Ruheman (1929) found bipyridine and hydrogen as the major products at $900-1020^0K$, hydrogen cyanide became a major product at
higher temperatures, and ring scission was complete at 1200°K.

Floquin (1947) pyrolyzed pyridine at temperatures of 350-550°C and found the gas products to be mainly acetylenic hydrocarbons and hydrogen with small amounts of methylamine and ammonia. At higher temperatures hydrogen cyanide and ammonia cyanide were found. The liquid products distribution also depended on temperature; at low temperature the major products were piperidine, undecomposed pyridine, and pyrrole-indole was recovered at temperatures between 450 and 500°C.

Ring scission was postulated to occur by ring hydrogen migration followed by scission to yield a four carbon biradical and an imine. Formation of pyrrole occurred either by reaction of the four carbon radical with ammonia or by ring scission of pyridine to form a methylimine followed by self condensation and elimination of a carbon atom to form the pyrrole ring.

Krumholz (1949) found the following products from pyrolysis of pyridine at 850°C; polypyridines, quinoline, pyrrole, indole, hydrogenated skatole, benzonitrile, and cyanopyridine.

Hurd and Simon (1962) found pyridine to be more stable to pyrolysis than picolines. Quinoline, benzonitrile, acrylonitrile, acetonitrile, and benzene were found to be products of pyridine pyrolysis. Production of nitriles increased at higher temperatures and hydrogen cyanide was present, but not measured at all temperatures above 775°C.

Linnell (1962) pyrolyzed pyridine at 750-850°C and found the gas product to be almost entirely hydrogen. The other
major product was bipyridine; minor amounts of acridine, hydrogen cyanide, and cyanogen were also identified. Linnell concluded that ring decomposition under the conditions of his experiments was very slight.

Axworthy (1957) decomposed pyridine at temperatures from 700-1000°C and found hydrogen cyanide to be the most important nitrogen product. He was not able to identify any ammonia. Other products from pyridine pyrolysis were methane, benzene, benzonitrile, and anthracene.

Hurd and Simon (1962) and Axworthy (1975) have generated data sufficient to extract pseudo-first order rate constants; these values are shown in Figure VIII-6. Decomposition mechanisms were proposed by Ploquin and Hurd, et al. (1962). Ploquin's mechanism provides a formation of the pyridyl radical by hydrogen migration and a means of producing pyrrole from decomposition of pyridine. Hurd's mechanism is more detailed, will form the basis of a mechanism proposed here, and will be discussed later.

Axworthy has pyrolyzed pyridine in the presence of 5 and 10% oxygen. The rate of decomposition of pyridine was accelerated but kinetics and products have not as yet been reported.

Axworthy has studied the pyrolysis of pyrrole at temperatures of 850-1000°C. The rate constants derived from his measurements are presented in Figure VIII-6. The major products identified were methane, acrylonitrile, methylnitrile,
benzene, benzonitrile, and unknown hydrocarbons.

Picoline pyrolysis has been studied by Roberts and Szwarc (1948) and Hurd and Simon (1962). Roberts and Szwarc determined bond energies of benzyl radical formation of the various picolines. Rate constants derived from their data are not presented in Figure VIII-6 except as a generalized equation since the values have been tabulated and corrected by Benson and O'Neal (1970) and are considered fundamental rate constants. Rates of reaction of pyridine base compounds are close to those for analogous benzene compounds. Hurd and Simon's data appear on Figure VIII-6 and are thought to represent overall pyrolysis of heterocyclic nitrogen compounds. The products identified from picoline pyrolysis at 700-850°C were an unidentified residue, isomeric picolines, acetonitrile, benzonitrile, acrylonitrile, and quinoline. At higher temperatures the quantity of residue and isomeric picolines decreased.

Pyrolysis of methylpyrazine by Hurd and Simon produced a high boiling residue, acetonitrile, acrylonitrile, and hydrogen cyanide. Methylpyrazine was found to be less stable than the picolines.

Quinoline and benzonitrile have also been pyrolyzed by Axworthy; oxygen has been added in some of the benzonitrile pyrolysis experiments. Rate constants derived from the data are presented in Figure VIII-6. Quinoline pyrolysis produced methylnitrile and acrylonitrile; benzonitrile produced
hydrogen cyanide, benzene, methane, bipyridine, and anthracene. It should be noted that pyrrole has been identified as a product of pyridine pyrolysis, quinoline as a product from pyridine, pyrrole, and picoline pyrolysis, and benzonitrile as a product from pyrolysis of all the nitrogen compounds reported except methylpyrazine.

VIII-2.2.4 Proposed Model for Nitrogen Pyrolysis from Coal

The previous sections have established most of the information needed to postulate a simplified model of nitrogen pyrolysis from coal. The model to be proposed will be composed of elementary reactions that provide competition between nitrogen removal in small units and condensation of nitrogen compounds into larger units which are more difficult to remove.

Hurd, et al. (1962) has recommended a mechanism for picoline decomposition that can explain many of the features of model nitrogen compound pyrolysis and by extension some of the kinetic features of nitrogen removal from coal. This mechanism produces most of the products observed in more recent pyrolysis of model fuel nitrogen compounds, with few modifications. The major products found in pyrolysis of pyridine at temperatures around 1000°C are HCN, CH₄, benzene, benzonitrile, methyl nitrite, anthracene, acrylonitrile, and quinoline. Quinoline pyrolysis produced; benzene, benzonitrile, and CH₄, benzonitrile pyrolysis produced; HCN, benzene, CH₄, biphenyl, and naphthalene, and pyrrole pyrolysis produced;
CH₄, methylnitrile, acrylonitrile, benzene, benzonitrile, and some unidentified hydrocarbons. The proposed mechanism is
\[ \text{Py} \text{CH}_3 \rightarrow \text{Py} \text{CH}_2 + H^+ \quad \text{(VIII-5)} \]

\[ \text{Py} \text{CH}_3 + H^+ \rightarrow \text{Py} \text{CH}_2 + H_2 \quad \text{(VIII-6)} \]

\[ \text{Py} \text{CH}_3 + H^+ \rightarrow \text{Py} + \text{CH}_3 \quad \text{(VIII-7)} \]

\[ \text{Py} \rightarrow \text{N-CH-CH-CH-CH-CH} \quad \text{(VIII-8)} \]

\[ \text{Py} \text{CH}_3 + \text{CH}_3 \rightarrow \text{Py} \text{CH}_2 + \text{CH}_4 \quad \text{(VIII-9)} \]

\[ \text{Py} \text{CH}_3 + H^+ \rightarrow \text{Py} + \text{CH}_4 \quad \text{(VIII-10)} \]

\[ \text{Py} + \text{Py} \rightarrow \text{Py-Py} \quad \text{(VIII-11)} \]
\[ \text{N-CH-CH-CH-CH-CH} \rightarrow \text{N-CH-CH + CH-CH-CH} \quad (\text{VIII-12}) \]
\[ \text{N-CH-CH-CH-CH-CH} \rightarrow \text{N-CH + CH-CH-CH-CH} \downarrow_{HCN} \quad (\text{VIII-13}) \]
\[ \text{N} \rightarrow \text{C} + \text{CH}_2 \quad (\text{VIII-14}) \]
\[ \text{C} + \text{CH}_2 \rightarrow \text{C} \quad (\text{VIII-15}) \]
\[ \text{CH}_2\text{CH-CH} \rightarrow \text{CH}_2\text{CH-C≡N} \quad (\text{VIII-16}) \]
\[ \text{N} \rightarrow \text{C} + \text{N} \quad (\text{VIII-17}) \]
\[ \text{N} + \text{HX} \rightarrow \text{X} + \text{CH}_3\text{C≡N} \quad (\text{VIII-18}) \]
(VIII-19)

(VIII-20)

(VIII-21)

(VIII-22)

(VIII-23)
Further fused ring condensation by addition of the four carbon biradical and elimination of 2 peripheral element is possible.

Side substituents can migrate around aromatic rings. It has been suggested that hydrogen migration might saturate one or two elements in the aromatic ring and thus facilitate ring scission. The four carbon biradical produced from ring scission could react with a nitrogen group to yield pyrrole. Further additions of the four carbon biradical will lead to fused ring structures such as indole and carbazole, both have been identified in coal and other fossil fuel destruction products.

A simplified model can be postulated based on the following assumptions. (1) Most nitrogen in coal is contained in heterocyclic rings, (2) probably substituted pyridine nucleus, (3) groups containing two or more rings will undergo further decomposition prior to being volatilized, (4) few single nitrogen heterocyclic groups, at least in high rank coals, are bridged to the coal structure through an alphatic linkage, (5) most alphatic linkages are ethylene or methylene linkages. These assumptions lead to a model where nitrogen can be released only by scission of aromatic rings. The initial products from this model will consist of only nitrile compounds. The general model that would develop from the above assumptions would be primary destabilization of aromatic structures either through a first order thermal decomposition or through
abstraction by radicals previously produced by reactions such as VIII-5-10. The radical ring structures formed can then break into fragments as in reactions VIII-12-14, 17. The relatively small nitrogen containing fragments can then either condense, as in reactions VIII-11,15, 19, 20-23 to form nonvolatile products or break down to form relatively stable small nitrogen compounds that could escape as in reaction VIII-14, 16, 18.

Evidence was presented in a previous section supporting the postulate that most of the nitrogen in coal is contained in stabilized ring structures. This postulate is supported by the results of the present study which show that the rate of nitrogen released during the initial stages of pyrolysis is slow relative to the corresponding rate for hydrogen, oxygen, sulfur, and carbon. Other supporting evidence is provided by the chemical analysis of the nitrogen compounds in fossil fuels which show that most of the nitrogen is in compounds built up around a pyridine ring. Nitrogen containing aliphatic compounds are found only when the fuel has been severely degraded and could likely be a decomposition product of a heterocyclic ring.

The smaller aromatic units directly connected to the coal matrix by an aliphatic group contains at least two fused rings. This contention is supported by the best estimate of 2-4 rings (Tingley and Morrey (1973)) composing the average unit in lignite. The average number of rings per cluster increases
rapidly with carbon content so that anthracite coal is estimated to have more than 20 units per cluster.

A group containing only two or three rings will certainly be volatile at pulverized coal flame conditions but, at least for swelling coals, the dimensions of a two member ring will restrict exit of the volatile matter from the small pores. Most of the surface area of coal has been shown by Van Krevelen (1961), March (1965), Toda (1971), Nsakala (1975), and results of this study, reported in Appendix VII, to have pore restrictions of less than 120\(^{0}\)A. The internal surface area of bituminous coal becomes less available during devolatilization at temperatures above 1200\(^{0}\)K but access to the internal surface area of lignite improves after devolatilization. The surface area accessible at 77\(^{0}\)K (restrictions greater than 120\(^{0}\)A) of the North Dakota lignite studied by Nsakala, et al. increased from less than 0.5% of the total surface area, in the raw coal, to about 10% of the total surface area after devolatilization at 800\(^{0}\)C for 0.6 seconds. The increase in lignite surface area during devolatilization reported by Nsakala agrees with krypton surface areas reported for devolatilized lignite in Appendix VII.

