THERMAL REACTIONS OF FRESHLY GENERATED COAL TAR
OVER CALCIUM OXIDE

by

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ABSTRACT

A systematic study of the effects of cracking temperature
(in the 400 - 800°C range) on the pyrolysis reactions of freshly
formed tars, from a thin bed of Pittsburgh No. 8 Seam Bituminous
coil, in the absence and presence of CaO was performed. Selective
studies of the effects of stone origin, stone/feed ratio, gaseous
environment, types of stone, and volatiles contact time with the
CaO packed bed, on tar cracking reactions were also performed.
System pressure was typically 1.2 - 1.3 atm.

The vapor phase thermal cracking of tar was found to occur
mainly through breakage of the aliphatic linkages and of the
functional groups, rather than cracking of the aromatic ring
systems. The major products were CH₄, C₂H₄, C₃H₆, CO, CO₂ and
above 700°C, H₂, as well as coke formed on the reactor wall. The
tars that survived thermal treatment had decreasing average
molecular weight and aliphatic hydrogen contents with increasing
cracking temperature. Above 700°C, the phenolic content declined
and the metabolically induced bacterial cell (MIB) mutagenicity
of tar increased drastically.

At the same cracking temperature, the rate of cracking
reactions of tar over micron-size CaO from calcined Ca(OH)₂,
was increased by one to two orders of magnitude. The major
products were coke (about 80 - 85 Wt%) formed on the CaO surface
and H₂. The relative yields of light hydrocarbon gases were
significantly lower in the presence of CaO than in its absence.
The existence of special CaO-aromatics interactions that led to enhanced pyrolysis of the aromatic tar fractions, was indicated by a significantly higher aliphatic to aromatic hydrogen ratios when compared to thermally cracked tars at the same temperature. Conversion over CaO gave lower average MW and phenolic content of tars than for thermal cracking, suggesting that higher molecular weight constituents (when pore diffusion limitations were unimportant) and phenolics were selectively removed from the tar mixture through the CaO treatment. Tar MIB mutagenicity was generally moderated, especially at 700°C, when thermally treated over CaO, as compared to its absence.

The tar cracking activity of CaO decreased with increasing extent of coking. The activity could only be partially re-generated by O₂ burnoff of the coke. An effective stone regeneration protocol which involved hydration and recalcination of the coke-free, deactivated CaO, was identified. An adverse effect (to stone sintering) of sulfur content of CaO (due to sulfur pickup from the coal pyrolysis gases) was also observed.

The ability of CaO to selectively enhance the cracking of aromatics is believed to be related to the stone's electron-accepting (i.e., Lewis acid) property at high temperatures, even though the CaO surface is well-known to be basic at room temperatures. The reversal of CaO surface property was presumably achieved by diffusion of O⁻ ions (positively charged defects in the CaO crystal lattice) from CaO bulk phase to the surface at high temperatures. Present measurements of CaO electrical resistance above 400°C in this work lend strong support to this picture. The results indicated strong chemisorptions of H₂, toluene, and benzene on CaO while O₂ and aliphatic hydrocarbons were not adsorbed. These observations are also consistent with the fact that specific tar cracking activity of MgO was found to be lower (by about 50% at 700°C) than that of CaO, since the O⁻ concentration in MgO was expected to be lower due to the less favored peroxide formation in the oxide crystal.
The heterogeneous cracking reactions of coal tar were well described by a kinetic model which used molecular weight as a global parameter to characterize the different thermal reactivity of different tar constituents over CaO. The model described the stone deactivation by considering the site-poisoning mechanism, pore plugging due to formation of coke deposits on the CaO surface, and cracking activity of the resulting coke-CaO complex.

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To my wife, Wendy
and my parents
# Table of Contents

List of Figures .................................................. 13  
List of Tables ................................................... 19  
1. Summary ....................................................... 20  
2. Introduction ................................................... 62  
   2.1 Coal Devolatilization and Generation of Organic Contaminants ......................... 62  
      2.1.1 Potential Problems .................................. 62  
      2.1.2 Proposed Solutions ................................ 63  
   2.2 CaO-Aromatics Interactions ................................. 65  
      2.2.1 Program Rationale .................................. 65  
      2.2.2 Objectives of Proposed Research ...................... 67  
      2.2.3 Technical Feasibility and Potential Benefits ...................... 68  
3. Background .................................................... 70  
   3.1 The Preparation and Properties of CaO .................... 70  
      3.1.1 Physical Properties of CaO ......................... 70  
      3.1.2 Chemical Properties of CaO ......................... 73  
      3.1.3 Preparation of CaO from Limestone Calcination ......................... 75  
      3.1.4 Preparation of CaO from Ca(OH)$_2$ Calcination ......................... 80  
   3.2 Reactions of Organic Compounds in the Presence of CaO and Dolomitic Solids .......... 84  
      3.2.1 Pure Compound Studies (Below 400$^\circ$C) .............. 85  
      3.2.2 Pure Compound Studies (Above 400$^\circ$C) .............. 95  
      3.2.3 Pyrolysis of Coal Volatiles .......................... 103  
4. Experimental Apparatus and Procedures ....................... 107
4.1 Tar Generation/Pyrolysis Experiments .............. 107
  4.1.1 Rationale for System Design ..................... 109
  4.1.2 Reactor System Description ...................... 116
  4.1.3 Operation Mode and Procedures ................... 124
  4.1.4 Sample Preparation ............................ 132
4.2 Characterization of Calcium Oxide .................... 138
  4.2.1 Physical Properties ............................ 138
  4.2.2 Electrical Resistance Measurement ................ 140
4.3 Characterization of Pyrolysis Products ............... 143
  4.3.1 Coal Tar Characterization ....................... 143
  4.3.2 Gas and Light Oil Analysis ...................... 155
5. Results and Discussion ................................ 160
  5.1 Characterization of CaO Packed-Bed ................. 160
    5.1.1 Uniformity of CaO Distribution in the Bed .... 160
    5.1.2 Uniformity of CaO Surface Area in the Bed .... 161
    5.1.3 Physical Properties of CaO .................... 169
  5.2 Characterization of Feed (Primary Coal Tar) ....... 174
    5.2.1 Product Distribution .......................... 174
    5.2.2 Comparison with Other Works ................... 179
  5.3 Importance of External and Internal Mass Transfer ................................. 183
    5.3.1 Effect of Carrier Gas Flow Rate ............... 183
    5.3.2 Effect of Crystal Size of CaO ................. 186
  5.4 Effect of Cracking Temperature on Coal Volatiles Pyrolysis ................................. 190
    5.4.1 Tar Yields .................................... 194
    5.4.2 Gas Yields .................................... 202
5.4.3 Light Oil Yields ........................................... 208
5.5 Effect of Cumulative Feed/CaO Ratio on Coal Tar Pyrolysis ........................................ 212
5.6 Effects of Other Parameters on Coal Tar Pyrolysis .................................................. 217
  5.6.1 Primary Tar Concentration ......................... 217
  5.6.2 Origin of CaO ........................................... 221
  5.6.3 Gaseous Environment ................................... 226
  5.6.4 Other Alkaline Earth Oxide ...................... 234
5.7 Deactivation/Regeneration of CaO Activity ...... 238
5.8 Coal Tar Characterization .................................. 243
  5.8.1 NMR Analysis ......................................... 245
  5.8.2 GPC Separation and Analysis ................. 273
  5.8.3 Thermometric Titration ............................ 281
  5.8.4 Mutation Bio-Assay .................................. 285
  5.8.5 Elemental Analysis .................................. 291
5.9 Chemisorption Study via Measurement of the Electrical Resistance of CaO ................. 295
  5.9.1 Chemisorption Study over CaO ................... 296
  5.9.2 The Existence of $O^-$ Ion and Its Effect on the Surface Property of CaO .......... 300
5.10 Modeling of Tar Cracking Over CaO ................. 307
  5.10.1 Important Parameter(s) for Characterizing Tar Reactivity ............................... 307
  5.10.2 CaO Deactivation Due to Coke Formation ............................................. 313
  5.10.3 Formation of the Kinetic Model .................. 319
      — The Area Effectiveness Factor .................. 323
      — Comparison of Experimental Data and Model Predictions ....................... 327
6. Conclusions and Recommendations .......................... 341
  6.1 Conclusions .............................................. 341
  6.2 Recommendations ......................................... 347
7. References ..................................................... 351
8. Appendices ..................................................... 364
   A. Calculation of Volatiles Residence Time ............... 364
   B. Calculation of Evolution Rate of Gaseous Products .............................................. 368
   C. Redistribution of Extra Tars Recovered From Walls of Reactor and Valve .......... 369
   D. Calibration and Operating Procedures of the Thermometric Titration System .......... 371
   E. Computer Program Used For Calculating Gas Yields and Generating Summary Tables of Product Distribution ....................... 375
   F. Computer Program 'KINE' Used For Kinetic Modeling of Heterogeneous Cracking Reactions of Tar Over CaO ......................... 385
   G. Sample Input File ('DATA') to the Kinetic Model Program — 'KINE' (Given in Appendix F) .... 390
   H. Results of 'KINE' Model Prediction for Tar Cracking Reactions Over CaO .............. 393
   I. Summary of Product Distributions of Experimental Runs (Calculated by Program Given in Appendix E) ........................... 419
**List of Figures**

<table>
<thead>
<tr>
<th>Figures</th>
<th>Description</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1-1a</td>
<td>Crystal Structure of Calcium Oxide</td>
<td>72</td>
</tr>
<tr>
<td>3.1-1b</td>
<td>Crystal Structure of Calcite</td>
<td>72</td>
</tr>
<tr>
<td>3.1-1c</td>
<td>Crystal Structure of Ca(OH)$_2$</td>
<td>72</td>
</tr>
<tr>
<td>3.1-2</td>
<td>Calcium Hydroxide Samples Calcined in Vacuo at Various Temperatures</td>
<td>82</td>
</tr>
<tr>
<td>3.2-1</td>
<td>Changes in Basicity, Surface Area, and Dehydration Percentage of CaO with Calcination Temperature</td>
<td>88</td>
</tr>
<tr>
<td>3.2-2</td>
<td>Correlation of Basicity of CaO with Catalytic Activity for Esterification of Benzaldehyde</td>
<td>88</td>
</tr>
<tr>
<td>3.2-3</td>
<td>(A) Amount of Anion Radical of Nitrobenzene Formed on CaO vs. Calcined Temperature; (B) Polymerization Activity in Vacuum vs. Calcined Temperature</td>
<td>94</td>
</tr>
<tr>
<td>3.2-4</td>
<td>Effect of Calcium Oxide on the Thermal Decomposition of Thiophene</td>
<td>97</td>
</tr>
<tr>
<td>3.2-5</td>
<td>Comparison of the Effects of Calcium Oxide on the Thermal Decomposition of Benzene and n-Heptane</td>
<td>97</td>
</tr>
<tr>
<td>3.2-6</td>
<td>Methane Yield from Toluene Conversion over Quartz or CaO</td>
<td>99</td>
</tr>
<tr>
<td>3.2-7</td>
<td>Benzene Yield from Toluene Conversion over Quartz or CaO</td>
<td>99</td>
</tr>
<tr>
<td>4.1-1</td>
<td>Apparatus Flowsteet</td>
<td>108</td>
</tr>
<tr>
<td>4.1-2</td>
<td>Axial Temperature Profiles in Reactor-2 at Various Times After Beginning Bed Heatup</td>
<td>115</td>
</tr>
<tr>
<td>4.1-3</td>
<td>Schematic of Reactor Tube Assembly</td>
<td>118</td>
</tr>
<tr>
<td>4.1-4</td>
<td>Modes of Experiment</td>
<td>126</td>
</tr>
<tr>
<td>4.3-1</td>
<td>Schematic of the Thermometric Titration System</td>
<td>150</td>
</tr>
</tbody>
</table>
4.3-2 Block Diagram of Automatic Gas Analysis ............ 156
5.1-1 The Surface Areas of Calcined C.C.Q. in a Packed Bed ........................................ 165
5.1-2 Specific Surface Area of CaO, Prior to the Introduction of Coal Volatiles, as a Function of Cracking Temperature .............. 171
5.1-3 Pore-size Distribution in CaO Calcined from Ca(OH)$_2$ (Sample prepared for a 700°C Mode-4 experiment) ........................................ 173
5.2-1 Volatiles from Coal Pyrolysis ....................... 175
5.2-2 CO and CO$_2$ Evolution Rates as a Function of Reactor-1 Temperature (For Mode-1 Experiments) ........................................ 177
5.3-1 Effect of Ca(OH)$_2$ (CaO) Crystal Size on the Overall Conversion of Coal Tar .............. 189
5.4-1 Product Distributions for Mode-3 and Mode-4 Experiments, as a Function of Cracking Temperature ........................................ 191
5.4-2 Yields of Light Hydrocarbon Gases for Mode-3 and Mode-4 Experiments, as a Function of Cracking Temperature ......................... 192
5.4-3 Yields of CO$_2$, CO, H$_2$O, and H$_2$ for Mode-3 and Mode-4 Experiments, as a Function of Cracking Temperature ....................... 193
5.4-4 Cumulative Tar Yields for Mode-3 Experiments Performed at Different Cracking Temperatures, as a Function of Tar Formation Temperature .... 197
5.4-5 Cumulative Tar Yields for Mode-4 Experiments Performed at Different Cracking Temperatures, as a Function of Tar Formation Temperature .... 198
5.4-6 Fractional Tar Conversion for Vapor Phase Cracking (Mode-3) Experiments at different Cracking Temperatures, as a Function of Average Tar Formation Temperature ............. 199
5.4-7 Fractional Tar Conversion for Heterogeneous Cracking Reactions over CaO at Different Cracking Temperatures, as a Function of Average Tar Formation Temperature .......... 200
5.4-8  CH₄ Evolution for Mode-4 Runs at Different Cracking Temperatures, as a Function of Reactor-1 Temperature ........................................... 204

5.4-9  Effect of CaO and Cracking Temperature on Relative CH₄ Yield ........................................... 205

5.4-10 H₂ Evolution for Mode-4 Runs at Different Cracking Temperatures, as a Function of Reactor-1 Temperature ........................................... 207

5.5-1  Effect of Cumulative Tar/CaO ratio on Tar Cracking Activity of CaO ........................................... 215

5.6-1  Effect of CaO Source on the MWD of Coal Tars Subjected to Thermal Cracking over CaO ..... 225

5.7-1  Effect of Burnoff and Hydration/Recalcination on the Percentage Tar Conversion Over CaO ...... 240

5.8-1  A Typical ¹H-NMR Spectrum of a Tar Sample (from Mode-1 Runs) ........................................... 249

5.8-2  Alpha Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Cracking Temperature ...... 253

5.8-3  Beta Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Cracking Temperature ...... 254

5.8-4  Gamma Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Cracking Temperature ...... 255

5.8-5  Naphthenic Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Cracking Temperature ........................................... 256

5.8-6  Aromatic and Phenolic Hydrogen Fraction of Mode-3 and Mode-4 tars as a Function of Cracking Temperature ........................................... 257

5.8-7  Alpha Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Tar Conversion .............. 258

5.8-8  Beta Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Tar Conversion .............. 259

5.8-9  Gamma Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Tar Conversion .............. 260

5.8-10 Naphthenic Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Tar Conversion ..... 261
5.8-11 Aromatic and Phenolic Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Tar Conversion ........................................ 262

5.8-12 Comparison of Absolute Yield of Aromatic Hydrogen for Primary and Secondary Tars .......... 265

5.8-13 Comparison of $^1$H-NMR Spectra for Mode-1, Mode-3, and Mode-4 Tars. (Tar Cracking Temp. = 800°C) ............................................... 268

5.8-14a Carbon Aromaticity for Mode-3 and Mode-4 Tars as a Function of Cracking Temperature ...... 271

5.8-14b Carbon Aromaticity for Mode-3 and Mode-4 Tars as a Function of Tar Conversion ............. 272

5.8-15 Molecular Weight Distribution of Mode-1 Tars — Effect of Evolution Temperature ...... 275

5.8-16 Effect of Evolution Temperature on Number-Average Molecular Weight of Mode-1 Tars ........ 277

5.8-17 Effect of Evolution Temperature on Weight-Average Molecular Weight of Mode-1 Tars ........ 277

5.8-18 Effect of Cracking Temperature on the Number-Average Molecular Weight of Mode-3 and Mode-4 Tars ........................................... 278

5.8-19 Effect of Cracking Temperature on the Weight-Average Molecular Weight of Mode-3 and Mode-4 Tars ........................................... 279

5.8-20 Phenolic Content of Mode-3 and Mode-4 Tars as a Function of Cracking Temperature ......... 283

5.8-21 Effect of Cracking Temperature and CaO on Coal Tar Mutagenicity (With Metabolic Activation) ....................................................... 286

5.8-22 Effect of Cracking Temperature and CaO on Coal Tar Mutagenic Impact (With Metabolic Activation) ................................................... 288

5.8-23 Effect of Cracking Temperature and CaO on Coal Tar Mutagenicity (Without Metabolic Activation) ................................................... 289

5.8-24 Effect of Cracking Temperature and CaO on Coal Tar Mutagenic Impact (Without Metabolic Activation) ................................................... 290
5.9 -1 Effect of \( H_2 \) and \( O_2 \) Partial Pressures on the Electrical Resistance of CaO (Prepared from Calcining Iceland Spar) ................................. 299

5.10-1 Performance of the Prep-GPC Used for Separating Coal Pyrolysis Tars ............................................. 310