Tingey and Morrey (1973) have compiled evidence demonstrating that cluster units in lignite are connected by methylenes and ethylene bridges in approximately equal amounts. Higher rank coals appear to have about twice as many ethylene bridges as methylene bridges. The bridges are easily ruptured since the relatively stable benzyl radical is formed.
The simple model proposed here for nitrogen released during pyrolysis of lignite and higher rank coals would involve primary rupture of ethylene and methylene bridges. The fragments will, for the most part be too large to escape without further degradation. If the nitrogen is considered to be entirely contained in heterocyclic rings, then no nitrogen can be released without destruction of aromatic rings. These assumptions would imply that the primary nitrogen products leaving a particle are nitrile structures. Support for the early appearance of HCN is supplied by Milne and Beachey (1976). The volatile nitrogen fragments must escape through the molecular size restrictions of the coal pores. This is a slow process and the nitrogen fragments can condense and refracture along the pores out of the coal.

The initial benzyl and phenyl radicals can abstract hydrogen from other structures to form stable compounds, condense to form higher order biphenyl or fused ring structure, or undergo ring fusion. The fragments of ring fission can condense or rearrange to form small stable species that will comprise the volatile matter of the coal.

Cheong, et al. (1975) has proposed a mechanism similar to that above for thermal reactions of hydrogen and carbon in coal. Their mechanism does not include ring fissure. Axworthy has, however, identified benzene, benzonitrile, and methane as the major products of quinoline pyrolysis; benzene and benzonitrile are undoubtedly formed from the condensation
of products of ring rupture.

The work of Cheong, et al. (1975), Hurd and Simon (1962), Ploquin (1947) and Axworthy (1975) allow the following mechanism to be proposed as a first attempt to model nitrogen devolatilization from coal:

\[ \text{PhPh-CH}_2\text{-CH}_2\text{-PhPh(N)} \rightarrow \text{PhPhCH}_2 \cdot + \cdot \text{CH}_2\text{PhPh(N)} \]  
\[ \text{(VIII-24)} \]

\[ \text{PhPh-CH}_2\text{-PhPh(N)} \rightarrow \text{PhPh} \cdot + \cdot \text{CH}_2\text{PhPh(N)} \rightarrow \text{PhPhCH}_2 \cdot + \cdot \text{PhPh(N)} \]  
\[ \text{(VIII-25)} \]

\[ \text{PhPh} \cdot + \text{HX} \rightarrow \text{PhPh} + \cdot \text{X} \]  
\[ \text{(VIII-26)} \]

\[ \text{PhPhCH}_2 \cdot + \text{HX} \rightarrow \text{PhPhCH}_3 + \cdot \text{X} \]  
\[ \text{(VIII-27)} \]

\[ \cdot \text{PhPh(N)} + \text{HX} \rightarrow \text{PhPh(N)} + \cdot \text{X} \]  
\[ \text{(VIII-28)} \]

\[ (\text{N})\text{PhPhCH}_2 \cdot + \text{HX} \rightarrow (\text{N})\text{PhPhCH}_3 + \cdot \text{X} \]  
\[ \text{(VIII-29)} \]

\[ \text{PhPh-CH-CH}_2\text{-PhPh(N)} \rightarrow \text{PhPh-CH} = \text{CH-PhPh(N)} + \cdot \text{H} \]  
\[ \text{(VIII-30)} \]

\[ \text{PhPh-CH}_2\text{-CH-PhPh(N)} \rightarrow \text{PhPhPhPhPh} + \text{H}_2 \]  
\[ \text{(VIII-31)} \]

\[ \text{PhPh(N)} \rightarrow \text{Ph} \]  
\[ \text{(VIII-32)} \]

\[ \text{Ph} \cdot + \text{HX} \rightarrow \text{Ph} \cdot + \cdot \text{X} \]  
\[ \text{(VIII-33)} \]

\[ \text{Ph} \cdot + \cdot \text{H} \rightarrow \text{Ph} + \cdot \text{N} \]  
\[ \text{(VIII-34)} \]

\[ \text{Ph} \cdot \rightarrow \text{PhCH}_2 + \cdot \text{N} \]  
\[ \text{(VIII-35)} \]

The underlined fragments can react through mechanisms similar to the one described for picoline decomposition in equations VIII-5-23.
The rate of nitrogen removal from the coal will equal the rate of appearance of HCN, pyridine, pyrrole, acetonitrile, and acrylonitrile at the coal surface. The net rate of formation of the volatile nitrogen species involves a complicated radical mechanism for which many of the rate constants are not available at this time. The proposed mechanism cannot, therefore, be evaluated at this time.

This type of fundamental mechanism of coal pyrolysis will eventually lead to prediction of coal behavior based on the chemical structure of coal. When and if this occurs, model tests and empirical data fits no longer need be resorted to for each coal and each set of operating conditions to predict their behavior. Complete development of the type of model proposed here may require many years but the current methods for prediction of coal behavior are unsatisfactory and not likely to improve without detailed consideration of the chemical structure of coal.

VIII-3 Discussion of Oxidation Results

The results of the division of nitrogen between nitric oxide and residual char at widely varying fuel equivalence ratio will be discussed. Preliminary evidence shows higher flame temperatures result in lower conversions of fuel nitrogen to nitric oxide. The conversion of the residual nitrogen retained in previously devolatilized char will be shown to be lower than the conversion of nitrogen from coal. The differences
between the conversion efficiencies of nitrogen in the char and coal will be used to estimate the contribution of volatile and char nitrogen to total nitric oxide emissions.

VIII-3.1 Previous Work on Conversion of Fuel Nitrogen

Most of the previous work on reduction of the contribution of fuel nitrogen to nitric oxides emissions has been discussed in sections II and III. Pershing, et al., (1973), Pershing and Wendt (1976a and b) have demonstrated that the nitrogen contained in the coal accounts for approximately 75-80% of the total nitrogen oxides emission from pulverized coal flames.

A large quantity of data gathered on many practical combustion systems, shown in Figure II-3, indicates that the conversion efficiency of fuel nitrogen operating at a normal fuel equivalence ratio is about 30%.

Turner, et al., (1972b) has demonstrated the potential of two stage combustion for reducing nitrogen oxide formation from fuel nitrogen. McCann, et al., (1973) and Armento and Sage (1975) have demonstrated the effects of various control techniques on 500 lb/hr coal furnaces and found that the maximum practical reduction in nitrogen oxides emissions with existing techniques was about 50 to 60%. Field surveys of control techniques for nitrogen oxides by Crawford, et al., (1975) and Selker (1975) have confirmed the laboratory experience that a 50% reduction in nitric oxides emissions is
obtainable with present control techniques.

VIII-3.2 Aerodynamic and Thermal Characteristics of the Coal Burning of This Study

The system used in this study fed nominally 38-45 micron, or occasionally 75-90 micron coal particles through a 1-2 mm nozzle carried in an equal mass of air into a hot wall furnace, additional combustion air was added concentric to the fuel nozzle through a flow straightener. The particle size was designed to be in the range of interest for pulverized coal flames. The amount of primary air, approximately 15-25% of the stochiometric requirement, corresponds to values found in industrial practice. The secondary air is not swirled nor is it preheated, other than in the honeycomb straightener. These conditions do not correspond to industrial practice. In view of the differences between the mode of operation in this study and practical systems, the gross agreement in the data is remarkable. The conversion in our system for a fuel equivalence ratio of 0.7 agrees with the industrially observed value of 30%, carbon burn is high also in agreement with expectations from field results in the field.

The flame temperature in the system used in this study is unknown and probably does not correspond to the flame temperatures in pulverized coal units. Flame temperatures were estimated by optical pyrometry, a 1500°K furnace had a 1600°K flame temperature, but local regions of the flame
must have been considerably hotter than indicated by the pyrometer. Flame temperatures were varied by changing the surrounding wall temperature. This method certainly gives a relative measure of the flame temperature but absolute temperatures remain unknown.

Pershing and Wendt (1976b) investigated many of the variables that are uncertain in our system in a 6 lb/hr unit and found that efficiency of fuel nitrogen conversion to nitric oxide was affected by burner aerodynamics but not affected by flame temperature, provided the flame temperature was not too high. The results of Pershing and Wendt on fuel nitrogen conversion on a similar coal agree with the conversions of this study. For instance, at 15% excess air a Pittsburgh coal with 1.20% nitrogen showed about 28% conversion; the same value obtained for a similar coal in this study.

Pershing and Wendt injected coal through a divergent nozzle and an axial injector and found, when everything else was equal, about a 10% absolute difference in conversion efficiency between the two nozzles for a western Kentucky hvC bituminous coal and Montana sub-bC coal. The injector system used in this study is close to the axial injector system used by Pershing and Wendt. The burner design had no effect on char oxidation. The injector used in this study can not match the mixing conditions encountered in a pulverized coal flame but does represent a different flame; data can be
compared on a relative basis for this mixing condition and valid conclusions can be drawn about the effects of variables other than mixing for systems in general.

Pershing and Wendt used adiabatic flame temperatures as a comparison of temperature effects on fuel nitrogen behavior since they had no direct measure of the flame temperature. Comparison of the effects of flame temperatures on thermal and fuel nitrogen emission showed that thermal nitric oxide emissions increased greatly at higher temperatures but fuel nitrogen conversion did not increase until the adiabatic flame temperature reached about $2400^\circ K$. The stochiometric adabatic flame temperatures in helium for the coals of this study, disregarding dissociation, were about $2100^\circ K$ for the lignite and about $3000^\circ K$ for the bituminous coal; corrections for dissociation will lower the lignite temperature about $200^\circ K$ and the bituminous coal $300^\circ K$.

VII-3.3 The Effect of Flame Temperature on Fuel Nitrogen Conversion

Pershing and Wendt (1976b) report that nitric oxide emissions increased by about 100 ppm (15%) when the calculated adiabatic flame temperature of a Western Kentucky hvC bituminous coal was increased from 2500 to $2600^\circ K$; similar results were obtained when the flame temperature of a Colorado hvC bituminous was increased from 2600 to $2700^\circ K$. 
Comparison of the results in Figures VII-7 and VII-8 show that higher temperatures appeared to have lower fuel nitrogen conversions. At a normal operating fuel equivalence ratio of 0.7, the percentage of fuel nitrogen conversion to nitric oxide decreased by ten percentage points absolute when the furnace temperature was increased from 1500 to 1750°K. At the higher temperature, as would be expected, the burnout was markedly improved and the amount of nitrogen retained in the char drastically reduced.

The temperature effects on conversion of fuel nitrogen in this study are preliminary. Armento and Sage (1975) have reported that nitric oxide emissions decreased as the preheat increased for coal fired with normal excess air in a 500 lb/hr coal fired test furnace. When the excess air level was high the nitric oxide level increased as the preheat temperature increased, but this may be a consequence of increased fixation of atmospheric nitric oxide. That the level of nitric oxide decreased with increasing preheat at the normal levels of excess air, inspite of the increased nitric oxide contribution from thermal nitrogen fixation, suggests that the fuel nitrogen contribution decreases with increased temperature as was found in this study.