5.10-2 Oxygen Contents of Coal Tar Fractions ...................... 311

5.10-3 Phenolic Oxygen Content of Coal Tar Fractions .................. 311

5.10-4 Effect of Cumulative Tar/CaO Ratio on Conversion of Different Tar Lumps (Cracking Temperature = 500°C) .................... 314

5.10-5 Effect of Cumulative Tar/CaO Ratio on Conversion of Different Tar Lumps (Cracking Temperature = 525°C) .................... 315

5.10-6 Effect of Cumulative Tar/CaO Ratio on Conversion of Different Tar Lumps (Cracking Temperature = 550°C) .................... 316

5.10-7 Effect of Cumulative Tar/CaO Ratio on Conversion of Different Tar Lumps (Cracking Temperature = 600°C) .................... 317

5.10-8 Yield of Tar Lumps as a Function of Total Coke Content of CaO (Data and Model Predictions for Mode-4 Runs at 500°C Cracking Temperature) ................................. 329

5.10-9 Yield of Tar Lumps as a Function of Total Coke Content of CaO (Data and Model Predictions for Mode-4 Runs at 525°C Cracking Temperature) ................................. 330

5.10-10 Yield of Tar Lumps as a Function of Total Coke Content of CaO (Data and Model Predictions for Mode-4 Runs at 550°C Cracking Temperature) ................................. 331

5.10-11 Yield of Tar Lumps as a Function of Total Coke Content of CaO (Data and Model Predictions for Mode-4 Runs at 600°C Cracking Temperature) ................................. 332

5.10-12 Overall Tar Yields as a Function of Total Coke Content of CaO (Data and Model Prediction) ................................. 334
5.10-13 Effect of Volatiles Contact Time on Overall Tar Yield (Data and Model Prediction) .................. 335

5.10-14 Final Coke Content of CaO as a Function of Bed Depth (at 500 °C Cracking Temp.) .............. 337

5.10-15 Final Coke Content of CaO as a Function of Bed Depth (at 600 °C Cracking Temp.) .............. 338

5.10-16 Final Coke Content of CaO as a Function of Bed Depth (at 700 °C Cracking Temp.) .............. 339

D-1 A Typical Titration Curve for a Coal Tar Sample .......................................................... 373
# List of Tables

<table>
<thead>
<tr>
<th>Tables</th>
<th>Description</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1-1</td>
<td>Summary of Some Physical Properties of Lime</td>
<td>73</td>
</tr>
<tr>
<td>4.1-1</td>
<td>Typical Experimental Conditions</td>
<td>129</td>
</tr>
<tr>
<td>4.1-2</td>
<td>Characteristics of Coal Sample Studied</td>
<td>133</td>
</tr>
<tr>
<td>5.1-1</td>
<td>Percentage Weight Loss of C.C.Q. During Calcination</td>
<td>162</td>
</tr>
<tr>
<td>5.2-1</td>
<td>Comparison of Product Distributions for Pyrolysis of Pittsburgh No. 8 Seam</td>
<td>178</td>
</tr>
<tr>
<td></td>
<td>Bituminous Coal</td>
<td></td>
</tr>
<tr>
<td>5.3-1</td>
<td>Effect of Space Velocity of Carrier Gas/Feed Mixture on the Extents of Coal</td>
<td>185</td>
</tr>
<tr>
<td></td>
<td>Volatiles Conversion Over CaO (Cracking Temp. = 600°C, Contact Time = 0.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sec.)</td>
<td></td>
</tr>
<tr>
<td>5.4-1</td>
<td>Yield of Light Oils for Mode-3 and Mode-4 Experiments, at 700°C Cracking</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td></td>
</tr>
<tr>
<td>5.6-1</td>
<td>Effect of Coal Tar Concentration on Tar Conversion over CaO</td>
<td>219</td>
</tr>
<tr>
<td>5.6-2</td>
<td>Effect of CaO Source on Overall Yields of Coal Pyrolysis Tar</td>
<td>223</td>
</tr>
<tr>
<td>5.6-3</td>
<td>Effect of Steam on Tar Conversion over CaO</td>
<td>229</td>
</tr>
<tr>
<td>5.6-4</td>
<td>Effect of a Reactive Gaseous Environment on Tar Conversion over CaO</td>
<td>233</td>
</tr>
<tr>
<td>5.6-5</td>
<td>Comparison of Coal Tar Cracking over CaO and MgO</td>
<td>236</td>
</tr>
<tr>
<td>5.8-1</td>
<td>Results of NMR Analyses of a Simulated Coal Liquid Sample and the Experimental</td>
<td>252</td>
</tr>
<tr>
<td></td>
<td>% Errors</td>
<td></td>
</tr>
<tr>
<td>5.8-2</td>
<td>Elemental Analysis of Primary Tar and Secondary Tars from Runs at Cracking</td>
<td>292</td>
</tr>
<tr>
<td></td>
<td>Temperatures Between 400 and 800°C</td>
<td></td>
</tr>
<tr>
<td>5.9-1</td>
<td>Electrical Resistance of CaO as a Function of Gaseous Environment</td>
<td>301</td>
</tr>
<tr>
<td>D-1</td>
<td>Results of Titration of Standard Compounds</td>
<td>374</td>
</tr>
</tbody>
</table>
1. **Summary**

1.1. **Background**

Thermal devolatilization of coal occurs in many coal conversion processes such as coal gasification and coal pyrolysis. This process of coal transformation has potential for serious environmental and health problems. These include the generation of vapor phase pollutants such as hydrogen sulfide, sulfur dioxide, other organic sulfur compounds and volatile nitrogen compounds, and liquid products which contain many undesirable polycyclic aromatic hydrocarbons and other organic compounds, a number of which are carcinogenic or mutagenic.

Coal pyrolysis tars typically have a high content of organic oxygen compounds, many of which are phenolic. These compounds may cause such problems as storage instability, poor compatibility with petroleum liquids, and toxicity (Gould and Long, 1982). The cost of either complete or partial elimination of these unwanted chemicals using currently available technology is high. To make coal a satisfactory choice as an energy source, an economical and effective means is needed to control pollutants in its conversion products and waste streams.

Calcium oxide, because of its desirable chemical reactivity as well as its wide availability and relatively low cost, is of considerable industrial interest as an additive for improvement of coal conversion processes. Considerable investi-
gation of its use at high temperature (>1088 K) has been performed (e.g., Curran et al., 1967; Dawson, 1979; Lyon, 1977), where it acted mainly as a sulfur capturing reagent and CO₂ acceptor.

For temperatures in the range of 700-1033 K, researchers at our laboratory have initiated exploring the interactions of calcium oxide with the pyrolysis of coal (Yeboah et al., 1980; Franklin et al., 1981), and also its impact on the pyrolysis of pure organic compounds (Lai, 1986; Elig, 1981; Elig et al., 1985; Mead, 1979).

In the fluidized-bed pyrolysis of coal, the use of calcium oxide (Yeboah et al., 1980; Floess et al., 1985) resulted not only in the production of cleaner and higher heating value gas mixture, but also in decreased yields of tar with potentially improved qualities (e.g., higher H/C ratios and lower oxygen contents). Preliminary studies also indicated opportunity for decreasing the mutagenicity of coal tar with calcium oxide (Anderson, 1979; Longwell and Peters, 1983).

In the pure compound studies, calcium oxide was shown to be extraordinarily active in pyrolytic destruction of aromatics and phenolics, in contrast to its moderate activity for paraffin cracking. It is believed that the interesting effects observed in the coal pyrolysis programs are closely related to these special interactions of calcium oxide with aromatic compounds. A more comprehensive and quantitative understanding of the chemistry of calcium oxide interactions with coal tar
would be of great practical interest.
1.2. **Objectives**

The overall objective of this research was to investigate the role and potential application of calcium oxide chemistry to pollution control and product upgrading in coal gasification and pyrolysis processes. Specific objectives were to:

1. investigate the effects of calcium oxide on the global kinetics and product distribution of thermal decomposition of prompt coal pyrolysis tar, as a function of temperature, tar residence (contact) time, stone source, or composition of carrier stream (i.e., inert or reactive),

2. study the effect of calcium oxide on product tar properties, such as aromaticity, mutagenicity, molecular weight distribution, and heteroatom content,

3. study the change of calcium oxide activity with extent of utilization, and with method of regeneration,

4. develop a kinetic model for the heterogeneous reactions of coal tar over calcium oxide, accounting for the chemical complexity of the tar mixture as well as the deactivation behavior of calcium oxide activity due to coke formation and stone sintering,

5. elucidate the mechanism for the enhanced cracking of tar over calcium oxide surface.
1.3. **Experimental**

A reactor system, whose flowsheet is given in Figure 1, was designed and constructed to address these objectives. It consists of two fixed-bed tubular reactors (1.6 cm I.D.) employed in series, whose pressures were kept at 1.2-1.3 atm.

Prompt volatiles were generated from a thin bed of (about 0.1-2.0 gm) Pittsburgh No. 8 Seam bituminous coal, which was heated linearly at 3°C/min to 700°C within the upstream reactor (Reactor-1). The coal particles (with a size range 300-350 microns) were diluted with similar size SiC (1 to 12 W/W ratio), to prevent agglomeration. The primary volatiles were produced mostly at relatively low temperatures (about 95% below 550°C), and were rapidly swept downstream by a superimposed flow of preheated helium carrier gas, and thus had minimum opportunity for secondary reactions inside Reactor-1.

In selected runs (mode-1 experiments) these primary volatiles were quenched and collected directly upon exiting reactor-1 and were then recovered for various means of characterization. In typical runs, the fresh volatiles, which remained in the vapor phase, were introduced directly into a downstream reactor (Reactor-2) as reactants, and underwent secondary reactions either homogeneously in the vapor phase (mode-3 experiments where Reactor-2 was unpacked), or heterogeneously (as well as homogeneously) in the presence of a calcium oxide packed bed (mode-4 experiments) at a constant
volatiles cracking temperature between 400 and 800°C.

The volatiles contact times with the packed bed (about 0.06-0.24 sec) as well as the residence times in the homogeneous phase (about 2.0 sec) were varied by controlling the helium carrier gas flow rate through a thermal mass flow controller and by changing the depth of the CaO (about 0.25 - 1.0 gm) packed bed.

The conditions in Reactor-2 were such that cracking of light hydrocarbon gases and light oils were relatively unimportant. The major reactions studied were the secondary cracking of coal tars. By subtracting the effects of homogeneous cracking (determinable from the mode-3 runs) from the results of mode-4 runs, the contribution of calcium oxide interaction with the tars to the observed coal tar cracking behavior could be quantitatively assessed.

The calcium oxide was obtained by calcining reagent grade calcium hydroxide (Anachemia) in the form of calcium hydroxide-coated-quartz (C.C.Q.). This was prepared, to reduce the pressure drop and ensure uniform gas flow through the packed bed, from a 6/94 (W/W) mixture of Ca(OH)₂ powder (size < 5 micron) with quarts particle (300 - 350 micron size) as an inert diluent.

The calcination was achieved in-situ by heating the C.C.Q. bed from room temperature to 500°C at a 3°C/min rate and then holding at 500°C for 1.5 hours to achieve complete decomposition of Ca(OH)₂. The stone and the remaining reaction volume
of Reactor-2 were then cooled or heated to the desired cracking temperature prior to the introduction of coal volatiles from Reactor-1. The temperature of the CaO packed bed was determined to be uniform, both axially and radially, to within ± 2%, based on the absolute temperature scale.

The physical properties (e.g., surface area, and pore size distribution) of the CaO samples thus prepared at different cracking temperatures were characterized with a B.E.T. surface area analyzer using nitrogen as the adsorbate. Figure 2 shows the change of specific surface area of CaO (just before introducing the coal volatiles) with the cracking temperature, indicating significant stone sintering at temperatures above 700°C over a soaking period of about 120 minutes. Figure 3 shows the pore size distribution of a CaO sample prepared for a 700°C mode-4 run (where d is the width of the slit-shape pore in the CaO obtained by calcining Ca(OH)₂ (Beruto et al., 1980)).

Total tars (room temperature condensable coal volatiles) exiting the reactor system were collected in stainless steel traps packed with teflon wool and left at ambient temperature. Tar yields were determined gravimetrically. A 16-loop gas sampling valve which was switched pneumatically was employed to take gas samples at predetermined values of the temperature in the first (volatiles generation) bed. Yields of pyrolysis gaseous products, such as CO₂, CO and light hydrocarbon gases were determined by a packed column gas chromatograph (GC) using helium as the carrier gas. Hydrogen yields were
determined by a separate GC using argon as the carrier.

Water yield was determined gravimetrically after collection in a trap packed with 8 mesh Drierite (anhydrous CaSO₄). Light oils were collected further downstream in a cold trap which was immersed in a liquid nitrogen bath. Selected light oil samples were extracted from the trap with methylene chloride and were analyzed with a capillary column GC.

Yields of primary char remaining in Reactor-1 and of the coke formed on the surface of CaO in Reactor-2 were also determined gravimetrically. Yields of secondary coke on the walls of Reactor-2 were determined in selected runs by oxygen burnoff followed by catalytic conversion of the resulting CO to CO₂. The amount of CO₂ in the product gases was determined gravimetrically by precipitation as BaCO₃ powder.

To assist in the characterization of properties of coal tar, both primary (mode-1) and secondary (mode-3 and -4) tars were analyzed by a variety of techniques. These included gel permeation chromatography (GPC), which determines the molecular weight distribution, non-aqueous thermometric titration (Vaughan and Switchenbank, 1970), which measures the concentration of phenolic (or acidic) functional groups, ¹H NMR which gives average structural parameters, and elemental (C,H,O,N,S) analysis. Selected tar samples were also subjected to bacterial cell forward mutation bio-assays (Skopek et al., 1978a; b), which shed light on the mutagenicity of the tars to *Salmo-nella typhimurium*. 
A detailed description of the experimental system and the analytical techniques is given by Longwell et al. (1985) and Chang (1986).

The Pittsburgh No. 8 Seam bituminous coal which came from the Ireland Mind of the Consolidation Coal company, is representative of a strongly caking eastern U.S. bituminous coal. The coal particles used in this study were prepared by grinding coal lumps (> 5 mm in size) for 15 min in a stainless steel rod mill under a nitrogen blanket. The ground coal was then mechanically dry-sieved to collect the fraction of 300-350 micron particles which were further subjected to wet sieving to remove the electro-statically adhered fine impurities. The resulting coal samples were dried in a desiccator and stored under nitrogen atmosphere. The ultimate and proximate analysis of this coal are given in Table I.
1.4. **Results and Discussion**

1.4.1 **Product Distribution**

A systematic study of the effects of cracking temperature (in the 400 - 800°C range) on the pyrolysis reactions of primary tars both in the absence (mode-3) and presence (mode-4) of CaO was performed. All the other experimental parameters, i.e., amounts of coal (1 gm) and CaO (0.5 gm) used, the volatiles residence time in the homogeneous phase (about 2.0 sec), and contact time with the CaO bed (about 0.12 sec) were maintained constant.

Figures 4, 5 and 6 display product distributions as a function of volatiles cracking temperature. The product yields are calculated based on the amount of parent coal used. To characterize the input to the thermal treatment reactor, the yields of primary tar, light gases, and char, which were determined from average values of six duplicate mode-1 runs, are also shown in the figures.

The overall material balances for all modes of experiments typically fell in the range of 100 ± 5 Wt% of parent coal. As would be expected for packed bed carbonization at these operating conditions, char (which remained in Reactor-1) was the major coal pyrolysis product, accounting for about 60 - 62 Wt% of the parent coal (Figure 4).
The ultimate yield of primary tars accounted for 25 - 26 Wt% of the parent coal, which corresponded to a CaO to cumulative tar feed ratio (by weight) of about two in the mode-4 experiments. The yields of secondary tar decreased with increasing volatiles cracking temperature, and to a much greater extent in the presence of calcium oxide (Figure 4). The rate of cracking reaction of tar over CaO was found to be typically one to two orders of magnitude higher than the rate of a duplicate vapor phase cracking run.

The major components of mode-3, secondary tar cracking products were light hydrocarbon gases (mainly as CH₄, C₂H₄ and C₃H₆) (Figure 5), CO and CO₂ (Figure 6), for temperatures below 700°C. At 800°C, effects of reactor surface became important, resulting in the formation of 5 - 8 Wt% (of parent coal) of secondary coke formed on the reactor wall (Figure 4), along with the increased evolution of CH₄, C₂H₄ (Figure 5), CO, CO₂ as well as H₂ (Figure 6).

In the presence of CaO, the additional tar pyrolysis products (excluding the contribution from concurrent, vapor phase cracking reactions) were mainly secondary coke formed on the CaO surface (Figure 4) (accounted for 80 - 85 Wt% of total cracked tar), a significant amount of hydrogen gas (Figure 6), and (below 700°C) small amounts of CH₄ and C₂H₄ (Figure 5).

The ratios of increased methane yields to amounts of tars cracked over CaO were significantly lower than those from vapor phase tar cracking reactions (Figure 7). This phenomenon
of lower relative methane yield in the presence of CaO had also been observed in a series of studies in this laboratory on the pyrolysis of methyl-substituted pure aromatic compounds over CaO (Ellig, 1981; Ellig et al., 1985; Lai, 1986).

The changes in yields of \( \text{H}_2 \) and oxygenated light gases (\( \text{CO}, \text{CO}_2 \) and \( \text{H}_2\text{O} \)) were greatly complicated by the presence of CaO. In the absence of other reactions, the CO yields should increase with increasing cracking temperature for vapor phase tar pyrolysis reactions. This is supposedly due mainly to the thermal cracking of ethers and phenolics in the tar mixture, with CO as the major oxygenated gaseous product (Schlosberg et al., 1983; Cyprés and Bettens, 1975). The CO yields should be higher from mode-4 runs when compared with duplicate mode-3 experiments, as a result of enhanced cracking of phenolics over CaO (which will be discussed later).

The experimentally observed CO yields were actually lower for the runs with CaO present. The same trend was also observed for \( \text{H}_2\text{O} \) yields. These suggest occurrence of the water gas shift reaction catalyzed by CaO.

The \( \text{H}_2 \) produced from this reaction as well as from steam gasification of coke deposited on the CaO surface, would at most account for about 30 - 50 relative percent of the difference in \( \text{H}_2 \) yields between mode-4 and mode-3 runs at temperatures above 600°C. The additional \( \text{H}_2 \) production must have resulted primarily from dehydrogenation of tar molecules, which was enhanced in the presence of CaO.
Below 500°C, about half or more of the CO₂ were apparently removed by CaO through recarbonation reactions over a relatively short contact time, 0.12 sec. Above 600°C, however, little recarbonation reaction would have occurred, since the typical partial pressure of CO₂ (< 10⁻³ atm) in the gas stream of the pyrolysis products was lower than its equilibrium value in the presence of CaO.

The relative significance of the water-gas shift reaction and steam-carbon reaction could not be quantitatively address here, due to the lack of information on the instantaneous water concentration in the pyrolysis gases and coke content on CaO surface.

The total light oil yields were estimated to be 1-2 Wt% (of parent coal) from results of capillary column GC analyses of selected samples. The yields of major components (i.e., benzene, toluene, xylenes, m-cresol, and naphthalene) were found to be little affected by the presence of CaO, even at 700°C cracking temperature where significant increases in tar conversion took place.

The effects of other parameters on tar pyrolysis reactions over CaO or other stone, were also selectively studied. At 700°C, the source of CaO (i.e., Ca(OH)₂ or CaCO₃) had a minor effect on overall tar conversion. The specific activity for tar cracking (based on unit surface area) of another alkaline earth metal oxide, MgO, was found to be about half of that of CaO.
At 650°C, the presence of 0.3 atm steam decreased the overall tar conversion over CaO by about 20% (relative), but increased the H₂ yields by as much as 30 – 50%. At 800°C, the cracking activity of CaO was reduced by about 15% in the presence of a reactive gas mixture (i.e., 5% CO₂, 22% CO, 22% H₂, 1% CH₄, and the balance helium). The activity decline in the latter two cases was mainly due to the reduction in stone's surface area (by about 35 and 50%, respectively), which was greatly enhanced by the steam and CO₂.

1.4.2 Change in Tar Properties

The average properties of coal tar also changed significantly through thermal reactions with or without the presence of CaO. The elemental composition of both primary and secondary tars is given in Table II. The H/C atomic ratio shows the usual decreasing trend with cracking temperature, but the value is typically higher for mode-4 runs with CaO present when compared to the duplicate mode-3 runs at the same cracking temperature. The difference is significantly greater when the comparison is made at the same level of overall tar conversion.

The nitrogen and sulfur contents of mode-3 tars appear to be insensitive to the temperature, while oxygen content shows a decreasing trend. Tars cracked in the presence of CaO typically have lower contents of nitrogen, sulfur and
oxygen than those of mode-3 runs, with the latter two values generally declining with increasing temperature.

The changes in average molecular weights (MW) of coal tar are given in Figures 8a and 8b, as a function of cracking temperature. The GPC analyses (as well as NMR and thermometric titration measurements) were done both for low temperature tars (A-tar, which evolved from coal pyrolysis below 430°C and survived secondary thermal cracking), and for high temperature tars (B-tar, evolved between 430 - 700°C). The effect of tar formation temperature on the various tar properties we analyzed, was found to be minor.

The secondary tar that underwent vapor phase pyrolysis reactions generally had a decreasing trend for average MW with increasing cracking temperature (i.e., increasing extent of tar conversion). A comparison of the GPC chromatogram for primary and secondary tars suggested that while the cracking of tar molecules to form lighter products was dominant, there were some heavier tars formed through recombination reactions of lighter tars. This redistribution of molecular weight of tar through pyrolysis was also reflected by the increasing trend of polydispersity index (i.e., ratio of weight average MW to number average MW) of coal tar with increasing temperature.

Thermal cracking reactions over CaO reduced the average MW of secondary tars even further. The results indicate that, in the absence of pore diffusion limitations, higher MW tar
(generally with higher number of condensed aromatic rings) have a higher affinity for the CaO active sites, and are cracked preferentially. Results of pure compound work performed in this laboratory (Lai, 1986; Ellig et al., 1985) also support this picture.

It was found that heavier tar molecules (e.g., with MW > 500 gm/mole) were removed more efficiently when CaO prepared from CaCO₃ (instead of Ca(OH)₂) was used, based on the same level of overall tar conversion (i.e., about 75% at 700°C cracking temperature). This pointed to the existence of significant diffusion limitations for these large tar molecules in the CaO pores. The limitation would be less severe in the CaO prepared from CaCO₃ (with pores of cylindrical shape and of size about 10 nm in diameter (Beruto et al., 1980)), than that from Ca(OH)₂ (having slit-shaped pores with most common slit width of about 5 nm).

The hydrogen distributions, determined from ¹H-NMR analysis of coal tars are summarized in Figures 9a to 9d. The hydrogen fraction data must be interpreted carefully, since an apparent increase in one fraction could be due to the loss of another fraction at a greater than average rate. The absolute yield of a specific hydrogen fraction (Y_f, g/100 g coal) can be calculated, to determine if there is a net change of that fraction due to tar pyrolysis, as follows:

\[ Y_f = (H_f^*) (H) (Y_T) \]  
\[ \text{Eq.(1)} \]
where

\[ H^*_f = \text{hydrogen fraction from NMR analysis} \]
\[ H = \text{hydrogen content of tar (g/g tar)} \]
\[ Y_T = \text{tar yield (g/100 g coal)} \]

The absolute yields of aromatic hydrogen in the primary and secondary tars thus calculated are given in Figure 10, as a function of tar conversion. It was found that the value was relatively constant for mode-3 tars that survived vapor phase cracking, up to about 35% of tar conversion (at 800°C). This indicated that the aromatic rings of coal tar are largely intact in the mode-3 secondary reactions, under the conditions studied in this work.

The apparent increase in the aromatic H fraction (see Figure 9a) of mode-3 tar was mainly due to cracking of the aliphatic (side) chains. The fact that beta and gamma hydrogen fractions decreased monotonically (Figures 9c and 9d), while alpha hydrogen fraction remained relatively constant (Figure 9b), with increasing extent of tar conversion, indicates that the preferred aliphatic bond breakage occurred at positions beta or further away from the aromatic ring.

This is because the energy needed for opening up these alkyl bonds is at least 20 kcal/mole less than that for bonds alpha to the aromatic ring (Benson, 1976). The resulting aliphatic, free radical chain then continued bond breakage by beta-bond scission mechanism with ethylene and methane as the
major products. This is in good agreement with the experimental result of significant increases in methane and ethylene gas yields for mode-3 tar cracking runs at temperatures above 600°C.

Hydrogen distributions of tar samples from mode-4 experiments showed interesting differences from those of mode-3 runs. The results strongly indicate that tar pyrolysis reactions over CaO were taking place through vastly different pathways from those of vapor phase cracking reactions. At the same level of tar conversion, mode-4 secondary tars contained significantly lower aromatic hydrogen fraction and retained higher aliphatic hydrogen contents. In contrast to the free radical, dealkylation mechanism that accounted for the vapor phase tar cracking, CaO enhanced the tar conversion by selectively promoting the removal of the aromatic-rich fractions of the coal tar mixture.

This observation of special CaO-aromatics interactions is in good agreement with the results of pure compound studies (Mead, 1979; Elleg et al., 1985; Lai, 1986) where CaO was shown to greatly enhance the cracking of aromatics, as compared to its moderate activity for cracking aliphatics.

The important implication here is that upgrading of coal tar mixtures (to yield products of higher aliphatic contents), could potentially be achieved by this CaO-aromatics chemistry under appropriate conditions (e.g., below 600°C, where vapor phase cracking is unimportant) without additional, expensive
hydrogenation processes. This is especially effective for those tars where most aliphatic components exist as separate compounds not as side chains on the aromatic tar constituents.

The acidic content of coal tar was determined by thermometric titration. Since the acidic functional groups in Pittsburgh Seam No. 8 bituminous coal were suggested to be mostly (>90%) phenolic (Whitehurst et al., 1981; Attar and Hendrickson, 1982), and the carboxylic, carbonyl, and ester functional groups were considered to be so reactive that they would not survive even mild thermal processing (Ruberto and Cronauer, 1978), the acidity change of the tars in this study can be considered mainly as change in the phenolic content.

The titration results, presented as phenolic oxygen content (Wt% of tar) in Figure 11, indicated that the phenolic fraction of tar became susceptible to vapor phase thermal treatment at temperatures above 700°C. This was also in agreement with a corresponding increase in the yields of carbon oxide gases, especially the carbon monoxide.

The phenolic contents of mode-4 tars were consistently lower than those for mode-3 tars, suggesting the existence of special CaO-phenolics interactions. In the pure compound study performed in this laboratory (Lai, 1986; Lai et al., 1986), the conversion of m-cresol was found to be greatly enhanced over CaO. Below 500°C temperature, the formation of a calcium half-salt through the base-acid interaction was proposed (Schlosberg and Scouten, 1983; Lai et al., 1986).
At higher temperatures, cracking of m-cresol over CaO resulted in the formation of toluene and carbon monoxide as products. The same mechanism is expected for the removal of phenolic fractions from the coal tar mixture through thermal treatment with CaO.

The results for specific mutagenicity and mutagenic impact of coal tars, measured by a metabolically activated bacterial cell forward mutation bio-assay, are shown in Figure 12a and 12b respectively. In Figure 12a, the higher the value on the ordinate indicates a lower value for the mutagenic potency of the tar sample. Thermal treatment without CaO at high temperatures (700 - 800°C) produced secondary tars (with 20 - 40% conversion) which were significantly more mutagenic than the primary tar. Additional treatment over CaO generally resulted in surviving tars with reduced mutagenic potency, with the effect being most dramatic at 700°C cracking temperature.

The mutagenic impact (Figure 12b) is in effect a measure of the total amount of material, mutagenic to bacterial cells, evolved from the coal as surviving tars. In this figure, the higher the value on the ordinate means the greater the total mutagenicity of the coal evolved as surviving tar. High temperature (700 - 800°C) thermal treatment of primary coal tars without CaO produced tar residues of significantly higher mutagenic impact.

Cracking in the presence of CaO at these conditions resulted in a cumulative tar destruction of about 75 - 80%. As a result,
CaO was effective in reducing the total indirect mutagenic impact of secondary tars to levels comparable to that of primary tar. Opportunities for detoxification of high temperature (above 700°C) coal tars are therefore suggested, by controlled thermal treatment over CaO at appropriate conditions (e.g., 700°C).
1.4.3 Regeneration of CaO Activity

The regenerability of cracking activity of coked CaO, by burning off the coke at 700°C with pure O₂, was studied at 700°C cracking temperature and 0.24 sec volatiles contact time. It was found that the activity could only be recovered by about 85 - 90% after each regeneration cycle. The overall tar conversion over a repeatedly cycled CaO bed, was decreased from about 90% initially, to about 63% after the fourth regeneration cycle, as shown in Figure 13. The major reason for the declining CaO reactivity was the reduction in its surface area, presumably caused by the stone sintering in the presence of H₂O and CO₂, generated both by coal pyrolysis and by coke burn-off.

An alternative regeneration technique was applied to the coke-free CaO sample after the fourth burnoff cycle, by first hydrating it at room temperature, then recalcining it as usual to produce CaO in-situ. It was found that the cracking activity, almost as high as that of the original (unused) CaO, was attained (see Figure 13) even though the crystal lattice had already become partially sulfated in the presence of sulfur-containing gases (e.g., H₂S) derived from coal pyrolysis.

Additional cycles performed after the hydration/recalcination step, however, showed a faster decline in stone's cracking activity than that of the original, fresh CaO. This was presumably due to the enhanced sintering or site poisoning due to
the higher content of sulfate (with much lower melting point) accumulated in earlier cycles.
1.4.4 Proposed Mechanism

Both the aromatics and CaO (when titrated at low temperatures) are well known to be basic (electron donating) in nature (Take et al., 1971; Lai, 1986). It was therefore unexpected and interesting to find out that CaO exhibits a strong activity for enhanced thermal cracking of both the aromatic fraction of coal tars and pure aromatics.

Another interesting phenomenon which also deserved special attention, was the repeatedly observed evolution of CO (and some CO₂) during pyrolysis of oxygen-free, pure hydrocarbons over CaO (calcined from Ca(OH)₂ or CaCO₃) in an inert environment (Elliott, 1963; Eliig et al., 1985; Lai, 1986). The fact that the CO yield decreased with pyrolysis of successive aliquots of hydrocarbon introduced over the same packed bed of CaO (Lai, 1986), indicated that the oxygen mainly originated from CaO, and was not due to air leakage or impurities from carrier gas.

The work of Martens et al. (1976) on the calcination of Mg(OH)₂ could shed some light on the source of these oxygen species. Evolution of H₂ and atomic oxygen was observed mass spectrometrically, even after the water evolution from Mg(OH)₂ decomposition was over. It is believed that a small amount of residual OH⁻ groups remain within the oxide crystal even after the calcination is apparently complete. The evolution of H₂ is therefore attributed to the decomposition of residual
OH\(^-\) anions.

This leads to the formation of O\(^-\) ions which are equivalent to singly charged positive defects in the MgO, since a regular (defect-free) sublattice exactly balances the positive charges of the Mg\(^{2+}\) sites by a corresponding number of O\(^2-\) sites. An overall charge balance must be maintained, therefore the defect-containing crystal has the formula Mg\(^{2+}\)O\(^{2-}\)\(_{1-x}\)O\(^-\)\(_{2x}\), i.e., the oxide acquires an excess of \(\delta\) (a small value, on the order of 10\(^{-2}\) to 10\(^{-3}\) for the MgO case) oxygen atoms per Mg atom.

Although similar observations for Ca(OH)\(_2\) calcination were yet unavailable in the literature, excess O\(^-\) ions are also believed to exist in CaO (and other alkaline earth metal oxides) obtained from calcining the corresponding hydroxide or carbonate. The O\(^-\) ions become unstable in the crystal matrix at higher temperatures (e.g., above 800 K for MgO) and diffuse from the bulk to the surface of the oxide. They can then recombine with one another, and undergo the following disproportionation reaction,

\[
2\ \text{O}^- (s) \rightarrow \text{O}^{2-} (s) + \text{anion vacancy} (s) + \text{O} (g) \quad \text{Eq.(2)}
\]

which leads to the evolution of oxygen atoms. The excess O\(^-\) ions are also likely sources for the unexpected CO evolution discussed above.

This diffusion of O\(^-\) ions effectively carries positive charges from the bulk to the surface of the oxide. At low to
moderate temperatures, the CaO surface is probably negatively charged as indicated by the basicity found in the titration measurements. At high temperatures, the process of $O^-$ ion diffusion is believed to eventually reverse the CaO surface charge to a positive value. The CaO surface therefore would become electron-accepting (acidic) at high temperatures.

To assess the applicability of the above picture for CaO, one must find a method that can titrate the CaO surface in-situ at high temperatures. The method we chose was to measure the effects of chemisorption (at temperatures between 400 to 500°C, to avoid the occurrence of cracking reactions) of various gases or vapors on CaO surface, on the electrical resistance of the calcine.

It was found that there was a strong and fast chemisorption reaction of $H_2$ on the CaO surface, indicated by a significant reduction of the CaO resistivity. The reversible chemisorption reaction was hypothesized as

$$H_2(g) + 2 O^{2-}(s) \rightarrow 2 OH^-(s) + 2e^-(s) \quad \text{Eq.(3)}$$

The availability of more mobile charge carriers, namely the electrons liberated through the reaction given in Eq.(3), is a possible explanation for the observed decrease in the electrical resistance of the CaO upon introducing $H_2$ (Ashmore, 1963). Increase in concentrations of mobile ionic species in a solid electrolyte, such as CaO with crystal defects, could be another explanation (Choudhary et al., 1980). However, the precise mechanism responsible for this effect is as yet
uncertain.

Reduction of the CaO resistivity was also observed in the presence of toluene and benzene which contain aromatic \( \pi \)-electrons, and thus can act as electron-donating (basic) agents. On the other hand, essentially no such change was measured when \( O_2 \) (an electron-accepting species), heptane, cyclohexane, or ethylene was introduced over CaO.