The levels of nitrogen oxides typically produced in flames are below the equilibrium concentrations for the $N_2O_2$ reaction being limited by the kinetics of the thermal fixation of atmospheric nitrogen. The situation is different when fuel nitrogen is the source of nitrogen oxide emissions. In
early regions of the flame quantities of nitrogen compounds will be present in excess of the concentration that would be predicted from equilibrium considerations. The kinetic rates that control the paths to various species during relaxation will have a large effect on the ultimate nitrogen oxide emissions.

If it is assumed that the primary nitrogen species released in flames is hydrogen cyanide, as has been argued here, then HCN will react to produce other nitrogen species, probably N$_2$, NO, and NH$_3$. The rates of the competitive paths to N$_2$ and NO will control the overall conversion of fuel nitrogen into nitrogen oxides. Conversion of N$_2$ to nitric oxide in regions of the flame where this reaction is favored will be slow so that reduction of hydrogen cyanide into N$_2$ in the early regions of the flame is greatly advantageous.

Higher flame temperatures in coal flames will increase the rich regions of the flame, remove more nitrogen from the char, and increase the rate of all reactions. Reactions with high activation energies which might not be competitive with reactions with lower activation energies at low temperatures can become competitive at high temperatures. Long residence times of nitrogen species in rich regions of the flame will favor reduction to N$_2$ and will mean lower overall conversion of fuel nitrogen to nitrogen oxides.

Figure VIII-9 shows the equilibrium distribution of nitrogen products for devolatilized bituminous coal and Figure VIII-10 for lignite. The curves were calculated at
FIGURE VIII-10. Equilibrium distribution of nitrogen from devolatilized lignite.
the devolatilization temperatures of this study and the mole ratio were choosen as the ratio of the volatile matter lost at one second for temperatures up to 1750°K and at times corresponding to the asymptotic weight losses at 1940 and 2100°K. The data points are preliminary measurements of the gas phase nitrogen distribution in the gas leaving the furnace. The gas residence time was about 4 minutes; long enough for most gas phase reactions to approach completion. The data points are shown to indicate the direction of the shift in nitrogen distribution to be expected in the pyrolysis of gases.

Nitrogen is seen to be the most favored nitrogen product under all conditions; hydrogen cyanide and ammonia are the only other two nitrogen products that have appreciable concentrations. Ammonia has a higher concentration below 1200°K than hydrogen cyanide for bituminous coal, above 1400°K hydrogen cyanide is the only nitrogen species, other than molecular nitrogen, of significance. The measured values agree in ranking of magnitudes with the values obtained from the equilibrium calculations. At 1000°K the ammonia measured accounted for more nitrogen than hydrogen cyanide but at 1500°K more nitrogen was present as hydrogen cyanide than as ammonia. Measured N₂ concentrations were lower than predicted by equilibrium but consistently higher than other nitrogen species concentrations.

Similar trends are shown for lignite in Figure VIII-10. One notable difference is that the hydrogen cyanide concentration for lignite does not exceed the ammonia concentration
until the temperature exceeds $1600^\circ$K. The equilibrium results, again, agree with preliminary measurements.

Equilibrium calculations in fuel rich devolatilization regions, where oxygen has not penetrated, over a temperature range from $1000^\circ$K, typical of gasifiers and fluidized beds, to $2100^\circ$K, typical of pulverized coal flames, predict that most of the fuel nitrogen will be converted into $N_2$, although ammonia can account for a troublesome fraction of the nitrogen at low temperatures and hydrogen cyanide can account for almost 1/10th of the nitrogen at the higher temperatures.

If the primary fuel nitrogen product is hydrogen cyanide, equilibrium predicts considerable reduction to $N_2$, a most desirable occurrence. A kinetically rapid path must now be demonstrated for reduction of fuel nitrogen that is competitive with oxidation of fuel nitrogen to nitric oxide.

The most interesting, and the most poorly understood aspect of nitrogen gas phase reactions is the competition between reactions to produce either nitric oxide or nitrogen. Work on ammonia and hydrogen cyanide flames have supplied information of the oxidation mechanism of these simple nitrogen compounds. A number of speculative mechanisms have been advanced for the reduction of nitrogen compounds to molecular nitrogen. The mechanisms, postulated to produce molecular nitrogen, in general, are not satisfactory and many of the reactions do not appear to be elementary processes.

Oxidation of ammonia can generally be described by the following set of reactions after normal hydrogen abstraction
by radicals

\[ \text{NH}_2 + O = \text{HNO} + H \]  
(VIII-36)

\[ \text{HNO} + X = \text{NO} + \text{HX} \]  
(VIII-37)

\[ \text{NO} + \text{NH} = \text{N}_2\text{O} + H \]  
(VIII-38)

\[ \text{NO} + \text{NO} = \text{N}_2\text{O} + O \]  
(VIII-39)

\[ \text{NO} + X = N + \text{OX} \]  
(VIII-40)

\[ N + \text{NX} = \text{N}_2 + X \]  
(VIII-41)

\[ \text{N}_2\text{O} + X = \text{N}_2 + \text{OX} \]  
(VIII-42)

Hydrogen cyanide oxidation follows a similar mechanism

\[ \text{CN} + \text{OX} = \text{NCO} + X \]  
(VIII-43)

\[ \text{NCO} + O = \text{NO} + \text{CO} \]  
(VIII-44)

\[ \text{NCO} + X = \text{NX} + \text{CO} \]  
(VIII-45)

\[ \text{CN} + \text{NO} = \text{N}_2\text{O} + C \]  
(VIII-46)

\[ \text{CN} + X = \text{CX} + N \]  
(VIII-47)

\[ \text{N}_2\text{O} + X = \text{N}_2 + X \]  
(VIII-48)

\[ N + \text{NX} = \text{N}_2 + X \]  
(VIII-49)

The importance of homogenous reactions leading to the formation of molecular nitrogen has been evaluated based on a comparison of the characteristic reaction times with the time
scales of interest in pulverized coal flames. Rate constants were selected from compilations by Kondratiev (1972) and Engleman (1976). Four centered reaction, which are often hypothesized to lead directly to molecular nitrogen, are not included in the analysis because the author believes that four centered reaction will not be as rapid as the alternate two step mechanism. There appear to be only four species (N, NCO, NH, N₂O) that can lead to the production of molecular nitrogen. In the fuel-rich regions expected to have super-equilibrium concentrations of fuel nitrogen compounds the following reactions might supply important paths for formation of N₂:

\[
\begin{align*}
\text{NO} + \text{H} &= \text{N} + \text{OH} \\
\text{NO} + \text{CO} &= \text{N} + \text{CO}_2 \\
\text{CN} + \text{OH} &= \text{NCO} + \text{H} \\
\text{CN} + \text{O}_2 &= \text{NCO} + \text{O} \\
\text{NCO} + \text{H} &= \text{NH} + \text{CO} \\
\text{NCO} + \text{NO} &= \text{N}_2\text{O} + \text{CO} \\
\text{NH} + \text{NO} &= \text{N}_2\text{O} + \text{H}
\end{align*}
\]

(VIII-50)  
(VIII-51)  
(VIII-52)  
(VIII-53)  
(VIII-54)  
(VIII-55)  
(VIII-56)

No rate data was available for reactions 21, 23, and 24, but they are all exothermic, spin conserved, and so are retained as possible reactions. Reaction 21 is expected to be fast
by analogy with reaction 22. Reactions 19 and 20 are expected to be important only at high temperatures and reaction 25 will be important only when the NH radical concentration approaches 1ppm.

The above intermediates can all undergo additional reaction to produce $N_2$. The above species can form $N_2$ in the following ways; monotonic N can react rapidly with any molecule containing an exposed nitrogen atom; NCO can, additionally, react with NO to form $N_2O$; NH can react with NO to form $N_2O$, and $N_2O$ can easily be reduced to $N_2$ by a number of oxygen abstraction reactions.

It is impossible to determine the effect of temperature on the competition between the nitrogen oxidation and reduction scheme without a complete kinetic evaluation. This will be done in future work but it should be noted that reactions producing N are likely to be highly temperature sensitive and these reactions appear to be important in production of $N_2$.

**VIII-3.4 Oxidation of Char**

One possibility for control of the fuel nitrogen contribution to nitrogen oxides emissions is to control the split of nitrogen between the char and volatiles. At the start of this study no information existed on the conversion of fuel nitrogen to nitrogen oxides when char was heterogenously oxidized, a gap which has been filled by the results of the present study reported by Pohl and Sarofim (1976) and a parallel effort reported by Pershing and Wendt (1976).
The evidence on the oxidation of char from this study showed that the conversion efficiency was lower by about 10% absolute at a fuel equivalence ratio of 0.7. Other than the lower efficiency of conversion the trends observed for conversion of the fuel nitrogen in the raw coal were similar to those observed for oxidation of the char. Burnout of the char was poorer than burnout of the raw coal at rich fuel equivalence ratios. Additionally more nitrogen was retained in the unburned char compared to the unburned coal.

Pershing and Wendt (1976b) report conversion efficiency to NO of a char containing 0.99% nitrogen oxidized using both a divergent nozzle and an axial injector. There was no difference in conversion between the two different nozzles. The conversion efficiency was about 13% which agreed with the conversion found in this study using a char devolatilized at 1500°C for one second which had 1.07% nitrogen. It seems reasonable that mixing should have much less effect on the slow heterogenous oxidation reactions.

That the conversion to nitric oxide of fuel nitrogen when char is oxidized should be less than that for raw coal can be explained by the nature of reactions subsequent to heterogenous oxidation. Figure VIII-6 shows the equilibrium distribution under several postulated boundary conditions. Molecular nitrogen is not shown although it is the major product in every case. The figure is prepared on the assumption that all elements in the char are oxidized or volatilized in the same
EQUILIBRIUM DISTRIBUTION OF COAL N NEAR BURNING SURFACES

ONLY COAL OXYGEN

$1500^\circ K$ CHAR

$\text{CH}_0.03 \rightarrow \text{CO} + 0.015 \text{ H}_2$

$\text{NO} \quad \text{N}_2$

$\text{AIR}$

$\text{CO}_2 + 0.015 \text{ H}_2\text{O}$

TEMPERATURE ($^\circ K$)

ratio as in the char. Three oxidation conditions are shown: the top figure assumes only the oxygen in the coal is available for oxidation, the second assumes that enough oxygen is added to oxidize the carbon to carbon monoxide, the bottom graph assumes enough oxygen is added for complete combustion. The graphs on the left side of the paper assume only oxygen is added, the graphs on the right assume the oxygen is added as air. The temperature range covers interests ranging from fluidized beds, at 800°K, to pulverized coal flames, at 2200°K.

The major conclusion is that under all conditions, except stoichiometric air addition at high temperatures, the nitric oxide levels do not approach those observed in coal or char flames. The nitric oxide production accounts for slightly over 100% of the nitrogen from the fuel when char is oxidized with a stoichiometric amount of air at 2200°K. The excess nitrogen is contributed by atmospheric nitrogen. Comparison of the bottom two graphs indicates that the major portion of nitric oxide produced when air is added is the result of the oxidation of atmospheric nitrogen and not fuel nitrogen.