The results of our chemisorption studies strongly support the picture of high temperature surface charge reversal for CaO (and other alkaline earth metal oxides). The ability of CaO to selectively enhance the cracking of aromatics may thus be due to the promotion of an electron donor-acceptor chemisorption reaction, by an electropositive (acidic) CaO surface at high temperatures. Once chemisorbed on the CaO surface, the aromatics undergo further reactions (mainly polymerization and dehydrogenation) to form coke, the major product. The dehydrogenation may arise from reversal of reaction (3).
1.4.5 Model for Tar Cracking Over CaO

External mass transfer limitations were shown to be insignificant in this study of coal tar-CaO interactions, since the overall tar conversion over CaO was insensitive to the change (and only the change) of carrier gas flow rate. The overall tar conversion was also found to be largely unaffected, when the size of CaO particle was varied from $<5$ micron, i.e., the powder typically used in this work, to about 40 micron.

This suggested that, at least for the lighter tar molecules (perhaps $<600$ g/mole), the pore diffusion limitations may be unimportant when powder form CaO was employed. The global kinetics, for tar cracking over CaO powder, obtained in this work could therefore be considered to be an adequate approximation to the 'intrinsic' kinetics.

A useful, global kinetic model describing tar cracking behavior over CaO should account for the chemical complexity of the coal tar mixture as well as treat the transient behavior of calcium oxide activity due to coke formation on the oxide surface.

It was observed, at least qualitatively, that tar fractions of different molecular weight (MW) cracked over CaO at different rates. This was so, presumably because (in the absence of pore diffusion limitation) the molecular size (or more appropriately, the number of aromatic ring clusters) of a tar molecule (which can be associated qualitatively with the MW), is closely related
to the cracking reactivity of different aromatics system over CaO. Furthermore, it was found that there was no preferential distribution of oxygen hetero-atom and phenolics (which exhibit high reactivity with CaO) among tar sub fractions of different MW.

The MW was therefore chosen as the major structural parameter for characterizing the coal tar reactivity. A simplifying approach of lumping the whole tar into four sub fractions (with MW ranges of \(< 340\), \(340 - 395\), \(395 - 575\), and \(> 575 \text{ g/mole}\), respectively) was determined to be adequate for modeling purposes. The first two fractions corresponded to major peaks of tar sample separable by the GPC.

It was found that the response, per unit mass of tar, of the UV detector (at 405 nm) used for GPC, was approximately uniform over the MW range studied. The weight fraction and yield of each tar lump could then be determined from the corresponding GPC areas (assuming 100% tar recovery from the GPC column) and knowledge of the corresponding total yield of tar surviving thermal treatment.

The CaO deactivation behavior due to surface coke deposition was examined by studying how the CaO activity for cracking coal tars, changed as a function of cumulative feed to CaO weight ratio (which was varied from about 0.05 - 0.5). The cracking experiments were carried out over the 500 - 700°C temperature interval to give a wide range of % tar conversion (Figure 14).
The general trend observed was that for a given cracking temperature the cracking activity of CaO initially decreased rather rapidly with increasing tar/CaO ratio (or equivalently, coke content of CaO), and then declined at a much slower rate with further increase in this ratio. The change of % conversion for each tar lump, with increasing tar/CaO ratio, also showed the similar trend. These observations were in agreement with the results of corresponding pure compound studies where the effect of cumulative feed of pure compound (instead of coal tar) on CaO activity was examined (Lai, 1986).

The initial 'fast' deactivation was presumably due mainly to direct site suppression, i.e., the CaO lost activity because the active site was covered by coke. The activity of CaO was never deactivated completely in the 'slow' deactivation regime, even after coke equivalent to several monolayers was deposited on the CaO surface. This residual cracking activity might be due to the contribution from coke-enhanced cracking and/or residual activity of CaO.

A small fraction of the CaO surface could be constantly available for tar cracking, even after extensive coking, presumably through segregation of surface deposits to form 3-dimensional islands of multilayer coke on the CaO, a process similar to that proposed by Somorjai and Zaera (1982) for surface reactions on platinum catalysts. The multilayer coke could also be formed by a growing filament mechanism (Baker and Harris, 1978) above surface activated sites. The slow
decrease in cracking activity of stone during this latter stage could be mainly caused by the monotonically increasing plugging (choking) of the pores by coke deposits.

Based on the above discussions, a model was developed to describe the kinetics of tar cracking reactions over a packed bed of CaO. Since the concentration of coal tar was so dilute (typically less than $10^{-7}$ mole/cm$^3$) that there was no discernible temperature changes measured during a pyrolysis reaction, the packed bed was considered isothermal.

By considering a material balance, a set of continuity equations for each of the four tar lumps and the total coke formed on the CaO surface were derived as

$$\frac{\partial f_i}{\partial z} = -\rho_s \frac{A_d}{F} r_i , \quad i=1,4$$  \hspace{1cm} \text{Eq. (4)}

and

$$\frac{\partial C}{\partial \theta} = \frac{\epsilon \rho_A d}{FM_1} r_c$$  \hspace{1cm} \text{Eq. (5)}

where

$\text{d}_b$ : bed depth (m);

$z$ : dimensionless axial distance from the top of packed bed, scaled by $\text{d}_b$;
\( \rho_s \): bulk density of catalyst (kg/m\(^3\) of reactor volume);

\( A \): reactor cross-sectional area (m\(^2\));

\( F \): molar flow rate of feed (helium + tar), (mole/min);

\( \epsilon \): bed void fraction;

\( \rho_1 \): vapor density of tar lump 1 at the cracking temperature (kg/m\(^3\));

\( M_1 \): mean MW of tar lump 1 (kg/mole);

\( \theta \): dimensionless time, scaled by \( \epsilon \rho_i d_B A F \);\( M_1 \);

\( f_i \): mole fraction of tar lump i in the fluid;

\( C \): CaO coke content (kg coke/kg of CaO);

\( r_i \): rate of disappearance of tar lump i

\[ \text{[mole of lump } i/(\text{min } \times \text{kgCaO})] \];

\( r_c \): rate of coke formation on CaO,

\[ \text{[kg coke/(min } \times \text{kgCaO})] \].

The heterogeneous reactions of coal tar over CaO is presumable best described by a Langmuir-Hinshelwood type kinetics. However, first order kinetics would be a good simplifying approximation if the reactant concentrations were very dilute, such as in this study. The rate terms in Eq. (4) were proposed as
\[ \rho_{s_{i}} = c_{A_{s}} N[\phi_{k_{i}} f_{i} + (1-\phi)k_{c_{i}} f_{i}] \phi_{A} \quad \text{Eq. (6)} \]

where

- \( k_{i} \): specific rate coefficient for tar lump \( i \) cracking over cokeless CaO, \((\text{min} \times \text{m}^{2}/\text{g of CaO})^{-1}\);
- \( k_{c} \): rate coefficient for tar cracking over coke or coked CaO, \((\text{min} \times \text{m}^{2}/\text{g of stone})^{-1}\);
- \( N \): total concentration at the cracking temperature \((\text{moles/m}^{3} \text{ of fluid})\);
- \( A_{s} \): specific surface area of cokeless CaO \((\text{m}^{2}/\text{g})\);
- \( \phi \): deactivation function;
- \( \phi_{A} \): area effectiveness factor.

The rate of coke formation was then proportional to the total cracking rate of lumps 1 through 4 (the conversion factor (by weight) for coke from cracked tar was experimentally determined to be about 0.8 - 0.85).

The first term in the bracket of Eq.(6) accounted for the initial rapid decay of the CaO activity, which has been suggested to be adequately described by an exponential type deactivation function (Froment and Bischoff, 1979),

\[ \phi = \exp(-\alpha C) \quad \text{Eq. (7)} \]
where $\alpha$ : deactivation coefficient (kg coke/kg of CaO)$^{-1}$.

The second term accounted for the residual activity of CaO after extensive coking had taken place. Since the effective surface area of CaO available for tar cracking varied with cracking temperature (Figure 2) and the coke content of CaO (due to pore plugging), the term $\phi_A$ was included in the model. The term $\phi_A$ is a ratio of available surface area of CaO, at any time during tar cracking, to its initial area prior to tar introduction.

The assumptions that the specific (per unit surface area) cracking activity of CaO was constant, and that coke formation on CaO was uniform, were made in deriving Eq.(6). The relationship between cumulative surface area and pore (slit) width of CaO, determined from pore size distribution analysis, was also used for calculating $\phi_A$.

The coupled equations (4) and (5) were solved numerically. The parameters in Eq.(6) and (7), determined by best fitting the data (i.e., changes of conversion of tar lump i vs. tar/CaO ratio) between 500 - 600$^\circ$C cracking temperature (i.e., conversion was less than 100%), and were found to be

$$k_1 = 7.57 \times 10^7 \exp (-26100/RT)$$
$$k_2 = 3.82 \times 10^5 \exp (-15800/RT)$$
$$k_3 = 1.27 \times 10^5 \exp (-13800/RT)$$
$$k_4 = 3.60 \times 10^4 \exp (-12200/RT)$$
$$k_c = 1.80 \times 10^6 \exp (-24200/RT)$$
$$\alpha = 30.9$$
The model (with parameters determined below 600°C and 15 Wt% coke content of CaO) was also found to properly describe the tar cracking kinetics over CaO at 700 and 800°C and up to 20 Wt% of CaO coke content (Figure 15). The apparent decrease in CaO activity at 800°C was mainly due to the reduction (by more than 50%) of its surface area, compared to that at 600°C. Furthermore, the effect of volatiles contact time on overall tar yield, shown in Figure 16, was also largely predicted by this model.
1.5. **Conclusions**

1) The presence of CaO significantly enhances the cracking rate of prompt coal tar (by one to two orders of magnitude in this study) when compared to that for the vapor phase tar pyrolysis in the absence of CaO.

2) The major products for tar cracking over CaO are coke and hydrogen. The relatively yields of light hydrocarbon gases (based on the amount of tar loss) are significantly lower in the presence of CaO than in its absence.

3) Vapor phase thermal cracking reduces the average molecular weight (MW) of secondary tars mainly through breakage of the aliphatic linkages rather than the aromatic ring systems. Tar pyrolysis over CaO reduces the average MW by selectively enhancing the removal of higher MW molecules.

4) At the same conversion level, secondary tars have significantly higher aliphatic to aromatic hydrogen ratios when cracked over CaO, suggesting the existence of special CaO-aromatics chemistry that enhances the pyrolysis of the aromatic-rich fraction of tar.

5) The acidic content (mainly phenolics) of coal tar decreases
above 700°C when cracked in the vapor phase alone. In the presence of CaO it is reduced in the 400 – 800°C temperature range. The CaO presumably enhances the removal of phenolics through the formation of calcium half-salts, at least at low temperatures (below 500°C).

6) The specific bacterial cell mutagenicity of coal tar increases drastically due to homogeneous thermal cracking at 700°C or 800°C, but is moderated in the presence of CaO, especially at 700°C.

7) The tar cracking activity of coked CaO can only be partially regenerated by O₂ burnoff of the coke deposits. However, essentially complete regeneration of activity can be achieved by appending the O₂ burnoff by hydration of the coke-free, deactivated CaO sample, and then recalcining it in-situ. The presence of sulfate in CaO enhances the stone sintering process.

8) The results of high temperature (400 – 500°C) chemisorption experiments lend strong support to the picture that the surface of solid CaO functions as a Lewis acid (electron acceptor) at high temperatures (perhaps ≥ 400°C). The ability of CaO to selectively enhance the cracking of aromatics is presumably due to the promotion of electron donor chemisorption reactions of these compounds on the
CaO by its acidic surface at high temperatures.

9) A model is developed that uses molecular weight as a global parameter to characterize the different thermal reactivity of different tar fractions over CaO. The model describes the deactivation of CaO activity by considering both the site-poisoning mechanism and the process of pore plugging (choking) due to coke deposition on the CaO surface. It is shown to describe the heterogeneous cracking of coal tar over a wide range of conditions, i.e., 0.05 - 0.5 (g/g) cumulative tar/CaO ratios, 0.06 - 0.24 s volatiles contact times, and 400 - 800°C cracking temperatures.

Acknowledgement

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References


Table I. Proximate and Ultimate Analyses of the Pittsburgh No. 8 Seam Bituminous Coal\textsuperscript{a}

<table>
<thead>
<tr>
<th>prox. anal.</th>
<th>Wt% as-received</th>
<th>elem. anal.</th>
<th>Wt%, dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>volatiles</td>
<td>38.5</td>
<td>C</td>
<td>71.5</td>
</tr>
<tr>
<td>fixed carbon</td>
<td>50.5</td>
<td>H</td>
<td>5.1</td>
</tr>
<tr>
<td>moisture</td>
<td>1.5</td>
<td>O</td>
<td>8.2</td>
</tr>
<tr>
<td>ash</td>
<td>9.5</td>
<td>N</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ash</td>
<td>9.6</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Heating value, 7250 cal/g.

Table II. Elemental Analysis of Primary Tar and Secondary Tars from Runs at Cracking Temperatures Between 400 and 800\textdegree C

<table>
<thead>
<tr>
<th>tar</th>
<th>thermal treatment</th>
<th>crack temp. \textdegree C</th>
<th>Wt%</th>
<th>H/C at ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>primary</td>
<td>none</td>
<td></td>
<td>81.6</td>
<td>6.97</td>
</tr>
<tr>
<td>secondary</td>
<td>vapor phase</td>
<td>500</td>
<td>80.7</td>
<td>7.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>600</td>
<td>81.5</td>
<td>6.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>700</td>
<td>82.3</td>
<td>5.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>86.4</td>
<td>5.49</td>
</tr>
<tr>
<td>secondary</td>
<td>over CaO</td>
<td>400</td>
<td>83.2</td>
<td>7.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>81.2</td>
<td>6.78</td>
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<td>600</td>
<td>83.2</td>
<td>7.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>700</td>
<td>76.6</td>
<td>6.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>84.5</td>
<td>6.22</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Determined by difference.
Figure 1. Apparatus Flowsheet
Figure 2. Specific Surface Area of CaO, Prior to the Introduction of Coal Volatiles, as a Function of Temperature.

Figure 3. Pore-size Distributions in CaO Calcined from Ca(OH)$_2$. (Sample prepared for a 700°C Mode-4 experiment)
Figure 6. Yields of CO₂, CO, H₂O, and H₂ as a function of cracking temperature.
- Symbol △ is for mode-1, ○ for mode-3, × for mode-4.
- "homo" = 2.0%, "hetero" = 0.12%.

Figure 7. Effect of CaO and cracking temperature on relative CH₄ yield.
Figure 8a. Effect of Cracking Temperature on the Number-Average Molecular Weight of Mode-3 and Mode-4 Tars.

Figure 8b. Effect of Cracking Temperature on the Weight-Average Molecular Weight of Mode-3 and Mode-4 Tars.
Figure 9a. Effect of Tar Conversion on Aromatic + Phenolic Hydrogen Fraction.

Figure 9c. Effect of Tar Conversion on Beta Hydrogen Fraction.

Figure 9b. Effect of Tar Conversion on Alpha Hydrogen Fraction.

Figure 9d. Effect of Tar Conversion on Gamma Hydrogen Fraction.
Figure 10. Comparison of Absolute Yield of Aromatic Hydrogen (g/100g Coal) for Primary and Secondary Tars.

Figure 11. Phenolic Content of Mode-3 and Mode-4 Tars as a Function of Cracking Temperature.
FIGURE 12a. Effect of Cracking Temperature and CaO on Coal Tar Mutagenicity. (With Metabolic Activation)

FIGURE 12b. Effect of Cracking Temperature and CaO on Coal Tar Mutagenic Impact. (With Metabolic Activation)
Figure 13. Effect of Burnoff and Hydration/Recalcination on the Percentage Tar Conversion Over CaO.

Fresh CaO was employed in Run #0 for tar cracking. In between Run #0 to #8, coked CaO was kept at 700°C overnight before regenerated by O₂ burnoff. After Run #4, the regenerated CaO was first hydrated, then recalcined in-situ before Run #5.

Figure 14. Effect of Cumulative Tar/CaO Ratio on Tar Cracking Activity of CaO.

Tar cracking temperature, \( t_{\text{hetero}} = 0.12 \) s.
Figure 15. Total Tar Yields as a Function of Total Coke Content of CaO.

Figure 16. Effect of Volatiles Contact Time on Overall Tar Yield.
2. **Introduction**

2.1 **Coal Devolatilization and Generation of Organic Contaminants**

Thermal devolatilization of coal occurs in many coal conversion processes such as coal combustion, gasification, and pyrolysis processes. Depending on the operating conditions, this process of coal transformation has great potential for serious environmental and health problems. It produces various amounts of organic contaminants such as soot and tars, the latter being very complex mixtures of many different (aromatic-rich) compounds spanning a boiling point range from 80 to $>350^\circ C$, and including hydrocarbons, phenolics and many other heteroatom compounds.

2.1.1 **Potential Problems**

If the process is uncontrolled, these products from coal devolatilization could cause major problems in the management of coal gasification (or pyrolysis) waste and product streams. These include:

1. the generation of vapor phase pollutants such as hydrogen sulfide, sulfur dioxide, other organic sulfur compounds and volatile nitrogen compounds;

2. the production of liquid products (tars) which contain many undesirable polycyclic aromatic hydrocarbons which are toxic,
i.e., mutagenic, carcinogenic, etc. It constitutes a significant health hazard for both plant personnel (as fugitive emissions and in handling of waste or by-products), and for the general public (as stack emissions and in the waste streams):

(3) the production of tars many of which are corrosive or easily form coke or other deposits in downstream equipment, causing fouling of heat exchangers, clogging of valves, and interference with $\text{H}_2\text{S}$ removal processes.