Nitric oxide will be first produced in a rich environment where conversion to N₂ is favored. This is a possible explanation for the lower conversion to nitric oxide of char nitrogen compared to coal nitrogen.

Reduction of NO to N₂ is also suspected to take place on char surfaces. Pereira, et al., (1975) have observed that nitric oxide is depleted when char is added in a fluidized bed.
This was interpreted as reduction of nitric oxide by char. More fundamental work has been done on the reaction between nitric oxide and char by Watts (1958), Bedjai, et al., (1958), Shelef and Otto (1969), and Edwards (1972) but not enough kinetic information is available to evaluate the effect of the heterogeneous reduction of nitric oxides by char surfaces for either the fluidized bed or the pulverized coal flame. The reaction seems to have an activation between about 12 and 20 kcal/g-mole, probably around 15 kcal/g-mole, but the pre-exponential factor is poorly defined.

Most studies on the nitric oxide char reaction were aimed at removing the nitric oxide and not much attention was paid to developing kinetic parameters. This reaction deserves more careful study so that the effect of nitric oxide reduction by char can be evaluated for the fluidized bed and the pulverized coal flame.

The implication of lower conversion of fuel nitrogen in the char than in coal is that it is advantageous to keep as much nitrogen as possible in the char to be heterogenously oxidized instead of pyrolyzing the nitrogen into the gas phase where the nitrogen compounds can be homogenously oxidized. Unfortunately the advantage of heterogenously oxidizing the majority of the nitrogen is offset by more rapid pyrolysis which creates a larger rich region surrounding the coal particle where gas phase production of N₂ can also occur.
VIII-3.5 The Contribution of Volatile and Char Nitrogen to Nitric Oxide

Very little information exists on the contribution of nitric oxide produced from the oxidation of char and from the oxidation of volatiles. Pereria, et al., (1975) has shown, in a fluidized bed, the volatile contribution to be negligible at temperatures below 1000⁰K but to increase until the nitric oxide produced from volatile matter accounted for 2/3 of the total emission at 1200⁰K. These figures agree qualitatively with the results of this study, although the systems, temperatures, and mixing patterns must be considerably different.

The data from Figures VII-7 and VII-9 can be used to obtain preliminary estimates of the fractions of the NOₓ formed in pulverized coal flames that are contributed by the volatiles and char. As a first order approximation it will be assumed that the conversion efficiencies to nitric oxide of the nitrogen in the char and volatiles are independent. The fate of the fuel nitrogen during combustion of coal can be represented by the following simplified scheme
where 'a' is the fraction of the coal nitrogen that is released as volatiles, \( n_1 \) the fraction of the volatiles that is converted to \( \text{NO}_x \), c is the fraction of the char nitrogen that is consumed, and \( cn_2 \) is the fraction converted to \( \text{NO}_x \). The overall conversion \( n^* \) of coal nitrogen to \( \text{NO}_x \) is then given by

\[
    n^* = an_1 + (1-a)cn_2 \quad (\text{VIII-57})
\]

For a furnace temperature of 1500\(^{\circ}\)K, the value of a as determined from VII-6 is 0.67. The values \( n^* \) and \( cn_2 \) are reported as functions of fuel equivalence ratio in Figures VII-7 and VII-9. From this information it is possible to derive values of both the efficiency of conversion, \( n_1 \), of the volatile nitrogen to \( \text{NO}_x \) and the fraction of the total \( \text{NO}_x \) contributed by the volatiles \( (n_1a/n^*) \). The values thus derived are shown as a function of equivalence ratio in VIII-12. The curve suggests that for a furnace temperature of 1500\(^{\circ}\)K, 60 to 80 percent of the \( \text{NO}_x \) is contributed by the volatiles.

The contribution of the oxidation of bound nitrogen in the volatiles to \( \text{NO}_x \) will, of course, increase with increasing temperature and time in the pyrolysis zone.

The fractional conversion \( n_1 \) of the volatiles to \( \text{NO}_x \) decreases with increasing fuel equivalence ratio in a manner similar to previously reported data on premixed (Fenimore (1972) and Sarofim, et al., (1975)) and laminar diffusion flames (Sarofim, et al., (1975)).
FIGURE VIII-12. Contribution of the oxidation of volatile nitrogen to total nitric oxide.
VIII-4. Practical Implications of This Work

The purpose of this work was to better understand the processes operating in large flames that produce nitric oxide from fuel nitrogen. The object was to characterize the mechanism of fuel nitrogen conversion and recommend combustion modifications to minimize nitric oxide emission. Combustion process modifications have already reduced the nitric oxide emission levels by about half by such techniques as two stage combustion, biased firing, and delayed mixing.

The parameters that can be modified in a pulverized coal flame are temperature distribution, local richness, and mixing patterns. Mixing patterns were not a part of this study and will not be discussed, except as the mixing patterns effect the local fuel equivalence ratio which alters the conversion of fuel nitrogen. A rich early part of the flame is desirable so that a large fraction of fuel nitrogen can react to form molecular nitrogen: The molecular nitrogen is not as reactive to oxidation as fuel nitrogen components.

Experience suggest that modification of the temperature has little effect on the conversion of fuel nitrogen. Pershing and Wendt (1976b) support this conclusion at temperatures below about 2400°K. Data from this study, Armento and Sage (1975) and kinetic reasoning suggest otherwise. The evidence does not appear to be adequate at this time to ascertain the effect of temperature on fuel nitrogen conversion.

There are subtle interactions between the devolatilization
and oxidation steps in pulverized coal combustion which complicate the development of NO\textsubscript{x} control strategy. Low temperature operation favors retention of the nitrogen by the char; inasmuch as the conversion efficiency of the nitrogen in the char to nitrogen oxides is lower than that of the volatiles at a given fuel equivalence ratio low temperature operation should favor low NO\textsubscript{x} emissions for a single stage combustor. As the temperature is raised, however, increases in the devolatilization kinetics increase the local fuel equivalence ratio tending to offset the effect of having a larger fraction of the fuel nitrogen burned in the volatiles. Available data suggest that changing temperature alone does not have a significant effect on fuel nitrogen conversion in coal-fired combustors, possible as a consequence of compensation by the two opposing effects described above.

Delayed mixing burners take advantage of a large rich zone to allow reduction of fuel nitrogen components to molecular nitrogen. It is unclear if temperature changes would have any effect on the conversion of fuel nitrogen in the slowly mixed systems.

Two stage combustion has proven to be an effective control technique to suppress fuel nitrogen conversion. The richness of the first stage is controlled by flame stability, usually no less than 80% of the air requirements can be added in the first stage. This places a severe limitation on the flexibility of this control technique. Even so, the temperatures of the two stages can be modified within limits. A hot first stage
will produce a richer zone with faster kinetics but also remove more nitrogen from the char. Figure VIII-13 shows the effects of temperature and amount of air added to the first stage using the 1500°K data from this study.

This figure predicts, ignoring practical considerations for the moment, that either the first stage must be fired unacceptably rich or that the first stage must be unusually cold to minimize fuel nitrogen conversion. A very low first stage temperature implies that most of the nitrogen will remain in the char to be heterogenously oxidized in the second stage. A very rich first stage would give ample opportunity for fuel nitrogen to react to molecular nitrogen prior to extensive oxidation.

This figure should not be taken as representative of the magnitude of reductions in practical systems but the maximum reduction predicted for fuel nitrogen is only about 65% when the furnace temperature is such that unburned char persists. For higher temperature (1750°K) complete oxidation of the char is attainable under fuel rich conditions with less than 10% conversion of the fuel nitrogen to nitric oxide. The lower conversion of fuel nitrogen to nitrogen oxides at higher flame temperatures and the improvement of carbon burnout suggest that a very rich hot first stage followed by a lean second stage will give low nitrogen oxides emissions.
FIGURE VIII-13. Potential reduction of nitric oxide emissions from two stage combustion.
IX. CONCLUSIONS

Data developed in this thesis allows the following conclusions to be made about the behavior of fuel nitrogen in pulverized coal flames:

A. Pyrolysis Results

1. Evolution of nitrogen from coal is kinetically controlled for conditions encountered in typical pulverized coal flames. Nitrogen does not form structures stable to pulverized coal flame conditions but carbon does.

2. When coal is slowly heated in crucibles to different temperatures most of the volatile matter evolution occurs at temperatures below that of the ASTM Proximate Analysis test (1023°K) whereas most of the nitrogen is evolved at higher temperatures.

3. Although carbon forms a stable char through condensation reactions, no comparable stabilized nitrogen structures are formed, consequently, nitrogen can be completely eliminated from the char at temperatures above 1740°K.

4. Only small amounts of nitrogen are lost from coal during the ASTM Proximate Analysis.

5. The major portion of the ultimate volatile matter lost from coal slowly heated in crucibles occurs under the conditions of ASTM Proximate Analysis.

6. The early stages of pyrolysis of nitrogen from coal can be empirically correlated, for the two coals
studied, by a pseudo-first order rate constant with the value

\[ k = 9.3 \times 10^3 \exp(-22,700/RT) \text{ sec}^{-1} \]

7. A mechanistic model developed for nitrogen rings typically of those found in coal involves a large number of competing parallel, and consecutive radical reactions leading to formation of small volatile products containing all the fuel nitrogen and large condensed carbon products. Hydrogen cyanide appears to be the primary stable species of coal pyrolysis.

8. Little nitrogen is lost until 10-15% of the weight of the coal has been devolatilized. After this initial period associated with loss of side chains and scission of aliphatic bridges in coal, the rate of fractional nitrogen loss is found to be proportional to the rate of fractional total weight loss.

B. Oxidation Results

1. Conversion of fuel nitrogen to nitric oxide decreased with increasing fuel/air ratio, falling to negligible values at equivalence ratios greater than 1.5. At temperatures of 1500\textdegree K and below, however, some of the coal persists as unburned char which may contain a significant fraction of the original nitrogen.

2. Conversions to nitric oxide of nitrogen contained in the char are 2-3 times lower than the corresponding values for coal.
3. For the conditions of the present study, approximately 60-80% of the nitric oxide in a pulverized coal flame is produced by oxidation of volatile nitrogen.

4. Nitric oxide is probably reduced to molecular nitrogen by both homogenous reactions and heterogenous reactions with the char. The efficiencies of conversion of the volatile nitrogen decrease with increasing fuel/air ratio and fall between the values reported in the literature for premixed and diffusion flames.

5. Lower conversion efficiency of fuel nitrogen to nitric oxide, better carbon burnout, and less nitrogen in the residual char were obtained for higher oxidation temperatures.
X. RECOMMENDATIONS

Several recommendations for improvement of the experimental procedure and future work have come out of this study. These recommendations are listed below:

1. Future work should be conducted in a cold wall furnace with heat supplied by conduction from preheated gas. Cold walls will allow particle temperatures to be measured which proved impossible in the current study.

2. A wider variety of coals be studied so that more general and detailed information on the effect of coal structure on nitric oxide emission can be obtained.

3. The fundamental mechanistic approach should be extended and numerical predictions of model compound and coal pyrolysis be compared.

4. The temperature of the oxidation experiments be varied over a wider range, particularly to higher temperatures, to investigate the extent that fuel nitrogen conversion can be suppressed by operation at higher temperatures under fuel rich conditions.

5. Oxidation of chars prepared under different conditions from different coals be studied to confirm the results on the lower conversion efficiency of nitrogen bound in the char compared to that in coal.

6. Kinetics and mass transfer of the nitric oxide char reaction be investigated so that parameters can be
supplied for modeling fluid beds and pulverized coal flames.
### APPENDIX I

**FUEL CONVERSION FACTORS FROM LINDEN (1973) AND HOTTEL & HOWARD (1971)**

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### APPENDIX II

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<td>93.8</td>
<td>-</td>
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<td>77.6</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
</tr>
</tbody>
</table>

* Includes Imports
APPENDIX III

LIST OF U.S.B.M. TECHNICAL PAPERS

"ANALYSIS OF ___________ COALS"

<table>
<thead>
<tr>
<th>State</th>
<th>Report #</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALA.</td>
<td>347</td>
<td>1925</td>
</tr>
<tr>
<td>ALAS.</td>
<td>682</td>
<td>1946</td>
</tr>
<tr>
<td>ARIZ.</td>
<td>696</td>
<td>1947</td>
</tr>
<tr>
<td>ARK.</td>
<td>416</td>
<td>1928</td>
</tr>
<tr>
<td>CALIF.</td>
<td>696</td>
<td>1947</td>
</tr>
<tr>
<td>COLO.</td>
<td>574</td>
<td>1937</td>
</tr>
<tr>
<td>IDA.</td>
<td>696</td>
<td>1947</td>
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<tr>
<td>ILL.</td>
<td>641</td>
<td>1942</td>
</tr>
<tr>
<td>IND.</td>
<td>417</td>
<td>1927</td>
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<tr>
<td>IOWA</td>
<td>269</td>
<td>1921</td>
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<tr>
<td>KAN.</td>
<td>455</td>
<td>1929</td>
</tr>
<tr>
<td>KY.</td>
<td>308, 652</td>
<td>1922, 1944</td>
</tr>
<tr>
<td>MD.</td>
<td>465</td>
<td>1930</td>
</tr>
<tr>
<td>MICH.</td>
<td>700</td>
<td>1948</td>
</tr>
<tr>
<td>MO.</td>
<td>366</td>
<td>1926</td>
</tr>
<tr>
<td>MONT.</td>
<td>529</td>
<td>1932</td>
</tr>
<tr>
<td>NEV.</td>
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<td>1947</td>
</tr>
<tr>
<td>N.M.</td>
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<td>1936</td>
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<tr>
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<td>1948</td>
</tr>
<tr>
<td>OHIO</td>
<td>344</td>
<td>1923</td>
</tr>
<tr>
<td>OKLA.</td>
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</tr>
<tr>
<td>OREG.</td>
<td>696</td>
<td>1947</td>
</tr>
<tr>
<td>PENNA. (Bit.)</td>
<td>590, 645</td>
<td>1939, 1942</td>
</tr>
<tr>
<td>PENNA. (Anthracite)</td>
<td>659</td>
<td>1944</td>
</tr>
<tr>
<td>S.D.</td>
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<td>1948</td>
</tr>
<tr>
<td>TENN.</td>
<td>356, 671</td>
<td>1926, 1945</td>
</tr>
<tr>
<td>TEX.</td>
<td>700</td>
<td>1948</td>
</tr>
<tr>
<td>UT.</td>
<td>345</td>
<td>1925</td>
</tr>
<tr>
<td>VA.</td>
<td>365, 656</td>
<td>1926, 1944</td>
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<tr>
<td>WASH.</td>
<td>491, 618</td>
<td>1931, 1941</td>
</tr>
<tr>
<td>W.VA.</td>
<td>405, 626</td>
<td>1928</td>
</tr>
<tr>
<td>WYO.</td>
<td>484</td>
<td>1931</td>
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</table>
U.S. LIGNITE COAL RESERVES

28.4% of Total, 78.3% in N.D., 19.5% in Mont.
Slightly less than 0.1% N/10^3 Btu, N decreases ~ 0.2% for a 1% increase in S.

<table>
<thead>
<tr>
<th>Location</th>
<th>Heating Value Btu/lb</th>
<th>Wt % N</th>
<th>Wt % S</th>
<th>( \frac{\text{lb NO}_2}{10^6 \text{ Btu}} )</th>
<th>( \frac{\text{lb SO}_2}{10^6 \text{ Btu}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adams, N.D.</td>
<td>7,340</td>
<td>0.6</td>
<td>1.4</td>
<td>2.69</td>
<td>3.81</td>
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<tr>
<td>Adams, N.D.</td>
<td>7,630</td>
<td>0.5</td>
<td>1.6</td>
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<td>4.19</td>
</tr>
<tr>
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<td>6,620</td>
<td>0.6</td>
<td>1.0</td>
<td>2.98</td>
<td>3.02</td>
</tr>
<tr>
<td>Burleigh, N.D.</td>
<td>6,760</td>
<td>0.5</td>
<td>0.9</td>
<td>2.43</td>
<td>2.66</td>
</tr>
<tr>
<td>Divide, N.D.</td>
<td>7,270</td>
<td>0.7</td>
<td>0.7</td>
<td>3.16</td>
<td>1.93</td>
</tr>
<tr>
<td>Divide, N.D.</td>
<td>7,710</td>
<td>0.8</td>
<td>0.4</td>
<td>3.41</td>
<td>1.04</td>
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<tr>
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<td>2.00</td>
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<tr>
<td>McLean, N.D.</td>
<td>7,190</td>
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<td>1.39</td>
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<td>0.5</td>
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<td>1.58</td>
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<tr>
<td>Ward, N.D.</td>
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<td>0.72</td>
</tr>
<tr>
<td>Mercer, N.D.</td>
<td>7,140</td>
<td>0.6</td>
<td>0.7</td>
<td>2.76</td>
<td>1.96</td>
</tr>
<tr>
<td>McLean, N.D.</td>
<td>7,000</td>
<td>0.3</td>
<td>0.3</td>
<td>1.41</td>
<td>0.86</td>
</tr>
<tr>
<td>McKenzie, N.D.</td>
<td>7,010</td>
<td>0.7</td>
<td>0.6</td>
<td>3.28</td>
<td>1.71</td>
</tr>
<tr>
<td>McKenzie, N.D.</td>
<td>6,470</td>
<td>0.6</td>
<td>0.7</td>
<td>3.05</td>
<td>2.16</td>
</tr>
<tr>
<td>Williston, N.D.</td>
<td>6,460</td>
<td>0.6</td>
<td>0.6</td>
<td>3.05</td>
<td>1.86</td>
</tr>
<tr>
<td>Williams, N.D.</td>
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<td>0.6</td>
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<tr>
<td>Bowman, N.D.</td>
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<tr>
<td>Burleigh, N.D.</td>
<td>6,620</td>
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<td>1.0</td>
<td>2.98</td>
<td>3.02</td>
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<tr>
<td>Divide, N.D.</td>
<td>7,270</td>
<td>0.7</td>
<td>0.7</td>
<td>3.16</td>
<td>1.93</td>
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<tr>
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<td>0.6</td>
<td>2.86</td>
<td>1.74</td>
</tr>
<tr>
<td>Daniels, Mont.</td>
<td>6,850</td>
<td>0.6</td>
<td>0.4</td>
<td>2.87</td>
<td>1.17</td>
</tr>
<tr>
<td>Daniels, Mont.</td>
<td>6,470</td>
<td>0.5</td>
<td>2.0</td>
<td>2.54</td>
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<tr>
<td>Dawson, Mont.</td>
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<tr>
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<td>0.2</td>
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<tr>
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<td>0.6</td>
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<tr>
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<td>0.7</td>
<td>0.4</td>
<td>3.35</td>
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</tr>
</tbody>
</table>
**U.S. SUBBITUMINOUS COAL RESERVES**

24.6% U.S. Reserves, 34% Mont., 27.8% Wy., 18.3% Alas., 13% N.M., and 4.7% Colo.

0.1% N/10^3 Btu, S <1% Except for two Mont. and One Carbon, Ut. Point

<table>
<thead>
<tr>
<th>Rank</th>
<th>Location</th>
<th>Heating Value</th>
<th>Wt % N</th>
<th>Wt % S</th>
<th>10^6 lb NO₂</th>
<th>10^6 lb SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Btu/lb</td>
<td></td>
<td></td>
<td>Btu</td>
<td>Btu</td>
</tr>
<tr>
<td>sub C</td>
<td>Campbell, Wyo.</td>
<td>7,970</td>
<td>0.6</td>
<td>0.7</td>
<td>2.47</td>
<td>1.76</td>
</tr>
<tr>
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<td>Carbon, Wyo.</td>
<td>11,620</td>
<td>1.1</td>
<td></td>
<td>3.11</td>
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<td>Fremont, Wyo.</td>
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<td>0.5</td>
<td>4.16</td>
<td>1.06</td>
</tr>
<tr>
<td>sub B</td>
<td>Lincoln, Wyo.</td>
<td>10,010</td>
<td>0.9</td>
<td>0.7</td>
<td>2.95</td>
<td>1.40</td>
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<td>Sheridan, Wyo.</td>
<td>9,150</td>
<td>1.0</td>
<td>0.3</td>
<td>3.59</td>
<td>0.66</td>
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<tr>
<td>sub B</td>
<td>Sweetwater, Wyo.</td>
<td>10,490</td>
<td>1.2</td>
<td>0.5</td>
<td>3.72</td>
<td>0.94</td>
</tr>
<tr>
<td>sub A</td>
<td>Sweetwater, Wyo.</td>
<td>12,000</td>
<td>1.4</td>
<td>0.9</td>
<td>3.83</td>
<td>1.50</td>
</tr>
<tr>
<td>sub C</td>
<td>Rosebud, Mont.</td>
<td>9,080</td>
<td>0.8</td>
<td>0.4</td>
<td>2.89</td>
<td>0.88</td>
</tr>
<tr>
<td>sub A</td>
<td>Musselshell, Mont.</td>
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<td>0.9</td>
<td>0.4</td>
<td>2.71</td>
<td>0.733</td>
</tr>
<tr>
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<td>Rosebud, Mont.</td>
<td>9,290</td>
<td>0.8</td>
<td>0.8</td>
<td>2.83</td>
<td>1.72</td>
</tr>
<tr>
<td>sub A</td>
<td>Musselshell, Mont.</td>
<td>10,820</td>
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<td>0.5</td>
<td>3.04</td>
<td>0.92</td>
</tr>
<tr>
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<td>2.3</td>
<td>4.65</td>
<td>4.34</td>
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<tr>
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<td>Gallatin, Mont.</td>
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<td>0.6</td>
<td>2.70</td>
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<tr>
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<td>Judith Basin, Mont.</td>
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<td>3.9</td>
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</tr>
<tr>
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<td>Roosevelt, Mont.</td>
<td>9,020</td>
<td>0.9</td>
<td>0.4</td>
<td>3.28</td>
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<tr>
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<td>3.03</td>
<td>0.67</td>
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<td>0.5</td>
<td>3.03</td>
<td>0.84</td>
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<tr>
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<td>0.7</td>
<td>3.34</td>
<td>1.29</td>
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<tr>
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<td>El Paso, Colo.</td>
<td>8,750</td>
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<td>0.3</td>
<td>3.00</td>
<td>0.69</td>
</tr>
<tr>
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<td>Noarth, Alas.</td>
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<td>0.3</td>
<td>3.70</td>
<td>0.61</td>
</tr>
<tr>
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<td>Yukon, Alas.</td>
<td>9,700</td>
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<td>0.6</td>
<td>2.71</td>
<td>1.24</td>
</tr>
<tr>
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<td>Yukon, Alas.</td>
<td>10,600</td>
<td>0.9</td>
<td>0.5</td>
<td>2.79</td>
<td>0.94</td>
</tr>
<tr>
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<td>Nenana, Alas.</td>
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<td>0.1</td>
<td>2.35</td>
<td>0.24</td>
</tr>
<tr>
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<td>8,640</td>
<td>0.6</td>
<td>0.1</td>
<td>2.28</td>
<td>0.23</td>
</tr>
</tbody>
</table>
U.S. BITUMINOUS COAL RESERVES