The pyrolysis tars typically have a high content of organic oxygen compounds, many of which are phenolics. The phenolics are believed to cause such problems as corrosiveness, instability on storage, incompatibility with the conventional petroleum-derived liquids, and toxicity of coal pyrolysis tars (Gould and Long, 1982).

2.1.2 Proposed Solutions

To make coal and pyrolysis tar satisfactory choices as alternative energy sources, an economic and practically implementable process is desirable for the control of pollutants in coal conversion products.

Calcium oxide, because of its desirable chemical reactivity as well as its wide availability and relatively low cost, is of considerable industrial interest as an additive for improvement of coal gasification and pyrolysis processes. It is proposed to overcome the problems discussed above, by identifying
proper operating conditions under which in-situ thermal treatment of coal pyrolysis volatiles, with calcium oxide (or calcined dolomite) would result in either total contaminant destruction or some combination of contaminant removal plus quality improvement that makes the surviving products suitable for better and safer utilization.
2.2 CaO-Aromatics Interactions

2.2.1 Program Rationale

Considerable investigations of the use of CaO at high temperatures ($> 1088$ K) have been performed in the areas of:
(a) fluidized-bed production of low BTU gas (Chemically Active Fluidized Bed Process) (Craig et al.; Lyon, 1977), where it served principally as a sulfur remover; and (b) in steam gasification in the CO$_2$ Acceptor Process (Curran et al., 1966; 1967), where in addition to its ability to remove CO$_2$ and sulfur compounds from the gas stream, a concurrent increase in hydrogen and methane content resulted in product gas of high heating values.

More recently, the effects of CaO have been investigated in the so-called COHOGG Process (Dawson, 1979), where the sulfur-capturing properties of calcium oxide are utilized as coal and lime are pyrolyzed in a fluidized bed at 1144 K.

For temperatures in the range 700 - 1033 K, researchers at M.I.T. have explored the chemistry of calcium oxide interactions with the pyrolysis of coal (Yeboah, 1979; Yeboah et al., 1980; Franklin, 1980; Franklin et al., 1981), and also its impact on the pyrolysis of pure organic compounds (Mead, 1979; Abrishamian, 1978; Ellig et al., 1985; Ellig, 1981; Lai, 1986).

In the fluidized bed pyrolysis of Illinois No. 6 bituminous coal or a 55:45 (W/W) mixture of Texas lignite/Illinois No. 6 coal, over the temperature range 700 - 1033 K under 1 atm pressure
using N₂ as a fluidizing gas in a 5.1 cm I.D. (about 30 cm bed, 45 cm free board) fluidized bed, the addition of calcium oxide or calcined dolomite stones to the bed instead of sand resulted in the following improvements in the products (Yeboah, 1979): (a) major decarbonation of the product gas over the temperature range 700 - 923 K; (b) virtually total desulfurization of the product gas at all temperatures studied, including removal of vapor phase organic sulfur compounds such as thiophene, 2-methyl thiophene, methyl-, and ethyl-mercaptan, and dimethyl sulfide; (c) greater proportion of the coal heat content converted to pyrolysis gas; (d) increased heating value per unit volume of product gas due not only to removal of CO₂ but also to the increased production of hydrocarbon gases and hydrogen; and (e) decreased absolute tar yields but product tars of improved quality (higher H/C ratios and lower oxygen contents). In addition, dilution of Illinois No.6 coal with calcium oxide allowed the caking coal to be fed to the above scale fluidized bed pyrolyzer without bogging problems.

While the removal of non-thiophenic sulfur compounds and of CO₂ were consistent with earlier findings at higher temperatures (from the CO₂ Acceptor Process), effects (c) to (e), and probably the removal of the thiophenic sulfur compounds, apparently derive from an unexpected cracking activity of calcium oxide for coal pyrolysis tars, and are of special interest.

A program on rapid coal pyrolysis has also shown that the addition of calcium oxide to demineralized coal resulted in
reduced tar yields and an increased yield for carbon monoxide (Franklin, 1980). Other exploratory studies from our group found that addition of calcium oxide to a small packed bed of coal reduced the mutagenic potency of tars produced on subsequent pyrolysis of the coal at 600°C (Anderson, 1979).

Studies of interactions between calcium oxide and pure organic compounds were also undertaken in our laboratory in the past few years. Calcium oxide was shown to be extraordinarily active in pyrolytic destruction of aromatic compounds, in contrast to its moderate activity for paraffin pyrolysis (Elliott, 1963). It is believed that the interesting effects observed in the coal pyrolysis research programs are closely related to these thermal reactions of calcium oxide with aromatic compounds.

2.2.2 Objectives of Proposed Research

The overall objective of this research was to investigate the role and potential application of calcium oxide chemistry to improving product yields and quality and to the control of pollutants in coal gasification and pyrolysis processes. Specific goals were to:

(1) Investigate the effects of calcium oxide on the global kinetics and product distribution of thermal decomposition of prompt coal pyrolysis tar, as a function of temperature, tar residence (contact) time, coal/CaO ratio, stone source, and
type, and composition of carrier stream (i.e., inert or reactive);

(2) study the effect of calcium oxide on product tar properties, such as aromaticity, mutagenicity, molecular weight distribution, and heteroatom content;

(3) study the change of calcium oxide activity for tar cracking with extent of utilization, and with method of regeneration;

(4) develop a kinetic model for the heterogeneous reactions of coal tar over calcium oxide, accounting for the chemical complexity of the tar mixture as well as the deactivation behavior of calcium oxide activity due to coke formation and stone sintering;

(5) elucidate the possible mechanism for the enhanced cracking of tar over calcium oxide surface.

2.2.3 Technical Feasibility and Potential Benefits

The results of this research are believed to be useful in defining and assessing means for controlling pollutants and improving product quality and hence economics, in coal gasification processes.

Specific benefits could include identification of strategies for: (1) increasing product gas yields, heating values, and desulfurization, resulting in a more marketable fuel gas that would also have lower transportation and storage costs;
and (2) improving the by-product value of the tars that are formed concurrently — specific effects would include reduced aromaticity, heteroatom content, mutagenicity and toxicity and possibly improved stability.

Possible problem with the use of calcium oxide in practical scale processes would include the cost of the CaO and increased solid disposal problems because of the formation of calcium sulfide and sulfate as part of waste stones. Nevertheless, special interest in application of the results of this program would be expected in processes in which calcium oxide is already employed, such as those involving fluidized bed combustion of coal or char.

Furthermore, a potentially very significant advantage of using calcium oxide in thermal processing of coal is the possibility of being able to feed caking coals to practical scale fluidized bed reactors without encountering bed bogging problems.
3. **Background**

3.1 **The Preparation and Properties of CaO**

One of the major focuses of this research is to investigate the special activities of CaO for organic reactions, especially in the high temperature (>500°C) range. Unfortunately, there appears to be little literature information regarding the precise role the CaO surface (and presumably its active sites) plays in the high temperature (pyrolytic) reactions. However, studies on the catalysis of many organic reactions, although mostly carried out at temperatures lower than those of primary interest in this work (about 20-400°C vs. 400-800°C), are abundant in the literature. These studies identify the importance of method of stone preparation as well as its physical and chemical properties in determining the reactivity of CaO in low temperature catalytic reactions. It is hoped that a survey on these studies can perhaps shed some light on understanding the high temperature pyrolysis reactions involving CaO.

3.1.1 **Physical Properties of CaO**

Calcium oxide, generally known as lime or quicklime, exhibits a white color in its pure form. All quicklimes are
crystalline, but crystallite conglomerates vary greatly in size and spacing in their matrices, owing to the differences in origin of CaO and in its preparation methods. X-ray diffraction reveals that a pure calcium oxide possesses a face-centered cubic system (see Figure 3.1-1a), the type of crystal lattice similar to that of sodium chloride, with a coordination number of 6 for both the calcium and oxygen ions. The length of each edge of the cube is 4.797 Å, with calcium atoms located midway in between.

The surface area of quicklime varies from \( < < 1 \text{ m}^2/\text{g} \), when it is dead-burned, to as high as 133 \text{ m}^2/\text{g}, when derived from Ca(OH)\(_2\) calcined in vacuo at proper temperatures (Beruto et al., 1980). The porosity of commercial lime also covers a wide range in percent of pore space (from 18 to 54\%), depending on the structure of the source limestone and severity of calcination.

The critical dimensions and shapes of CaO pores are also found to be strongly dependent on the sources of stone. Beruto et al. (1980), from the nitrogen adsorption and desorption isotherms, concluded that lime from calcining CaCO\(_3\) powder in vacuum at 510°C has pores of cylindrical symmetry, with the most probable diameter of 100 Å, while that from Ca(OH)\(_2\) (calcined at 320°C) has slit-shaped micro fissures, with the most common slit width being about 27 Å.

This geometrical difference in CaO micro-structure, though without direct information available from literature as yet,
Fig 3.1-1a. Crystal structure of calcium oxide. (Boynton, 1980)

Fig 3.1-1b. Crystal structure of calcite. (Boynton, 1980)

Fig 3.1-1c. Crystal structure of Ca(OH)$_2$. (Boynton, 1980)
might cause differences in chemical and catalytic properties of the lime from different sources of stone. Other important physical properties of CaO such as the specific gravity, melting point, thermal conductivity, etc., are summarized in Table 3.1-1 for reference.

Table 3.1-1 Summary of Some Physical Properties of Lime
(Boynton, 1980)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>True specific gravity (zero porosity)</td>
<td>3.34</td>
</tr>
<tr>
<td>Apparent specific gravity</td>
<td>1.6-2.8</td>
</tr>
<tr>
<td>Thermal conductivity (cal/cm. sec. °C)</td>
<td>0.0015-0.002</td>
</tr>
<tr>
<td>Coefficient of expansion (0-1700°C)</td>
<td>1.38*10^{-5}</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>2570</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>2850</td>
</tr>
<tr>
<td>Specific heat (0-2500°C) (cal/g.°C)</td>
<td>0.17-0.32</td>
</tr>
<tr>
<td>Heat of formation (cal/mole)</td>
<td>151,900</td>
</tr>
<tr>
<td>Surface energy (erg/cm²) (23°C)</td>
<td>1310 ± 200</td>
</tr>
</tbody>
</table>

3.1.2 Chemical Properties of CaO

The surface of calcium oxide crystals has long been known to be basic at low temperatures, with the existence of basic sites exhibiting a wide range of basic strength. The basic
strength is defined as its proton-accepting ability, following the Brönsted concept. The base-strength distribution of the solid surface has been determined at room temperature by wet chemistry techniques such as titration of the solids suspended in cyclohexane with benzoic acid, using a series of H-indicators (Take et al., 1971).

It was found that basicity (and surface area) of the lime can vary greatly with calcination temperatures (Iizuka et al., 1971; Tanabe and Saito, 1974). The change in stone's basicity could not be totally accounted for by the change in its surface area, indicating that these are likely independent events. The proposed nature of these basic (mainly O^{2-}) sites and their relationship with certain catalytic activity of CaO will be discussed in more detail in the next section (3.2.1).

Acidic sites which are believed to be coordinatively unsaturated Ca^{2+} ions were found to be present on CaO surface, and were also responsible for catalyzing reactions such as the isomerization and exchange reactions of butenes (Hattori and Satoh, 1976; Tanabe and Saito, 1974). Calcium oxide derived from calcination in vacuum has been shown to possess electron donating power in low temperature reactions (Iizuka et al., 1971; Cordischi and Indovina, 1976; Morrison, 1975). These reducing sites are generally observed by spectroscopic techniques (such as electron-spin-resonance (ESR) absorption and visible reflectance spectroscopy) which will also be described in more detail in the next section. The concentration of reducing sites is also found to change greatly with the calcination temperature.
3.1.3 Preparation of CaO from Limestone Calcination

Since CaO is industrially derived mainly from the calcination of high-calcium limestone, its calcination chemistry and variables that affect the lime properties will be discussed first. Calcite (CaCO$_3$) is the most abundant of all minerals in limestone; therefore, the term 'limestone' will refer to CaCO$_3$ in this work.

X-ray diffraction shows that calcite is crystallized in the rhombohedral system whose unit-cell is given in Figure (3.1-1b), with a cell edge of 6.360 Å in length. The limestone calcination, which probably represents one of the most straightforward and oldest chemical reactions, is described by equation (3.1-1):

$$\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2,$$

$$\log K = 7.24 - \frac{8476}{T} \quad \text{Eq. (3.1-1)}$$

Even though many studies regarding this single reaction have been undertaken by researchers in the lime industry, controversy still exists, simply because the structural changes during stone dissociation and crystallite rearrangement are not fully understood yet.

A unit cell of calcite contains two molecules of CaCO$_3$ and has a crystal volume of about $122 \times 10^{-24}$ cm$^3$ (Hedin, 1961). A unit cell of CaO, on the other hand, includes four CaO molecules, but its volume is only about $108 \times 10^{-24}$ cm$^3$ (Hedin, 1961). This implies that in the process of calcination, the
solid should undergo a 55% reduction in volume. However, it is found that the increase in the bulk density of the stone is often considerably less than the increase in specific gravity (Hedin, 1961), indicating that the CaO structure formed after dissociation can differ significantly from the ideal case of a perfect packing model.

Based on results of the fairly extensive work by Glasson (1956, 1961, 1967), several major calcination parameters which can significantly influence the characteristics of the product lime are identified as follows:

(1) source of stone,
(2) calcination temperature, heating rate and time,
(3) particle size of stone,
(4) calcination environment,
(5) presence of other minerals.

Effect of the Type of Limestone

The complex nature of the effect of stone type on properties of product lime can be illustrated by the study of McClellan and Eades on the calcination of two high purity calcitic limestones (1970). Iceland spar, which is the purest form of natural limestone, yields a lime of consistently higher surface area and smaller pore size than that of limestone 89 (USDA reference sample 89) at all temperatures. Another example is available based on Murray's work (1954). It can be concluded that the nature of the original carbonate does exert signifi-
cant influence on the properties of the resulting CaO.

**Effects of Calcination Temperature, Heating Rate and Time**

The equilibrium dissociation temperature of CaCO$_3$ under 1 atm CO$_2$ pressure is about 900°C. It has been observed that, for calcination in nitrogen or open atmosphere, a minimum heating temperature of 900°C is needed for complete decarbonation within 2-3 hours, even when the limestone is in powder form (Boynton, 1980).

According to Glasson's suggestion (1961), three physical changes occur during the production of CaO which affect stone properties, such as specific surface area (SSA) or porosity, in the following manner: (a) formation of CaO, still having a pseudo-lattice of CaCO$_3$ (or Ca(OH)$_2$), does not significantly change SSA, (b) recrystallization of the pseudo-lattice, by mutual interchange of surface molecules via diffusion, to the stable normal face-centered cubic CaO-lattice, causes the SSA to increases (and this production of new surface lags behind the decomposition because of the limited rate of recrystallization), (c) sintering of the recrystallized CaO decreases SSA. Mayer and Stowe (1964) as well as Hedin (1961) supported this calcination theory. Beruto et al. (1980), however, proposed a somewhat contrary mechanism involving no induction period for recrystallization, based on their work on calcination of CaCO$_3$ and Ca(OH)$_2$ in vacuum.
In view of the effects of calcination conditions on the properties of lime derived from CaCO$_3$, most researchers agree that generally a higher temperature and heating rate and longer period of calcination exert adverse effect on process (b) and enhance process (c) mentioned above, thus forming a lime with higher shrinkage and density, lower surface area and porosity, and lower chemical reactivity (Boynton, 1980).

Effect of Particle Size

Since the partial pressure of CO$_2$ normally builds up and dissociation always penetrates gradually from the surface into the interior of stone, the larger size particles are more difficult to calcine uniformly. Glasson (1961), along this line, found that the crystallite size of the CaO formed in the outer sections of the one inch limestone spheres tends to be smaller than that formed in the core, due to the difference in the nucleation rates during recrystallization of the oxide.

Frequently, overburn of the surface layer at high temperatures (>1200°C) necessary to expel CO$_2$ from within large size stones and incomplete dissociation of the core may occur. This condition is aggravated when the particle size distribution is broad, since the smaller sizes tend to be completely calcined first at lower temperatures, thus resulting in stones of non-uniform quality.

Boynton suggests that uniformity and optimal quality of
the product lime can be achieved by calcining stones of small dimension and of uniform size and shape (1980). Mullins and Hatfield (1970), using calcite in 81-645 micron size range, noticed that the extent of calcination for all particles is similar under the same thermal treatment, and that pore volume, however, increases with decreasing stone size.

**Effect of calcination environment**

Glasson (1958) studied the decomposition of calcium carbonate at 750°C in vacuo and observed the production of active lime whose specific surface (about 36 m²/g) is four times as much as that derived from the same limestone calcined in air at 800°C. He attributed this to the higher nucleation rate achievable in the vacuum case (where product CO₂ was removed promptly), which resulted in forming larger numbers of much smaller size crystallite and, therefore, higher surface area of CaO.