46% of Total, 18.7% Ill., 14.7% W. Va., 10.86% Mo., 8.6% Colo.,
8.0% Penna., 5.8% Ohio, 5.1% W. Ky., 4.8% Ind., 4.1% E. Ky.,
3.8% Ut., 2.9% Alas., 2.9% Kan., 1.8% Mont.

Sulfur varies widely. High values from Mo., Kan., W. Ky., and Ill.
Slightly greater than 0.1% N/10^3 Btu, nitrogen content decreases 0.2% for every percent increase in sulfur.

<table>
<thead>
<tr>
<th>Rank</th>
<th>Location</th>
<th>Heating Value</th>
<th>Wt % N</th>
<th>Wt % S</th>
<th>lb NO_2 / 10^6 Btu</th>
<th>lb SO_2 / 10^6 Btu</th>
</tr>
</thead>
<tbody>
<tr>
<td>hvB-b</td>
<td>Emery, Ut.</td>
<td>12,940</td>
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<td>0.7</td>
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<td>1.08</td>
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<td>Sanpete, Ut.</td>
<td>13,150</td>
<td>1.6</td>
<td>0.6</td>
<td>4.00</td>
<td>0.91</td>
</tr>
<tr>
<td>hvA-b</td>
<td>Walker, Ala.</td>
<td>13,800</td>
<td>1.8</td>
<td>1.3</td>
<td>4.21</td>
<td>1.88</td>
</tr>
<tr>
<td>hvA-b</td>
<td>Cherokee, Kan.</td>
<td>12,550</td>
<td>1.4</td>
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<td>3.66</td>
<td>5.10</td>
</tr>
<tr>
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<td>Lincoln, Wyo.</td>
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<td>0.7</td>
<td>2.91</td>
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<tr>
<td>hvC-b</td>
<td>Jackson, Ohio</td>
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<td>1.4</td>
<td>0.9</td>
<td>3.81</td>
<td>1.49</td>
</tr>
<tr>
<td>hvB-b</td>
<td>M. Kittanning, Ohio</td>
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<td>3.5</td>
<td>3.52</td>
<td>5.77</td>
</tr>
<tr>
<td>hvB-b</td>
<td>Muskingum, Ohio</td>
<td>12,260</td>
<td>1.2</td>
<td>4.9</td>
<td>3.22</td>
<td>7.99</td>
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<tr>
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<td>3.17</td>
<td>9.64</td>
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<tr>
<td>hvC-b</td>
<td>Adair, Mo.</td>
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<td>3.6</td>
<td>2.83</td>
<td>6.88</td>
</tr>
<tr>
<td>hvC-b</td>
<td>Missouri City, Mo.</td>
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<td>2.9</td>
<td>3.14</td>
<td>6.00</td>
</tr>
<tr>
<td>hvC-b</td>
<td>Henry, Mo.</td>
<td>11,470</td>
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<td>3.9</td>
<td>3.15</td>
<td>6.80</td>
</tr>
<tr>
<td>hvC-b</td>
<td>Boone, Mo.</td>
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<td>3.3</td>
<td>2.77</td>
<td>5.56</td>
</tr>
<tr>
<td>hvA-b</td>
<td>Kanawha, W. Va.</td>
<td>14,150</td>
<td>1.5</td>
<td>0.7</td>
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<td>0.99</td>
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<td>1.1</td>
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<td>1.57</td>
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<tr>
<td>hvA-b</td>
<td>Marion, W. Va.</td>
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<td>A.R.</td>
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</table>

Generally low in sulfur.

Slightly lower than 0.14% N/10,000 Btu.

4% of U.S. reserves, 98% in Pennsylvania.

U.S. Anthracite Coal Reserves
APPENDIX IV

Weight Loss Data

The work in this thesis was done in cooperation with Hisashi Kobayashi who was most concerned with the devolatilization kinetics. His results have been reported, Kobayashi (1976a and b) and will be summarized here since total weight loss is directly connected with nitrogen loss which is the subject of this thesis. The equipment used, the mode of operation, and the samples are the same as described in the main thesis body.

Figure A-IV-1 shows weight loss, d.a.f., versus time with furnace temperature as a parameter for the Montana Lignite used in this study. Weight loss was zero at 1000ºK and the short residence times studied. This run confirmed that the collection efficiency was very good to temperatures at least as high as 1000ºK. Maximum weight loss increased uniformly as temperature increased; weight loss was 0 at 1000ºK, 26% at 1260ºK, 42% at 1560ºK, 52% at 1740ºK, 59% at 1940ºK, and 63% at 2100ºK. The time to reach asymptotic weight loss decreased from about 200 milliseconds at 1260ºK to about 30 milliseconds at 2100ºK. Weight loss at one second, not shown in the graph, showed that for the lower temperatures weight loss marginally increased on the time scale of one second.

There is no reason to suppose that the ultimate weight loss is achieved at 2100ºK. If higher temperatures were used
the rate loss should be greater, even graphite has a finite loss of weight at high temperatures. Secondly, very slow weight loss appears to occur on a very long time scale after the initial weight loss. These results are consistent with pyrolysis being controlled by a complex kinetic mechanism that involve competitive reactions.

Figure A-IV-2 shows similar weight loss curves for the Pittsburgh Seam #8 hvA bituminous coal used in this study. The weight loss for the bituminous coal is very similar to that obtained for the Montana lignite used in this study. The weight loss for the bituminous coal appears to be slightly higher and the rate of weight loss somewhat faster, although the differences are minor. That two coals of such different rank, chemical, and physical structure should behave similarly was surprising. This is currently viewed as an unfortunate choice of coals but the trend should become clear as more coals are studied. Relatively large quantities were soot recovered after devolatilization of bituminous coal. Correction for soot formation will be discussed in Appendix V and would tend to increase the weight losses reported in Figure A-IV-2 by as much as 20%.

The following table lists the element analysis for all coal samples analyzed in this work. The listings are mostly self-explanatory. Listed in the tables for residual char and volatile matter are: weight percent, and atomic ratio. The percent retention of an element in the char is also listed.
FIGURE A-IV-2. Weight Loss from hvA Bituminous Coal.
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<th>WEIGHT (%)</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
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APPENDIX V

Discussion of the weight loss results presented by Kobayashi (1976)

The weight loss results for the data reported in this thesis were part of a complementary study by Kobayashi (1976). The results will be summarized here because total weight loss has an obvious effect on all element loss including loss of nitrogen.

Initial particle temperature measurement were thwarted by strong radiation from the hot walls. Measured two color pyrometer temperatures are equal to the wall temperature in the case of devolatilization where the particle is colder than the wall temperature. Thermocouple measurements are insensitive to the gas temperature because the thermocouple is largely heated by radiation from the wall. Initial trouble was encountered in attempts to measure gas stream temperatures with sodium D-line reversal. The problem was alignment of the optics on the small coal stream. These problems are not insurmountable and gas temperatures will be measured in the future by sodium D-line reversal and particle temperatures will be calculated from the known surrounding conditions.

In the absence of a direct temperature measure, temperature profiles were calculated. An integral approach was used to calculate both the velocity and temperature profile. The shape of the boundary layer must be known to use the integral approach to solution of the transport equations. The velocity
profile was chosen to match velocities measured with a laser doppler anemometer. The shape factor that best fit the data was 4.5; a shape factor of 2 would correspond to a parabolic profile and large shape factors approach flat profiles. Several different ratios were tried for the ratio of thermal profile to velocity profile.

The effect of variation of the shape factor from 1-3 for a temperature of 2100°C is shown in Figure A-V-1. The shape factor has little effect on calculated residence time or ultimate temperature but has a large effect on the temperature profile in the early heating stages.

A shape parameter of three was choosen based on weight loss at the different calculated temperatures. Figure A-V-2 shows weight loss versus calculated temperature for lignite and Figure A-V-3 is a similar prepresentation of bituminous coal. The criteria for choosing the shape factor as 3 is that it is the smallest shape factor that does not predict higher weight loss at lower furnace temperatures.

Many previous studies calculated weight loss based on the ASTM ash remaining constant regardless of temperature and time history. This can not be strictly valid because the ASTM ash test is a model test that measures the amount of mineral matter converted to oxides under specified conditions of time and temperature. For most conditions the ash content is an adequate measure of weight loss, although under some condition calculation of the weight loss assuming ash is
FIGURE A-V-1. Effect of shape factor on velocity and temperature profiles for a furnace temperature of $2100^\circ$K.
constant can lead to large errors.

Figure A-V-4 shows the correlation between apparent weight loss d.a.f. (directly measured weight loss) and the weight loss calculated using ash as a tracer component for free fall and crucible results of this study. The correlation for bituminous coal is shown to be excellent for free fall results but very low weight losses are predicted for samples held at temperatures above 1750\(^\circ\)K for long periods in crucibles. The low predicted weight losses are caused by significant ash losses at temperatures above 1750\(^\circ\)K.

A similar figure is shown for weight loss from lignite in Figure A-V-5. The predicted weight loss is always about 5% lower than the measured weight loss at temperatures below 1750\(^\circ\)K but is very significantly below the measured weight loss at higher temperatures. At 2000\(^\circ\)K use of the ash tracer to calculate weight loss would predict a negative weight loss. This implies that at this condition ash is lost more readily than coal. The residual char must be in a very stable form to have lower weight loss than the metallic oxides that compose ash. The ash has \(\text{CaCO}_3\) and \(\text{FeS}_2\) components that decompose differently under different conditions.

Comparison of ash tracer weight losses with measured weight losses for the fast flow experiments are shown in Figure A-V-6. The data is scattered partly because of the inherent experimental problems associated with obtaining devolatilization data at short residence times and high
FIGURE A-V-4. Correlation between apparent weight loss and weight loss calculated using ash as a tracer for bituminous coal.
FIGURE A-V-5. Correlation between apparent weight loss and weight loss calculated using ash as a tracer for lignite.
FIGURE A-V-6. Correlation between ash tracer and measured weight loss for rapid devolatilization of lignite.
temperatures, but the largest error is probably associated with the very small sample available for ash determination. Apparent weight losses are higher than predicted by the ash tracer method of weight loss estimation. If the scatter is ignored, the difference could represent differential char particle loss either in the furnace or through the filter. Tests have shown, however, that ash loss through the filter is more likely than char loss.

Similar results for the devolatilized bituminous coal are shown in A-V-7. Weight loss by use of ash as a tracer predicts higher weight losses than actually measured for weight losses above about 20%. The explanation for this effect is that large amounts of very small soot particles are manufactured in the gas phase when bituminous coal loses more than 20% of the original weight, and these soot particles are partially lost through the filter and partially trapped in the filter. The filter is made of 5 micron sintered bronze. The soot particles lost through the filter are counted as weight loss, and soot particles trapped in the filter are not counted as apparent weight loss but are counted when weight loss is estimated using ash as a tracer.

Both the amount of material lost from the original coal and the amount of material that condense are of interest in modeling gasifiers and pulverized coal flames. Large quantities of soot have been identified in similar systems: Eddinger, et al., (1966) found 5-16% soot, the results of Coates, et al.
FIGURE A-V-7. Correlation between ash tracer and measured weight loss for rapid devolatilization of bituminous coal.
(1974) indicate about 10% soot formation, Ubayakar, et al., (1976) found about 20% soot of which 80-90% was estimated to be formed in the gas phase. Alpern, et al., (1950) has clearly identified soot formation in samples from the Ijmuiden furnace. The soot particles were 100 to several thousand Angstroms in size, contained about 1% hydrogen, and were formed by condensation of heavy volatile matter evolved in the early stages of pyrolysis. The characteristics of the soot described by Alpern agrees with limited characterization of the soot found in this study.

Figure A-V-8, a plot of asymptotic weight loss, at different temperatures, with time shows that for lignite weight loss continues to occur at any temperature after an initially rapid loss. The slow increase of weight loss at long times further supports the type of competitive kinetic model developed in this study.

A similar plot for devolatilized bituminous is shown in Figure A-V-9. The trends of weight loss with time observed in the plot are not easily discernible. The asymptotic weight loss obtained from laminar flow experiments appeared to cross the results obtained from free fall experiments even though the longest residence time for the laminar flow experiments is 200 milliseconds compared to 1000 milliseconds for the free fall experiment. The difficulties with interpretation of this data are thought to be the effect of temperature, time, and experimental conditions on the quantity of soot formed and
FIGURE A-V-8. Increase in asymptotic weight loss with time for lignite
FIGURE A-V-9. Increase in asymptotic weight loss with time for bituminous coal.
collected. If a correction for the quantity of soot produced is made the curves, dark points, appear to resemble more closely the curves developed for devolatilization of lignite, where no soot is formed. The corrections are not entirely satisfactory and additional quantitative work on the quantity and nature of soot formed at pulverized coal flame and gasifier conditions is needed.

The pseudo-first order rate constant for total weight loss are plotted in Figure A-V-10 for Montana lignite and Figure A-V-11 for Pittsburgh bituminous. The trend in total weight loss is seen to be similar for the two coals used in this study and to be similar to the rates of nitrogen loss reported for the two coals in Figure VIII-6. The rate constant for the overall weight loss can be represented as

\[ k = 6.6 \times 10^4 \exp(-25,000/RT) \text{ sec}^{-1} \]

First order rate constants do not adequately represent the rate of weight loss, as has been discussed for pyrolysis of nitrogen. Only slight improvement is obtained by deriving rate constants at constant extent of reaction.

The rate loss of nitrogen, after an initial devolatilization period, is seen to be quite similar to total weight loss. The rate of loss of other elements is also similar to each other and to total weight loss. The rate of hydrogen, oxygen, and carbon loss are shown for lignite in Figure A-V-12 and for bituminous in Figure A-V-13. Similarity between the rate of various element losses would be expected if the units removed
FIGURE A-V-10. First order Arrhenius plot for weight loss.

Montana lignite.
FIRST ORDER ARRHENIUS PLOT FOR WEIGHT LOSS.
PITTSBURGH SEAM BITUMINOUS COAL.

Pittsburgh Seam bituminous coal.
FIGURE A-V-12. First order Arrhenius plot for retention of $\text{C}_n\text{H}_m\text{O}$. Montana lignite.
FIRST ORDER ARRHENIUS PLOT FOR RETENTION OF C, H, O.
PITTSBURGH SEAM BITUMINOUS COAL.

FIGURE A-V-13. First order plot for retention of C,H,O.
Pittsburgh Seam bituminous coal.
were large enough to have a statistical distribution of elements or the reactions leading to element loss are complex reactions involving radicals which discriminate little between elements.
APPENDIX VI

Coal Element Loss

Coal is composed of digested, compressed, and reacted plant material. The genesis paths followed by different coal elements and the rank of a particular coal is largely determined by the conditions under which chemical changes in the original plant material took place.

Figure A-VI-1 shows the genesis paths from cellulose to anthracite. Compositions of different coals and cellulosic materials are plotted on a H/C versus O/C basis.

Most coals are composed primarily of vitrinite elements or digested woody tissue. The vitrinites genesis path starts at cellulose, or more properly wood. As digestion and chemical changes occur in the original plant material—through loss of hydrogen, methane, and carbon oxides—peat, brown coals, and American lignites are produced. Between an O/C ratio of 0.25 and 0.05, oxygen is lost, or a combination of hydrogen, oxygen, and carbon losses such that the H/C ratio remains constant as the O/C ratio decreases. The flat portion of the curve encompasses the change in rank of bituminous coals. Complete oxygen loss results in anthracite coals. Graphite, the ultimate genesis product, retains only carbon.

Small quantities of fusinite appear in most coals. Fusinite is material that has the appearance and approximate composition of charcoal. It was once though fusinite was the result of forest fires; conventional genesis to produce
FIGURE A-VI-1. Coalification Diagram.
fusinite is now more acceptable.

Exinites represent inert plant material that has only been mildly digested through the coalification process. These bodies can typically be either resinous bodies or decayed resistance plant material such as spores, pollen, and cuticles. Exinite is usually easily decomposed when heated to temperatures above 400°C and exinite is believed to account for some of the strange physical behavior of bituminous coal that will be discussed in the next two sections.

Alginities are partially decomposed algae and form the major component of special coals, such as cannel. They have no importance in ordinary coals.

When coal is rapidly heated to high temperatures, the composition of the residual coal material passes through chemical stages similar to the stages the plant material passed through in coal generation. Figure A-VI-2 shows the chemical changes obtained by rapidly heating a lignite and bituminous coal to a temperature of 1500°C. The numbers along the curves represent the residence time in milliseconds, the "x's" represent the composition of the original. The changes in chemical composition of the lignite coal appear to be similar to the chemical changes that occur in vitrinite genesis and the changes in bituminous coal appear to be close to those changes that occur in exinite genesis.

The paths that would be followed by elimination of certain chemical components are also shown on the graph. The interpretation of chemical composition of the volatile elements is
FIGURE A-VI-2. Carbonization Diagram. 1500°K.
not unique but the elements chosen to represent loss are known to be present in volatile products of coal.

Initially lignite loses carbon monoxide and aliphatic groups. The long sloping regions could represent water loss, the flat portion would appear to represent oxygen loss or alternatively carbon monoxide and hydrocarbon loss. The final portion of the curves probably represents hydrogen loss.

The carbonization curve for bituminous coal appears quite different from the curve for lignite. The entire curve appears to represent a loss of hydrocarbons and water. Carbon monoxide is, however, identified in pyrolysis products. The carbon monoxide could be the results of secondary reaction between water fragments and the hydrocarbon but this is unknown.

Figure A-VI-3 shows all the chemical analysis performed for a number of different temperatures and different modes of experiment. Within the range of expected error, all the compositions seem to follow the general coalification paths discussed for the data taken under conditions of rapid heating and a maximum temperature of $1500^\circ\text{K.}$
APPENDIX VII
Surface Area

In order to develop models of coal behavior during devolatilization and burning, information must be available on the physical changes of the coal. The surface area and the nature of the restriction to the internal surface will effect the rate of devolatilization and condensation of the coal. Preliminary values of the surface of devolutilized char are presented in this appendix as an initial effort to characterize the physical structure of the char during the devolatilization process. Only krypton adsorption surface areas are reported here. It is recognized that at 77 K krypton can effectively enter only pores larger than about 12 Å. The surface area contained in pores this large accounts for only a small fraction of the total surface area but the surface area of these large pores is interesting because 12 Å is about the size of a two ring molecule, so compounds bigger than about two rings will not escape easily from coal during devolatilization. Adsorption of \( \text{CO}_2 \) at room temperature yields a more representative surface area-\( \text{CO}_2 \) adsorption as well as Kr adsorption. surface areas will be reported in future work.

The measured values of surface area are reported in Table A-VII-1. Surface areas of raw lignite and bituminous coal are the same but the surface area of the bituminous coal appeared to reach a maximum surface area at around 1500 K and then shrink, for residence times of one second, while the accessible
### TABLE A-VII-1

**Kr Surface Areas of Devolatilized Coal**

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<td>20.5</td>
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<td>1740.</td>
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<td>45.</td>
<td>1740</td>
<td>58.6</td>
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<td>1740</td>
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<td>LF-306</td>
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<td>55</td>
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<td>Raw</td>
<td>Bit</td>
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<td>-</td>
<td>-</td>
<td>1.25</td>
<td>2.1</td>
</tr>
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<td>ML-5</td>
<td>Bit</td>
<td>25.1</td>
<td>1000</td>
<td>1000</td>
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<td>0.7</td>
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<td>ML-6</td>
<td>Bit</td>
<td>32.2</td>
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<td>7.6</td>
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<td>ML-2</td>
<td>Bit</td>
<td>39</td>
<td>1750</td>
<td>1000</td>
<td>0.5</td>
<td>6.4</td>
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</table>
SURFACE AREAS OF DEVOLATILIZED COAL

Kr at 77°C K
% > 12 Å
1 Sec Residence Time
- Lignite, Polanti - Dubinin
- Lignite, B.E.T.
□ Bituminous Coal
Polanti - Dubinin
■ Bituminous Coal, B.E.T.

SURFACE AREA M²/g

32
28
24
20
16
12
8
4
0
300 1000 1500 2000
FURNACE TEMPERATURE

FIGURE A-VII-1. Surface area of devolatilized coal.
surface area of lignite appeared to increase to very large values as devolatilization continues. The data on bituminous coal is supported by Van Krevelen (1960) and the behavior of lignite is similar to that reported by Nsakala, et al., (1975).