Beruto et al. (1980) obtained CaO with a surface area as high as 78 m²/g from a high-purity CaCO₃, calcined at 510°C under a vacuum of 7 x 10⁻³ N/m². The same CaCO₃ gave a lime of only 1-2 m²/g surface area if decomposed in air at 900°C. Aside from the reason Glasson suggested, it is likely that vacuum calcination also has the effect of lowering the dissociation temperature of the stone, thus reducing the sintering rate of the crystals.
Effect of Mineral Impurities

The limestones that were prone to high shrinkage contracted less after pretreatment in NaCl and Na\textsubscript{2}CO\textsubscript{3} solutions for 16 hours [Murray, 1956]. The presence of NaCl has also been shown to slightly reduce the dissociation temperature of calcite by 10\textdegree{}C (Wieczorek-Ciurcwa et al., 1980). In an extensive study on the sintering of lime, Glasson (1967) observed that NaCl and CaSO\textsubscript{4} both accelerate the sintering process at 800-1100\textdegree{}C. Ferric oxide, having low Tammann temperature (650\textdegree{}C), readily permits ion diffusion into fissures of lime crystallite matrix, thus promoting its sintering at 800-1100\textdegree{}C. Alumina and silica, on the other hand, do not enhance lime sintering below 1100\textdegree{}C, which is probably due to the formation of calcium complexes with higher Tammann temperatures.

3.1.4 Preparation of CaO from Ca(OH)\textsubscript{2} Calcination

The Ca(OH)\textsubscript{2} crystal is a hexagonal-shaped plate with perfect basal cleavage and layered structure, but the physical particles can be of different sizes, depending on the degree of agglomeration of the microscopic crystallites. The unit cell crystallizes into the lattice of AX\textsubscript{2} type, similar to the structure of CdI\textsubscript{2} (see Figure 3.1-1c). Although there are not as extensive works in the area of Ca(OH)\textsubscript{2} calcination in the literature when compared to the CaCO\textsubscript{3} counterpart, the
major calcination parameters discussed in the last section are generally found to significantly affect the properties of resulting CaO, as well. Glasson (1956) has reported the production of CaO from calcination of calcium hydroxide, both in the air and in vacuo, as described by equation (3.1-2):

\[
\text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O} ; \quad \log K = 8.2 - \frac{5703}{T} \quad \text{Eq.(3.1-2)}
\]

It was observed that when calcined in vacuo at a constant temperature the surface area of the stone increases as the percentage decomposition increases, reaching a maximum (at A, B, C, and D as shown in Figure 3.1-2) when calcination is approximately complete; then slowly decreases with increasing heating time. The maxima (A, B, C, and D) shift progressively to shorter calcination times and to lower values as the decomposition temperature is raised presumably, due to the corresponding increasing rate of decomposition and more extensive sintering (Glasson, 1956).

Iizuka et al. (1971) studied the calcination of reagent-grade Ca(OH)\(_2\) in air at temperatures from 300 to 800\(^\circ\)C for a constant (3 hours) heating time. Surface area increased with temperature to a maximum of 16 m\(^2\)/g at 550\(^\circ\)C and then decreased with rise in temperature. Szabo et al. (1975), under the same condition, reported a value as high as 30 m\(^2\)/g when the lime is obtained from calcining Ca(OH)\(_2\) recrystallized in conductivity water. This again suggests that parameters such as source of stone, or calcination environment (e.g., whether
Fig. 3.1-2 Calcium hydroxide samples calcined in vacuo at various temperatures. (Glasson, 1956)
removal of evolved H₂O is hindered or not), can strongly influence the resulting properties of CaO. Furthermore, some of the error may be caused by the unstable nature of CaO, as suggested by Beruto et al. (1980). Lime has a strong propensity to form CaCO₃ and Ca(OH)₂ at room temperatures in an unprotected environment, as described by reversing equation (3.1-1) and (3.1-2).

Glasson (1956) and Beruto et al. (1980) both demonstrated that Ca(OH)₂ when decomposed in vacuo, generates a lime of very high surface area. A value of 133 m²/g was observed upon calcining Ca(OH)₂ in vacuum at 320°C (Beruto et al., 1980), two orders of magnitude higher than that obtained in nitrogen at 400°C. This increase in area can also be attributed to the enhancement of nucleation rate for recrystallization (Glasson, 1956) and/or to the reduction in crystallite sintering rate.

Another important property, the pore size distribution of calcium oxide, was also explored by Iizuka et al. (1971) and Beruto et al. (1980). The former group found that a significantly higher fraction of stone surface area was occupied by 30-100 Å diameter pores (with a effectively higher specific surface area) for samples prepared at 500°C, in comparison with those derived at 300 and 700°C. Most of the pores in the latter samples are 100-300 Å in diameter. Here the preparation was by calcining Ca(OH)₂ in air for 3 hours at 300, 500, or 700°C followed by heating in vacuo for 1 hour at 200, 400, or 600°C respectively.
3.2 Reactions of Organic Compounds in the Presence of CaO and Dolomitic Solids

This section by no means serves as an exhaustive listing of all possible reactions to which CaO can have significant contribution. There have been many studies of interactions of CaO with inorganic compounds which include (a) SO₂ removal as in-situ desulfurization during fluidized bed combustion of coal (Chrostowski, 1979; Hartmann and Coughlin, 1974; Doerr, 1979; Kyte, 1981), (b) H₂S removal in the contexts of clean fuels production via both pyrolysis and gasification of coal (and heavy fuel oils) for electric power generation (Camp, 1979; Squires, 1966; Attar & Dupuis, 1978; Yeboah et al, 1980; Yeboah, 1979), and (c) removal of CO₂ (Dedman and Owen, 1962). These works will not be discussed here, since the reaction of inorganics with CaO is outside the scope of this work.

However, extensive attention has been focused on the special activities of CaO for organic reactions and on the structure and nature of possible active sites on the stone surface which participate in these catalytic reactions. Through these studies, it is hoped that one can better understand the CaO chemistry, especially in the high temperature (> 500°C) range. This can be very informative, e.g., in determining the optimal operation conditions, such as stone calcination procedure, reaction temperature and reaction environment, etc., for best CaO performance in gasification and pyrolysis of coal.
3.2.1 Pure Compound Studies (Below $400^\circ C$)

There have been numerous studies on the effects of calcium oxide on the low-temperature ($2^\circ -400^\circ C$) reactions of organics. Although these investigations are not directly pertinent to the proposed research on coal volatiles, i.e., CaO interactions at temperatures from 500-1000$^\circ C$, they do shed light on some very special and interesting chemistry involving quicklime.

In general, the reactions are catalytic in nature and can be classified into three different categories: (a) basic-sites, (b) acidic-sites, and (c) reducing-sites catalyzed reactions (Iizuka et al., 1971; Tanabe and Saito, 1974). It was reported that three distinct types of sites, one basic, one acidic, the third reducing, can be identified on the surface of CaO obtained from Ca(OH)$_2$ calcination in the temperature range of 300 to 900$^\circ C$. The former two sites are catalytically active for acid/base catalyzed reactions, while reducing sites are for the reaction involving anion radical as intermediate. Most of the low temperature catalytic activities of CaO can be attributed to these sites.

Basic-sites Catalyzed Reactions

One good example of these reactions is the study of CaO catalytic activities for the esterification of benzaldehyde at 180$^\circ C$ by Iizuka, et al. (1971). Other related works include
hydrogen disproportionation and dehydrogenation of cyclohexene and cyclohexadienes, double-bond isomerization of olefins, hydrogenation of alkenes and of cyclohexene, dehydrogenation of alcohols (Schächter and Pines, 1968), double-bond migration of allylamine to enamine at 40°C (Hattori et al., 1980), isomerization of β-Carene (Shimazu et al., 1977), and isomerization and dehydrogenation of various menthadienes at 290–380°C (Albeck et al., 1971).

These investigations mainly focused on the catalytic chemistry of CaO interacting with these primarily aliphatic compounds at lower temperatures. Several specific reaction schemes for some above-mentioned reactions have been proposed (Hattori et al., 1980; Shimazu et al., 1977) which will not be discussed here. However, one interesting and common finding through all these studies is that the expected 'activity' of CaO, and hence dolomitic solids, can depend strongly on the preparation conditions and sources of the stone.

Schächter and Pines (1968) have observed that the most active catalysts for isomerization, and dehydrogenation reactions were prepared from calcium hydroxide which was calcined at 500°C. When the calcination was carried out at 900°C, the calcium oxide showed no catalytic activity towards the double-bond isomerization of olefins. The activity, however, could be restored when the catalyst was annealed at 500°C. Interestingly, CaO produced from calcining CaCO₃ at 900°C, with one hour annealing at 500°C, was very effective for 1-hexene iso-
merization. Its activity was unaltered even in streams of an equimolar mixture of O$_2$ and N$_2$, or of helium.

The researchers attributed the difference in catalytic activity of calcium oxides prepared by calcination of CaCO$_3$ and Ca(OH)$_2$ at 900°C, to differences in crystallographic dislocations which in turn depend on the starting materials (Renshaw and Thomas, 1966; Thomas and Renshaw, 1967). Similar existence of maximum stone activity was observed in the study of CaO-catalyzed esterification of benzaldehyde by Iizuka et al (1971).

This group also studied the variation with preparation temperature of the extent of dehydration, basicity and surface area of CaO/Ca(OH)$_2$ samples derived by calcining calcium hydroxide (presumably in air). As shown in Figure 3.2-1, rapid dehydration of Ca(OH)$_2$ starts at around 350°C while basicity becomes discernible at around 300°C and increases to a maximum at 500°C above which basicity decreases as calcination temperature increases. Interestingly, surface area also increases to reach a maximum at around 500°C but decreases only modestly with further temperature increases. This suggests that basicity changes are not solely a consequence of surface area changes and that surface area alone may not be the most important parameter in determining the reactivity of CaO.

Instead, it was found that there exists a good correlation of the stone's catalytic activity, as measured by the first-order rate constant of the reaction, with the basicity of lime
Fig. 3.2-1 Changes in basicity, surface area, and dehydration percentage of CaO with calcination temperature. (Iizuka et al., 1971)

Fig. 3.2-2 Correlation of basicity of CaO with catalytic activity for esterification of benzaldehyde: (○)—activity; (□)—basicity. (Iizuka et al., 1971)
generated at different calcination temperatures (Iizuka et al., 1971) (see Figure 3.2-2). This implies that basic-sites are (at least in part) responsible for the catalytic effects of CaO on the above-mentioned reactions.

Iizuka et al., (1971) through the infra-red study on adsorption of acidic molecules such as benzaldehyde and isopropyl alcohol onto calcium oxide, proposed that the basic sites on the stone consist of both a large number of strongly basic and a small amount of weakly basic OH− groups. Furthermore, they explained the decrease in observed basicity at higher calcination temperature by relating the basic sites to unstable crystal structure (e.g., coordination defects) of calcium oxide which became annealed and stabilized at high temperatures.

Acidic-sites Catalyzed Reactions

It is worth noticing that the surface acidic sites Ca2+ can also contribute to the stone's activity. The active O2− and Ca2+ sites may be formed if the CaO crystal cleaved along a face (the (111) face) containing only one of the two ions (Beruto, et al., 1981). Half of these ions should go to one and the remaining half to the other piece of crystal. On the resulting surfaces, one could then find cations (or anions) lacking one of their coordinating ligands. These coordinatively unsaturated sites can interact with allylic compounds to form Π-allyl complex and thus catalyze the reactions (Gates
et al., 1979).

In the follow-up studies of the conversion of benzaldehyde into benzyl benzoate, Tanabe and Saito (1974) observed that solid NaOH, NaOH/SiO$_2$, SrO$_2$ and BaO$_2$ which are strongly basic, did not show any catalytic activity. The fact that MgO and CaO activity was decreased by the addition of benzoic acid and almost lost entirely by introducing phenol or pyridine (a basic compound), suggests that the Lewis acid sites (metal ions of the oxides) and the basic sites (O$^{2-}$, OH$^-$) are both important as active sites in the catalytic reactions (Tanabe and Saito, 1974). Obviously, in this case basicity is a necessary, but not a sufficient, criterion for catalytic activity. Hattori and Satoh (1976) also found that incompletely coordinated metal ions (in CaO and BaO crystals) are part of the active sites which are responsible both for the isomerization and exchange reactions of butenes.

Another example of combined contribution of both basic-sites and the cations to the catalytic behavior of CaO, was given by Inoue and Yasumori (1981). The nature of the active sites on CaO for ethylene hydrogenation was explored by X-ray photoelectron spectroscopy. It is concluded that coordinately unsaturated metal cations (Ms) on sites located, e.g., at edges and corners of the CaO crystallites, as well as the O$^-$ (and to a lesser extent, O$^{2-}$) surface species, form certain combined structures that allow the formation of Π-allyl carbanions. The catalytic effect of CaO is considered to be the enhancement
of heterolytic splitting of hydrogen, with the induced charge polarization caused by the structure of these combined (basic and acidic) active sites.

**Reducing-sites Catalyzed Reactions**

The electron donor properties of CaO (as well as other alkaline-earth oxides) have been widely studied in recent years at temperatures less than 200°C. The capability of CaO, for example, of converting some molecules such as nitrobenzene and NO into the corresponding anions (Cordischi et al., 1976; Iizuka et al., 1976), of forming $O_2^-$ and $O_3^-$ ions from oxygen adsorption (Che et al., 1976; Cordischi et al., 1978; Ono et al., 1979; Zecchina et al., 1975), and of forming radical anions of 2-2'-bipyridyl (Coluccia et al., 1979), has been substantially reported. Results and conclusions of some controversy, however, are present and are briefly discussed here.

In one case, in the work of Iizuka et al. (1971), the amounts of reducing sites of CaO prepared from calcination of calcium hydroxide (both in air and in vacuum) at different temperatures were determined by observing visible reflectance spectra and electron-spin-resonance (E.S.R.) spectra of adsorbed nitrobenzene. The E.S.R. absorption data of this surface species, the anion radical of nitrobenzene, are shown in Figure 3.2-3 as a function of the calcination temperature. It is readily observed that the concentration of the anion
radical is strongly influenced by the calcination environment, the vacuum-calcined CaO being consistently superior to the air-calcined sample in reducing power.

Iizuka et al. (1971) reasoned that the reducing sites exist separately from the basic sites on the CaO surface, because
(a) the dependency, on calcination temperature, of anion radical concentration of the sample prepared in air is quite dissimilar to that of the basicity change (see Figures 3.2-1 and 3.2-3),
(b) the amount of the reducing sites is much smaller than that of basic sites, and
(c) the sites for anion radical formation (reducing sites are not poisoned by the adsorption of phenolphthalein, which is an acidic indicator.

Contrary to the conclusion of Iizuka et al. (1971), many other researchers found a correlation between the electron donor activity of alkaline-earth oxides and their Lewis base strength (Cordischi et al., 1976; Morrison, 1975), indicating a direct connection between basic centers and electron donor sites. (The CaO samples used in these studies were mainly obtained from calcination of Ca(OH)₂ in vacuum at temperatures of 600-950°C, for 2 to 15 hours, and had surface areas ranging from 50 m²/g to 200 m²/g.)

Morrison (1975), for example, has shown that basic centers can be coincident with sites for providing the surface states of reducing activity. In their later study of cis-trans inter-
conversion of 2-butene in the presence of CaO, Iizuka et al. (1976) also concluded that reducing sites can be ascribed to unusually strong basic sites.

A possible reducing site might be a point defect or a terminal of dislocation appearing on the surface (Iizuka et al., 1971). It is known that when point defect or edge dislocation occurs on calcium oxide crystal, oxide anions in high degrees of coordinative unsaturation become neighbor to each other, thus forming sites of high electron density. These $O^{2-}$ ions in sites of low coordination are often referred to as $O^{2-}$-cus.

The fact that the lower frequency bands (which characterize the lower coordinations) of visible reflectance spectra of surface states in CaO are eroded preferentially upon chemisorption of reactive gases such as $O_2$ or $N_2O$ (Zecchina et al., 1975), suggests that the higher the degree of coordinative unsaturation, the stronger the reducing activity of $O^{2-}$-cus site is. The decrease in radical amount formed on CaO when the latter is calcined at high temperature (see Figure 3.2-3) is considered due to the disappearance of point defect. The trend that the sample derived in air is consistently lower in radical amount than that treated in vacuum is also considered due to the annealing of defects which may be enhanced by the presence of both atmospheric and unremoved product moisture.

The good correlation between catalytic activity and the anion radical concentration of the sample CaO treated in vacuum is demonstrated both in the study of styrene polymerization
Fig. 3.2-3  (A) Amount of anion radical of nitrobenzene formed on CaO vs calcined temperature: (○) calcined in vacuum; (□) calcined in air.  (B) Polymerization activity in vacuum vs calcined temperature: (○) calcined in vacuum; (□) calcined in air. (Iizuka et al., 1971)
(Iizuka et al., 1971) (see Figure 3.2-3) and in that of cis-trans interconversion of 2-butene (Iizuka et al., 1976).

3.2.2 Pure compound Studies (Above $400^\circ$C)

Contrary to the case of low-temperature reactions, there have been relatively limited studies of high-temperature reactions of organics over CaO. Several important works on thermal cracking of pure compounds over CaO, most of which were performed in this laboratory, will be discussed first to gain some basic understanding of the special chemistry of interactions of lime with organics, especially with aromatics at temperatures above $400^\circ$C. The results of several studies concerning the effects of dolomitic compounds on coal utilization, which are most supportive of the importance for this research, will then be reviewed.

To our best knowledge, there are no systematic studies of selective cracking or heteroatom removal from aromatic compounds at temperatures above $450^\circ$C using calcium oxide or dolomitic stones, prior to work done by Mead (1979) in this department, who carried out exploratory investigations aimed at gaining a more basic understanding of the calcium oxide-organics interactions. A comparison study of the pyrolysis of several model aromatic compounds, (including benzene, thiophene, furan, and pyrrole) over sand, CaO, as well as alumina surfaces, was made. Some representative results on
the effect of temperature and stone type on thiophene pyrolysis are given in Figure 3.2-4. The unusual increase in the extent of cracking, on lime surface, of benzene, an aromatic compound, in contrast to that of heptane, an aliphatic hydrocarbon, is illustrated in Figure 3.2-5.