The development of large pore surface areas is reported in Figure A-VII-1 for free fall devolatilization with residence times on the order of a second. Surface areas are determined by both the BET equation and the Polyani-Dubinin equation. Since surface areas are only relative, it probably makes no difference which equation is used, although the Polyani-Dubinin equation is usually favored for determination of coal surface areas and gives slightly higher values.

Too little data has been collected as yet to make any definite conclusions on the behavior of the surface area at the short residence times typical of a pulverized coal flame. Preliminary data indicates that most of the large surface areas found for extensively devolutilized lignite occurs after the weight losses exceed 50%.
APPENDIX VIII
Changes in Physical Structure

During devolutilization, coking coal has a dramatic change in physical appearance. It has been recognized for a long time that some coal swell under certain devolutilization conditions. Sinnatt and Slater (1922) first identified swollen coal particles, Newall and Sinnatt (1924) coined the term cenosphere and investigated the effect of temperature on swelling, Lightman and Street (1967) have investigated swelling of coal under a number of experimental conditions, Street, et al., (1968) and Gray et al., (1975) studied the effect of atmosphere and lithotype on swelling. Efforts to relate the swelling of coals to combustion systems have been made by Newall and Sinnatt (1926), Littlejohn (1966), Street, et al., (1968), and the effect of particle size on burning has been reviewed by Mulcahy and Smith (1969). Additionally, Shibaoaka (1969) has studied the change in particle size during burning of a single particle.

One of the coals used in this study was non-swelling. Particle size determinations, shown in Figure A-VIII-1, show constant particle size and distribution with extensive weight loss. The difference in the structural changes that occur between a swelling and non-swelling coal during devolutilization are clearly represented by the polished sections of devolutilized coal presented in Figure A-VIII-2. The top micrograph represents one particle that has formed a cenosphere, the bottom micrograph
FIGURE A-VIII-2. Particle size of devolatilized lignite.
FIGURE A-VIII-2. Photomicrographs of a devolatilized coal: a single bituminous coal particle (top), a collection of lignite particles (bottom)
shows that the lignite coal retained the original particle size but developed large interior macropores.

Bituminous coking coal increases in size when volatile matter is removed under inert conditions. Figure A-VIII-3 shows the change in average particle size and dispersion as a bituminous coal loses volatile matter. The particles remain unchanged in size for weight losses up to 60% when the devolatilization temperature is greater than 1750°K. Noticeable swelling does occur at temperatures of 1500°K and below. At a furnace temperature of 1500°K the particle size increases from about 60 microns to a maximum of 450 microns at around 30% weight loss and then decreases as the particles break. Particles in the range of 400-600 microns were obtained when coal was devolatilized at lower temperatures and longer residence times.

The effect of residence time on particle swelling is demonstrated in Figure A-VIII-4. The coal was swollen by a factor of about four by the first data point (50 milliseconds) for a furnace temperature of 1510°K. By 60 milliseconds the char had reached its maximum swelling, a factor of about eight, at longer times the particles break.

The coal devolatilized at 1250°K showed swelling by a factor of 2-3 at around 100 milliseconds but a factor of 8-10 at 1000 milliseconds. When the furnace temperature was reduced to 1000°K bituminous coal showed a factor of two swelling at 250 milliseconds; the swelling increased to a factor of about
FIGURE A-VIII-4. Particle size of bituminous coal versus residence time.
FIGURE A-VIII-5. Early bubble development in Pittsburgh seam #8 hvA bituminous coal.
9 for coals devolatilized for 1000 milliseconds at 1000°K.

The bituminous coal swells because the coal becomes plastic at temperatures around 300-400°C and the large evolution of gas can not escape from the interior of the molten sphere without blowing holes through the plastic mass to the exterior and inflating the char in the process.

Early bubble development is shown in Figure A-VIII-5 for char with around 10% weight loss and temperatures of either 1000°K or 1250°K. When devolatilized at 1000°K for 155 milliseconds the coal loses 7% by weight and no swelling is detected, but bubbles 10 microns in size are visible. A very few bubbles have burst under these conditions to form small holes several microns in diameter. By the time the particles have been devolatilized for 244 milliseconds and lost 9% of the original weight, the coal has begun to form small spherical particles approximately twice the original diameter. Blow holes are more in evidence and larger than in the earlier picture.

A higher magnification picture taken of a particle that had been devolatilized for 69.2 milliseconds at 1250°K, conditions at which 10.9% weight loss occurred, showed only about 15% swelling and large bubbles some of which are broken. At the bottom of the picture a small spherical particle can be seen.

Figure A-VIII-6 shows void development with time for particles devolatilized in a 1500°K furnace. At 38 milliseconds the weight loss is 7% and no swelling or extensive bubble development is evident. After devolatilization for 51 milli-
FIGURE A-VIII-6. Void development in time for a Pittsburgh seam #8 hvA bituminous coal devolatilized at 1500°K.
seconds the coal has lost 14% of the original weight and
swollen by a factor of about 4. Void development can be
clearly seen. A weight loss of 23.2% has taken place by 63
milliseconds and the coal has swollen by a factor of 8 and
many small voids are visible. By 81 milliseconds the particle
has a weight loss of 33, 7% very large voids have developed
and the particles have begun to fracture. Fracture of the
particles and continued large void development are apparent
at 81 milliseconds.

The development of voids with temperature at a constant
residence time of ten minutes in a cup is shown in Figure
A-VIII-7. The average particle sizes are all about the same
and the weight losses range from 53.1% at 1000°K to 63% at
1750°K. The voids at low temperatures are few and relatively
large. As the temperature increased many more small voids
develop. The particles must, in this case, have had a
temperature time history that allowed maximum swelling since
all the temperatures had nearly the same average particle size
and distribution.

The nature of the swelling can be better visualized by
reference to the singel particle in Figure A-VIII-8. The
original size of the coal was about 60 microns. The swollen
particle is about 400 microns so the particle has swollen by
a factor of 7. A few large voids on the order of 20 microns
are visible as are many small holes less than one micron.
The particle can be seen to be hollow from the view inside the
VOID DEVELOPMENT WITH TEMPERATURE
PITTSBURGH SEAM #8 BITUMINOUS COAL, FREE FALL TO CUP (ASYMPTOTIC)

T = 1000*K
WL = 53.1 D.A.F.
X = 521.2 μm
σ = 173.3 μm

T = 1250*K
WL = 54.2 D.A.F.
X = 523.6 μm
σ = 108.4 μm

T = 1500*K
WL = 59.0 D.A.F.
X = 489.5 μm
σ = 138.6 μm

T = 1750*K
WL = 63.0 D.A.F.
X = 566.7 μm
σ = 145.3 μm

FIGURE A-VIII-7. Void development of Pittsburgh seam #8 hvA bituminous coal with temperature at asymptotic times.
FIGURE A-VIII-8. Electronmicrographs of a devolatilized bituminous coal particle
particle or by reference to Figure A-VIII-2 which shows a different particle. The surface of the particle shows that the particle was molten at one time.

Estimates of the amount of material contained in cenosphere shells indicates that there is slightly too much material to be accounted for by one particle. Figure A-VIII-9 shows the rare case of agglomerated particles that have not as yet fused together. Agglomeration does occur to some extent but the importance of agglomeration is uncertain at this time.

Finally, Figure A-VIII-10 shows electronmicrographs of ash particles from burned lignite and bituminous coal. The ash particles also form cenospheres because of release of water from hydrates and carbon dioxide from carbonates inside a molten shell. Ash cenospheres are typically 10 microns in size and no difference in physical characteristics could be seen between the lignite and bituminous coal ash.

\[ T = 1250^\circ K \]
\[ WL = 54.2 \text{ d.a.f.} \]
\[ \lambda = 523.6 \mu \text{m} \]
\[ \sigma = 108.4 \mu \text{m} \]

\[ T = 1500^\circ K \]
\[ WL = 59.0 \text{ d.a.f.} \]
\[ \lambda = 489.5 \mu \text{m} \]
\[ \sigma = 138.6 \mu \text{m} \]
FIGURE A-VIII-10. Electronmicrograph of ash obtained on the complete combustion of bituminous coal (top), lignite (bottom)
BIBLIOGRAPHY


Davis, J.D. and V.F. Parry, "Carbonizing of Subbituminous Coal from Puritan Mine, Dacono, Weld County, Colo.," U.S. Bureau of Mines Rept. of Invest., 3428 (1939).


Merryman, E.L. and A. Levy, "NO\textsubscript{x} Formation in CO Flames," presented at CRS Fundamental Research Contractors Meeting, Menlo Park, California (June 1975).


Pershing, D.W., J.O.L. Wendt, "Effects of Coal Composition on Thermal and Fuel NO\textsubscript{x} Production from Pulverized Coal Combustion," Presented at Central States Section, The Combustion Institute, Columbus, Ohio, April (1976a).


Selker, A.P., "Overfire Air as a NO\textsubscript{x} Control Technique for Tangential Coal-Fired Boilers," Presented at EPA Symposium on Stationary Source Combustion, Atlanta, Georgia, September (1975).


Snyder, G. "Flat Flame Burner Studies with HCN, NH₃, and NO," Presented at CRS Fundamental Research Contractos Meeting, Menlo Park, California (June 1975).


Vogt, R.A. and N.M. Laurendeau, "NO\textsubscript{x} Formation From Coal Nitrogen: A Review and Model," Presented at Central States Section Meeting The Combustion Institute, Columbus, Ohio, April (1976).


Tingey, G.L. and J.R. Morrey, "Coal Structure and Reactivity," 

Ubbayakar, S.K., D.B. Stickler, C.W. von Rosenberg, Jr., 
and R.E. Gannon, "Rapid Devolatilization of Pulverized 
Coal in Hot Combustion Gases," Paper to be Presented 
at Sixteenth Symposium (International) on Combustion, 

Gray, J.A., P.J. Donatelli, and P.M. Yavorsky, "Hydrogasification Kinetics of Bituminous Coal and Coal Char," 
ACS Division of Fuel Chemistry, Preprints, 20 (4), 130 
(1975).
BIOGRAPHY

The author, John Henning Pohl, was born at Fort Riley, Kansas May 29, 1944; the first son and second child of Ellen Henning and Herbert Otto Pohl. He attended public schools in Sacramento, California, graduated from Sacramento City College in 1964, earned a B.S. in chemical engineering from the University of California in 1966, and joined the du Pont Company the same year as a chemical engineer in Seaford, Delaware.

He married the former Judith Lynn Sykes of Sacramento in August, 1968. The author held a number of engineering jobs within the du Pont Company until 1970 when he returned to school at M.I.T. He has worked in the Fuels Research Laboratory since that time and earned an S.M. degree in 1973. Two sons, Otto and Clint Henning were born while the author was at M.I.T. On graduation the author will be employed by the Combustion Research Division of Sandia Laboratories in Livermore, California.

In addition to his master's thesis the author is the co-author of three technical publications with Adel F. Sarofim.


3. Fate of Coal Nitrogen during Pyrolysis and Oxidation,
presented at EPA Symposium on Stationary Source Combustion, Atlanta, Georgia, September (1975).


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