These data were obtained by passing vapor of the corresponding compound at a 5% (V/V) concentration in helium over a packed-bed of 355-425 micron particles of either sand or lime, or over 590-1190 micron particles of alumina, with an average residence time of 1 second for vapor in contact with stone. It is clear that the thermal decomposition of aromatics was preferentially accelerated by lime when compared to the other two solids, while only a moderate increase in cracking rate was observed for the aliphatic hydrocarbons.

This inversion in normal cracking reactivity (based on the thermodynamic considerations, aromatics should be more stable than aliphatics at high temperatures, and indeed this trend was normally observed (Fitzer et al., 1971)) is very significant and can be of great practical importance. The fact that despite its much higher specific surface area (210 m²/g) the alumina gave lower conversions under these conditions, suggests that the ability of lime to enhance cracking reactivity cannot be ascribed solely to the influence of surface area.

Ellig (1981) further studied benzene and extended the study to two alkylated aromatics, 1-methylnaphthalene and toluene. Thermal cracking reactions of these aromatic pure compounds
Fig. 3.2-4  Effect of calcium oxide on the thermal decomposition thiophene [global residence time=1 sec; feed gas was 5% thiophene 95% helium; pressure = 1 atm; stone size: 355-425 microns for lime and sand, 590-1190 microns for Al₂O₃] (Mead, 1979)

Fig. 3.2-5  Comparison of the effects of calcium oxide on the thermal decomposition of benzene and n-heptane (reaction conditions as in Figure 3.2-4. (Mead, 1979)
were performed over packed-beds containing CaO or quartz (which serve as comparison studies). Calcium oxide obtained by calcining calcium hydroxide at final reaction temperature was more active (on a unit weight basis) for benzene cracking than that obtained from limestone calcination under similar conditions. The temperature for aromatics removal from a helium hydrocarbon mixture in the presence of CaO was found to be lowered by 140-180°C from that observed over quartz. The major product from reactions over CaO was coke, with the reactivity of aromatic compounds increasing with the addition of a methyl group and a second aromatic ring to the structure.

The yields of methane, benzene (see Figures 3.2-6 and 3.2-7), and ethylene, presumably major light products from vapor phase free radical pyrolysis, were lower from toluene runs over CaO than those from experiments over quartz. (A similar trend was observed for the methylnaphthalene case.) All these interesting experimental findings suggest that CaO, as a good dehydrogenation catalyst at lower temperatures, also plays mainly a role of dehydrogenation (rather than dealkylation) catalyst (although the evolution of H₂ was not determined) in the high temperature reactions of aromatics which eventually leads to the formation of coke as the major product. The aromatics cracking activity of CaO is reduced after repeated use but can be at least partially regenerated by oxidation of the coke deposited on the surface (Ellig, 1981).

The results of n-heptane reactions over both CaO and
Fig. 3.2-6  Methane yield from toluene conversion over quartz or CaO*. (Ellig, 1981)

Fig. 3.2-7  Benzene yield from toluene conversion over quartz or CaO*. (Ellig, 1981)

* CaO derived from calcining Ca(OH)₂.
quartz show that the reduction in temperature for aliphatics removal was much less significant, and that there is little coke formation while the product distributions obtained over the two beds were similar to each other. These findings suggest that the special cracking chemistry of aromatics over CaO involves (at least in part) the interaction of stone surface active sites with the aromatic electrons of the hydrocarbons.

Another good example of heterolytic dehydrogenation over CaO was given by Sekiguchi et al. (1981). It was found that bibenzyl was dehydrogenated to stilbene over CaO (in the temperature range of 400-520°C), while, through a completely different course, it cracked to benzene, toluene, and ethylbenzene over glass beads (in the 520-620°C range).

There are several papers in the literature regarding the use of CaO as a cracking catalyst for thermal decomposition of aliphatic hydrocarbons. The catalytic cracking of methane over CaO at 900°C was studied by Solano et al. (1977), the major product being coke (and presumably H₂). In a comprehensive study of ethane decomposition over calcium oxide (Elliott, 1963), the major products were found to be ethylene and hydrogen as a result of ethane dehydrogenation. The lime was prepared from calcining CaCO₃ at 1000°C for 8 hours and heating the resulting CaO at 1400°C for 1 hour (presumably in air). Some methane, and between 600 and 980°C, a small amount of carbon monoxide
were also produced. Similar observations of CO evolution have been reported by Mead (1979) and Ellig (1981) in the pyrolysis of aromatics over lime.

Elliott (1963) suggested that the oxygen comes from calcium oxide lattice during the reactions. This assumption is indirectly supported by several interesting findings (Martens et al., 1976; Otto et al., 1979). Martens et al. (1976) studied the thermal decomposition of Mg(OH)$_2$ by analyzing the evolved gases with a mass spectrometer. They found that hydrogen is evolved in the temperature range 300-600°C (maximum at 450°C) and again between 600 and 900°C (maximum at 750°C). The amount of H$_2$ evolved is of the order of $10^{-4}$-$10^{-5}$ moles/g of MgO. An equivalent amount of (predominantly atomic) oxygen also evolves between 600 and 900°C. The following processes were proposed to occur:

\[
2\text{OH}^- \longrightarrow \text{O}^- + \text{H}_2
\]

at the lower temperature range, where H$_2$ molecules form within cation (Mg$^{2+}$) vacancies in the MgO neighbored by two adjacent OH$^-$ groups, and:

\[
\text{OH}^- \longrightarrow \text{O}^- + (1/2)\text{H}_2 \quad \text{and} \quad 2\text{O}^- \longrightarrow \text{O}_2^- + 0
\]

at the higher temperature range, where H$_2$ evolution is assigned to the dissociation of residual OH$^-$ groups.

The same process appears to be likely for CaO, derived from Ca(OH)$_2$, as the tendency to form peroxide increases.
passing from magnesium to calcium. If the amount of residual $0^-/OH^-$ group remaining on CaO, derived from calcining Ca(OH)$_2$ in the helium carrier gas, is of the order of that on MgO, i.e., $10^{-3}$-$10^{-4}$ moles/mole of metal oxide (which may be a lower-bound estimate), then the maximum amount of CO and CO$_2$ that can be obtained from reactions of residual $0^-$ ions (not the lattice oxygen) with deposited coke is on the order of $10^0$-$10^{-1}$ mg/g of CaO, enough to account for (at least most of) the CO/CO$_2$ evolution observed in above mentioned studies (Mead, 1979; Ellig, 1981).

The formation of $0^-$ species on the CaO surface upon heat treatment in vacuo was confirmed both by X-ray photoelectron spectroscopic (Inoue and Yasumori, 1981) and by ESR (Cordischi et al., 1978) studies. Furthermore, Inoue and Yasumori (1981) determined that the hydrogenation activity of CaO (at temperatures below 400$^\circ$C) is attributed to a combined structure of $0^-$ (not $0^{2-}$) and cations. They also found that the activity of the completely deactivated CaO can be recovered by pretreatment of the stone with water vapor at room temperature to such an extent that its surface is nearly covered by a monolayer of water, followed by evacuation at high temperatures.

This finding of the special functionality of residual $0^-/OH^-$ group can be significant if indeed CaO acts solely as a dehydrogenation/polymerization (coking) catalyst in the high temperature reactions of aromatics. The life-time and activity of the stone may, therefore, be influenced by the water vapor,
which inevitably exists in processes such as coal gasification or pyrolysis.

3.2.3 Pyrolysis of Coal Volatiles

Before the current interest of applying (catalytic) hydro-desulfurization to sweeten the sour oils, lime and related additives was used in several patents (Johnson, 1944; Moriarty, 1944; Schaafsma, 1944) to improve the quality of the crudes. These resulted in the significant removal of mercaptans as well as reductions in total sulfur from gasoline and visbreaker distillates, achieved through vapor-phase contacting of the oils with limestone (Johnson, 1944), marl (Moriarty, 1944), and partially slaked lime (Schaafsma, 1944), in the temperature range 370-450°C. It is interesting to note that the performance was improved as \(\text{Ca(OH)}_2\) particle size decreased and that the process was ineffective with direct use of pure quicklime (CaO) (Schaafsma, 1944).

Evidence in support of the importance of this study of reactions between lime and coal volatiles is suggested by the results of several Sc.D. (Yeboah, 1979; Franklin, 1980), M.S. (Mead, 1979; Ellig, 1981) and B.S. (Anderson, 1979) theses of this department. In Yeboah's study of coal pyrolysis in the presence of a high-calcium quicklime and several dolomitic stones, a 2-in I.D. nitrogen fluidized bed was operated near atmospheric pressure over a temperature range 700-1033K. It
was found that, in addition to the virtually total removal of
the sulfur content from the product gas, the pyrolysis tars
were cracked to a greater extent by the added solids, and that
increased amounts of the coal HHV were distributed in the gas
and char products.

Elemental analysis of the resulting tars revealed a higher
H/C ratio, higher HHV, and a significant reduction of oxygen
(and possibly nitrogen) contents, as compared to those obtained
from control experiment runs over sand. This implies that the
cracking activity of the dolomitic stones toward coal tars was
possibly selective for aromatics as was observed in the pure
compound studies.

Some preliminary studies (Anderson, 1979) suggest that
addition of lime to a packed bed of coal followed by pyrolysis
at 600°C for about 25 minutes can lower significantly the over-
all mutagenic activity of product tars (as measured by a bac-
terial cell forward mutation assay (Skopek et al., 1978b),
compared to those produced under otherwise identical conditions
but without lime.

Removal of heteroatoms, such as oxygen, from coal vola-
tiles was observed in the presence of CaO (Yeboah, 1979).
Franklin (1980) also suggests the special effect of CaO, on
the organic oxygen (mostly phenolic in nature) in the coals
and tars, which is of great practical interest. Tars produced
from coal by pyrolysis and hydropyrolysis, donor solvent or
catalytic liquefaction generally are known to exhibit such
problems as liquid instability, high viscosity, toxicity and incompatibility with petroleum feedstocks (Gould and Long, 1982). Significant concentrations of phenols in the tars (10-50\%) (Fleming and Talbot, 1982) are suspected to contribute to these problems. To minimize or eliminate phenols in coal-derived liquids efficiently and economically, is thus desirable. The vapor phase decomposition of phenols has been investigated by several workers (Cypres and Bettens, 1974; 1975; Pigman et al., 1954; Given, 1957; Griffiths and Mainhood, 1967).

The literature on the pyrolysis reactions of aromatic compounds in the absence of solid additives is pertinent to understanding competitive pathways and secondary (vapor phase) reactions in this study. This is a vast field and, therefore, will not be reviewed in detail here. Various aspects of this area have been reviewed in several documents from this laboratory (Yeboah, 1979; Mead, 1979; Franklin, 1980; Ellig, 1981). Relevant literature also includes selected studies on the pyrolysis of thiophene (Wynberg and Bantjes, 1959; Cullis and Norris, 1972), benzene (Hou and Palmer, 1965; Fields and Meyerson, 1966), pyrrole (Patterson et al., 1968; Jones and Bean, 1977), pyridine (Hurd and Simon, 1962) and phenolic compounds.

Thermal decomposition of polycyclic aromatic hydrocarbons is selectively reviewed in an excellent, annotated bibliography on the degradation of a wide variety of organic carcinogens (Slein and Sansone, 1980). Other significant information on
the thermal reactions of hydrocarbons in general is available in the books edited by Albright and Crynes (1976), and by Oblad et al. (1979). The latter present results of several recent kinetic and mechanistic studies. Studies on pyrolysis and cracking of tars are reviewed by Aristoff et al (1981) and Howard et al. (1981). The literature on the formation mechanism and yields of light aromatics (e.g., benzene, toluene, xylenes, phenolics, etc.) from vapor-phase cracking of coal-derived liquids is reviewed by Ladner et al. (1980). The important conclusion about achieving high yields of BTX, ethylene and propylene from these liquids, hydrogenated to varying degrees, has been drawn by Korosi et al. (1976) and Bernhardt et al. (1980).
4. **Experimental Apparatus and Procedures**

4.1 **Tar Generation/Pyrolysis Experiments**

The specific studies of the homogeneous and heterogeneous secondary reactions of tars from a Pittsburgh seam bituminous coal in the absence and presence of CaO were to be performed. To best approximate conditions of actual coal conversion processes, one would ideally study the formation and destruction of tars in a single bed. However, because of the complexity of the reactions involved, it would be extremely difficult to assess the relative importance of homogeneous (vapor phase) and heterogeneous reactions to coal tar cracking in such a system.

Therefore, a two-stage reactor system, whose flow sheet is given in Figure 4.1-1, was designed and constructed to attain maximum flexibility in operation, and to allow the proposed study of extraparticle (i.e., outside of coal particle) secondary reactions of coal tar.

A systematic study of the effect of major operating parameters (such as temperature, volatiles contact time, gaseous environment, feed/CaO ratio, type and source of stone, etc.) on overall tar conversion and on yields, compositions and rates of generation of the resulting products, was performed over ranges pertinent to coal pyrolysis and gasification processes.
4.1.1 Rationale for System Design

The apparatus consists of two fixed bed tubular reactors employed in series. The upstream reactor, called 'Reactor-1', has a thin bed of coal (mixed with diluent to prevent agglomeration). It is used to generate 'primary volatiles,' which are rapidly swept downstream by a superimposed flow of preheated carrier gas, and thus have minimum opportunity to undergo secondary reactions inside Reactor-1.

The downstream stage, called 'Reactor-2', is a heated tube of a fixed length and functions as an isothermal cracking reactor. It is used in two ways: (a) as an empty reactor where the contribution of homogeneous (i.e., vapor phase) pyrolysis reactions (and reactor wall effects) to the overall cracking behavior of the tars is assessed; and (b) as a fixed bed reactor, packed with CaO (or other stones), in which heterogeneous cracking of tars is studied. The CaO is obtained by calcining calcium hydroxide. It is then heated or cooled to the desired temperature prior to the cracking reaction studies.

This configuration facilitates determination of the effects of starting material, calcination history, and surrounding atmosphere on the stone cracking activity. Other advantages of this two-stage reactor system are: (a) separation of primary volatiles generation (Reactor-1) and secondary cracking reactions (Reactor-2); (b) large sample sizes (about 1 gm of coal), providing large quantities of products and hence less demanding
detectability in analytical instruments; and (c) relatively simple construction and low cost. Disadvantages include the long times required for run preparation and execution (6 - 8 hours).

Considerations for the Fixed-bed System

Care must be taken to minimize channeling, surface reactions at the reactor wall, and temperature non-uniformities within fixed-bed reactors. In the absence of agglomeration of particles of coal, char, diluent, or other stones, channeling problems should not arise since the ratio of reactor tube diameter to particle diameter is much greater than 10 in this study (Carberry, 1976). (Possible channeling problems associated with the reagent grade Ca(OH)$_2$, a very fine powder used in this program to generate active CaO, and the proposed resolution to this difficulty are discussed in Section 4.1.4.).

The tube wall is treated by the Alonizing process to minimize possible wall effects and to resist high temperature oxidation (Albright and Yu, 1979). Using a reactor tube of larger diameter will further reduce the relative contribution of reactor surface effects to the overall tar conversion reactions. In addition, this provides less opportunity for undesirable secondary reactions of volatiles with coal itself since a thinner bed is required to hold a given weight of coal.

On the other hand, some radial temperature gradients, both
in the preheat zone and in the packed-bed, inevitably arise in an externally heated fixed-bed reactor. This temperature non-uniformity must be minimized for the studies of kinetics for complex reaction system, such as coal tar cracking, where it is critical that data be obtained under isothermal conditions. Therefore, maintaining a uniform temperature profile, both axially and radially within the packed-bed, is essential for the acquisition of readily interpretable data.

Radial Temperature Uniformity of the Reactor

The temperature non-uniformity existing radially in an empty tubular reactor can be estimated by considering a reasonably simplified model. Assumptions made are given as follows:

(a) the carrier gas whose flow is laminar and fully developed at the reactor entrance is heated up to the desired (reaction) temperature by constant wall heat fluxes, Qw;

(b) natural convection of the gas due to the bouyancy effects are negligible when compared with the superimposed forced convection; and

(c) axial thermal diffusion is negligible, i.e., (Pe)z \gg 1.

The governing equation, derived from energy balance, can be shown to be

\[
\frac{\partial T}{\partial t} = v_{\text{max}} (1 - \left(\frac{r}{R}\right)^2) \frac{\partial^2 T}{\partial z^2} = \frac{\alpha}{r} \left( \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) \right)
\]

Eq. (4.1-1)
which is subjected to the boundary conditions

(1) \( T = T_0 \), at \( z = 0 \)

(2) \( \partial T / \partial r = 0 \), at \( r = 0 \)

(3) \( -k (\partial T / \partial r) = Q_w \), at \( r = R \)

where

\( T \) = carrier gas temperature
\( r \) = radial distance from the center line of the reactor
\( V_{\text{max}} \) = maximum (center-line) velocity of the carrier gas
\( R \) = radius of the tubular reactor
\( z \) = axial distance from the entrance of the reactor
\( \alpha \) = thermal diffusivity of carrier gas
\( T_0 \) = inlet temperature of carrier gas
\( k \) = thermal conductivity of carrier gas

The equation can be non-dimensionalized and solved to give

\[
\theta = 4 \rho + (\eta)^2 - (\eta)^4/4 - 7/24 \quad \text{Eq. (4.1-2)}
\]

where

\( \eta = r/R \)

\( \rho = (\alpha z / V_{\text{max}} \cdot R) \)

\( \theta = (T - T_0) / (Q_w \cdot R / k) \)
Let us consider the reactor to be radially isothermal when the relative difference between the carrier gas temperature near the reactor wall, $T_w$, and that at the center line, $T_c$, is less than $5\%$, i.e.,

$$D = \left(\frac{(T_w - T_c)}{T_w}\right) \times 100\%$$

$$= \left(\frac{0.75}{4\rho + 11/24 + \left(\frac{T_c \cdot k}{Q_w \cdot R}\right)}\right) \times 100\% < 5\% \quad \text{Eq. (4.1-3)}$$

Then the minimum length of preheating zone required to achieve 'uniformity' of the gas temperature radially is determined to be about 15 cm for a 2.5 cm O.D. reactor tube operating at atmospheric condition. This is done by considering the most severe case of preheating a carrier gas stream at a typical flow rate of 750 sccm, from room temperature (lowest possible value) to the final desired temperature, by the maximum power an existing (three-zone Marshall) furnace can supply.

The preheated carrier gas can in turn affect the radial temperature uniformity of the CaO (or coal) packed-bed. Actual experimental measurements (Longwell et al., 1983) showed that typical radial temperature differences within the packed-bed of coal in a 2.5 cm O.D. tubular reactor operated under conditions of interest were less than 2% of the absolute system temperature with a preheating zone of about 25 - 30 cm. Radial temperature non-uniformities were therefore taken as negligible in the present studies.
Axial Temperature Profile

Some test runs simulating experimental conditions were performed by increasing the temperature of an empty Reactor-2 linearly (at 3°C/min rate) to the final desired volatiles reaction temperature by the three-zone Marshall furnace. The axial temperature profile of Reactor-2 was monitored at various times during the heat-up and final soaking period. One set of the typical time-temperature profiles (desired reaction temperature = 700°C) is shown in Figure 4.1-2.

These results imply that aside from modest temperature gradients at the entrance and exit of the reactor tubes (about 10 cm from each side) due to gas preheating and heat loss through reactor ends, the axial temperature of the central zone (30 cm) of the reactor can be held relatively uniform at all times. Since coal pyrolytic reactions are considered to be relatively thermal neutral (Mahajan et al., 1976), and the concentration of coal volatiles is greatly diluted in the carrier gas, reaction heat effects are not considered to be significant in this study. The fact that there were actually no discernible temperature changes measured during all the tar cracking experiments, supports this argument.

Other Considerations

Radial mass diffusion should be minimal, since there exists
FIG. 4.1-2. AXIAL TEMPERATURE PROFILES IN REACTOR-2 AT VARIOUS TIMES AFTER BEGINNING BED HEATUP.
only small radial temperature gradient and the reactor inner wall is alonized to minimize surface contributions to volatiles cracking. Axial dispersion is usually not significant for an isothermal packed-bed whose bed depth to particle diameter ratio is greater than 50, for cases of Reynolds numbers greater than 10 (Carberry, 1976).

It is important to verify that the experiments involving coal volatiles cracking are carried out under conditions of chemical kinetic control. This is, however, extremely difficult to do for a complex gas-solid reaction system such as this, due to the lack of information on the physical and chemical properties of tar components. In general, the external mass transfer resistance can be reduced by increasing gas Reynolds number and decreasing reaction temperature (or purposely decreasing the reactivity of CaO). Intra-particle diffusion limitation, which may be a more likely problem, can be minimized by using very fine particles and lowering the temperature and/or stone activity (see also Section 5.3.2).

4.1.2 Reactor System Description

The reactor system, which is shown in Figure 4.1-1, basically consists of the carrier gas flow (control) system, the tubular reactors, the temperature controlling system, and the product collection system.
Carrier Gas Flow System

The carrier gas is supplied from standard high-pressure gas cylinders. Typically a mixture of 98 percent helium, 2 percent argon (as a tracer) is used. The gas is purified by using an in-line molecular sieve and activated carbon traps, held in a dry ice/isopropanol bath (-74°C) upstream of the entrance to Reactor-1. The mass flow rate of the carrier gas is kept constant by a Brooks mass flow controller (Model No. 5815 N2-1A), independent of pressure and temperature of the system.

This constant mass flow of gas passes downward through the two connected fixed-bed reactors. Pressures at several locations of the system are measured to monitor the pressure drop. After passing through the recovery trains, the exit-gas is conveyed into an exhaust suction hood via a pressure regulator and a rotameter. The standard flow rates range from 500 to 2500 scc/min (standard cubic centimeter per minute) for runs of different volatiles residence (contacting) times. Pressure relief valves are employed in case of system overpressure (see Figure 4.1-1). These valves also vent into an exhaust suction hood.

The Fixed-Bed Tubular Reactor

A sketch of Reactor-1 (or 2) is given in Figure 4.1-3. It consists of an outer tube of 2.5 cm O.D. x 1.9 cm I.D. 316 stain-
**Fig. 4.1-3.** SCHEMATIC OF REACTOR TUBE ASSEMBLY*

*Only the first stage of the reactor tube assembly is shown here. The second stage is designed similarly. Its dimensions, if different, are indicated in parenthesis.
less-steel tubing. The lengths of the outer tubes for Reactor-1 and -2 are 38 cm and 57 cm respectively. The two stages are connected together by Swagelok 316 stainless-steel unions which also have provisions for both internal temperature and pressure monitoring. The beds of coal or other stones are held in 1.9 cm O.D. x 1.6 cm I.D. 316 stainless-steel inner tubes and are supported on 150 mesh stainless-steel screens that are sandwiched in place as shown.

This design not only permits easy insertion and removal of the Pittsburgh seam bituminous coal which cakes strongly during pyrolysis, but also limits the bed thickness of coal (about 1 cm) to less than 3.8 cm, therefore minimizing the extent of undesirable tar secondary reactions with coal (or char) in Reactor-1. The inner wall of the inner tubing is alonized to minimize contributions to cracking and to inhibit corrosion of the reactor wall (Albright and Yu, 1979).

A quartz reactor setup, with the same I.D. dimension, is used in the later stage of this work, in place of its stainless-steel counter parts. The quartz reactor follows the similar design idea, and also allows easy insertion and removal of coal and CaO employed in the cracking experiments. It was found that results of tar conversions for selected duplicate runs were similar for either stainless steel reactor or quartz reactor. This suggested that the alonizing process was effective in deactivating the stainless-steel reactor wall.
Temperature Controlling System

Each stage of the reactor system is independently heated by a separate electrical furnace. Reactor-1 is heated by a 2.5 cm x 30 cm Lindberg single-zone furnace (Model No. 55035) and controlled by a two-zone Wizard temperature-programmable controller (Tetrahedron Assoc., Model No. 1601-22-110). The furnace used to heat Reactor-2 is a 3.8 cm x 51 cm Marshall three-zone furnace (Model No. 1116). It is controlled by:
(a) the Wizard controller when Reactor-2 is used to generate a bed of active CaO (or other solids) by calcining Ca(OH)$_2$ or other solid starting material at a constant heating rate, or
(b) two Omega set-point controllers (Model No. 4001 KC) to keep Reactor-2 isothermal. Control for each furnace is switched from one type of controller to the other by activating a set of relays. The Marshall furnace is equipped with shunt taps every two inches for adjusting and maintaining a uniform axial temperature profile in Reactor-2, which is of great importance in these experiments.

Product Collection System

After passing through the packed-bed reactor(s), the volatiles in the exit-gas are fractionated and trapped in the downstream product collection system. Typically at the exit of the reactor assembly are two tar traps in parallel, one in operation, and the other in a standby mode. This allows collection of tars
produced over known temperature intervals, by switching from one trap system to the other via turning a three-way valve. The valve is maintained at 220 - 240°C temperatures to minimize tar condensation prior to the trap.

Each trap consists of a 1.3 cm O.D. x 7.6 cm L. Stainless steel tube packed with about 2.5 gm of teflon 'wool' (Alltech No. 4082) which is conditioned at 150°C for 30 minutes before each run using a nitrogen gas purged at a flow rate of 750 scc/min, to remove the adsorbed atmospheric moisture. Although some heat is conveyed to the trap from the reactor system during the experiment, the tar traps are maintained essentially at room temperature. Most of the coal tar is collected in the first half of the trap. Test runs confirmed that backup traps are not necessary.

Following the tar traps, there is a gas sampling port for H₂ detection and, in series, a Valco 16-loop gas sampling valve (Model No, AH-4-ST-16-HPa), through which the reactor off-gas is continuously purged. During a typical run, the valve is pneumatically switched to take a sample at predetermined values of the temperature in the first (tar generation) bed. The valve temperature is maintained at about 120°C to prevent moisture condensation and adsorption of less volatile products onto the stainless steel sampling loops.

Downstream of the gas sampling valve, a trap for collecting water is installed which is composed of a 1.0 cm I.D. x 8.9 cm L. stainless-steel tube packed with Drierite (anhydrous CaSO₄, 8 mesh in size) particles. The trap is used because water exists in the
pyrolysis gases in such a low concentration that it can not be determined quantitatively with the thermal conductivity detector (TCD) of the available packed column GC for this study.

The H₂O trap is followed by a light oil trap which is composed of a 1.4 cm I.D. x 15 cm L. U-shaped, pyrex glass tube filled with DMCS (dimethyl-dichloro silane) treated glass wool (Alltech No. 4037). This trap is operated at liquid N₂ temperature and collects all the condensibles from the exit gas. The light oils (hydrocarbons ranging from C₆ to about C₁₂) are extracted by CH₂Cl₂ and then are analyzed by a capillary column gas chromatograph.

Steam Generation System

In many coal gasification/pyrolysis processes, steam, either derived from original coal moisture or added as gasifying reagent, exists among the coal volatiles at a significant concentration. To study the effect of steam on calcium oxide activity, and to assess the expected reduction in the extent of coking on the CaO and simultaneous catalyzed gasification of the finely dispersed coke from the CaO surface in the presence of steam, would therefore be of great practical interest.

Steam used in this study is produced by vaporizing liquid water introduced by a metering pump (model 314 Instrument Specialties (ISCO) high pressure precision syringe pump). The pump can meter 0.80 to 200 cm³/hr (+ 2% accuracy) of water from a
375 cm³ reservoir. Before it is used, pre-purified water is purged with nitrogen (at a approximately 250 cm³/min rate) for 30 minutes to reduce the level of dissolved oxygen.

The vaporizer is a 0.6 cm O.D. x 20 cm L vertical tubing made of 304 stainless steel, which is packed with stainless steel wool to promote heat transfer and provide extra nucleation sites for smoother boiling of the water. The tubing is heated externally by nichrome resistance wire wound around a thin, electrically insulating ceramic coating. A 1.3 cm thick coating of alumina cement is applied to secure the heating wire element in place and finally a 2.5 cm kaowool blanket provides further thermal insulation. The vaporizer outlet temperature is maintained at 200°C by adjusting the power output of a variac.

To dampen the pressure pulsations and steam flow fluctuations due to the inherently erratic water boiling, a surge pot is connected downstream of the vaporizer. It is constructed of type 304 stainless steel pipe (3.8 cm O.D. x 51 cm L. approximately 700 cm³ by volume) with welded end caps. Insulation is provided by a 2.5 cm layer of kaowool blanket and the temperature of the surge pot is kept at 200°C by electrically heating with a heating tape.

To further minimize upsets in steam flow, the surge pot is operated at 15 to 20 psig pressure controlled by adjusting a needle valve downstream of the pot exit. The pressure is monitored by a silicone-filled pressure gauge which is electrically heated and insulated to prevent steam condensation.
The superheated steam is then either introduced into the reactor system through the top of Reactor-2, or directed to the by-pass line. Two high temperature ball valves are used to control the direction of steam flow. All steam lines are wrapped with a 2.5 cm layer of kaowool insulation and electrically heated to approximately 200 - 225°C using heating tapes.

The steam generation system was calibrated to insure steady steam flow and minimal condensation losses in the lines, by separate experiments in which an ice bath was used to condense steam from a carrier gas exiting an unpacked reactor system operated at the reaction temperatures. The water balance was closed to within 5 percent.

Due to the relatively large thermal mass of the system, the time required for the vaporizer and surge pot temperatures and hence the steam flow to stabilize is about 1.5 - 2.0 hrs. Steam is therefore set on by-pass for more than two hours before it is introduced into the reactor system.

4.1.3 Operation Mode and Procedure

Modes of Operation

To reliably assess the separate contributions of homogeneous and heterogeneous secondary reactions to the cracking behavior of coal tar after thermal treatment, the following four modes of operation were employed:
1) Mode-1: to generate and characterize fresh tars used as feed to Reactor-2 (base run for mode-3 and mode-4),

2) Mode-2: to generate and characterize active CaO or other stones for tar cracking (reference run for mode-4),

3) Mode-3: to study homogeneous secondary reactions of fresh tars,

4) Mode-4: to study heterogeneous (as well as concurrently occurred homogeneous) secondary reactions of tars over CaO or other stones of interest.

A diagram summarizing the reactor configurations of the four modes is given in Figure 4.1-4.

A mode-1 experiment provided the information needed to characterize the 'feed stock', i.e., the primary pyrolysis products whose secondary reactions were to be studied. Primary volatiles, including tars, were generated under conditions such that they were essentially unaltered by secondary reactions, i.e., they were immediately quenched upon exiting Reactor-1. (Reactor-2 was not employed in these runs.) Samples of these 'primary' products were collected at definite intervals throughout a temperature-time history for Reactor-1, identical to that used in mode-3 and mode-4 experiments, and were characterized by various means (described in Section 4.3.1).

Mode-2 operation was designed to generate a packed bed of active CaO which would be used as contacting material in
Mode-1. Prepare Fresh Tar for Characterization of Feed

\[
\begin{align*}
T_0 & \rightarrow T_1 \\
\text{He} (\text{Ar}) & \rightarrow \text{Coal} \quad \text{VOLATILES} \quad \text{"REACTANT"}
\end{align*}
\]

Mode-2. Generate Active \( \text{CaO} \) Packed-Bed for Characterization

\[
\begin{align*}
T_0 & \rightarrow T_2 \rightarrow T_3 \\
\text{He} (\text{Ar}) & \rightarrow \text{Ca(OH)}_2 \rightarrow \text{CaO} \rightarrow \text{H}_2\text{O}
\end{align*}
\]

Mode-3. Study Homogeneous Secondary Reactions of Fresh Tar

\[
\begin{align*}
T_0 & \rightarrow T_1 \\
\text{He} (\text{Ar}) & \rightarrow \text{Coal} \quad \text{VOLATILE} \quad \text{"PRODUCT HC"}
\end{align*}
\]

Mode-4. Study Heterogeneous (+ Homogeneous) Secondary Reaction

\[
\begin{align*}
T_0 & \rightarrow T_1 \rightarrow T_3 \\
\text{He} (\text{Ar}) & \rightarrow \text{Coal} \rightarrow \text{CaO} \rightarrow \text{VOLATILE} \quad \text{"PRODUCT HO+HE"}
\end{align*}
\]

In general, \( T_0 < T_1 < T_2 < T_3 \)

Fig. 4.1-4. Modes of Experiment
the study of the heterogeneous secondary cracking reactions. Typically 0.66 gm of calcium hydroxide which mixed with 11 gm of quartz, was calcined in each run to produce CaO in-situ. This type of stone preparation was performed twice under identical conditions, once to prepare a CaO sample for characterization, and once to prepare a sample for use in (mode-4) heterogeneous cracking experiments.

Methods used for characterizing the chemical and physical properties of the calcined stones, such as surface area, pore size distribution, surface basicity (or acidity), etc., are given in Section 4.2.

The purpose of mode-3 experiments was to determine the effect of homogeneous secondary reactions on tars. In these experiments, the mode-1 runs were repeated but an unpacked cracking reactor (Reactor-2) was added immediately downstream. Reactor-2 was heated up to and maintained at a desired reaction temperature between 400 and 800°C. The temperature of Reactor-1 was then increased linearly to generate the 'feed' of fresh primary volatiles which were rapidly swept into reactor-2 where they underwent homogeneous cracking reactions. Product tars, light oils, gases, and char were analyzed as described in later sections.

The purpose of mode-4 operation was to investigate heterogeneous secondary reactions of tars. First, a bed of active CaO was generated in-situ in the second bed, using the procedure for a mode-2 run. Then, as in mode-3 the temperature of Reactor-1
was increased linearly causing a bed of coal to undergo pyrolysis and generate fresh volatiles. Unconverted feed and products from reactions with the packed bed of CaO, were collected downstream of Reactor-2 and analyzed.

Coked and (partially) deactivated CaO was also recovered, characterized, and compared with the unreacted stone generated in the corresponding mode-2 run to determine the extent of physical and chemical changes of the cracking stones. Correction for effects of homogeneous cracking (determinable from the mode-3 runs) allowed the heterogeneous cracking to be assessed quantitatively.

**Operating Conditions and Procedures**

The typical experimental conditions, summarized in Table 4.1-1, were determined by tradeoffs between limitations inherent in laboratory scale apparatus, and a desire to study reaction conditions pertinent to commercial practice. Since Reactor-1 was intended to be a 'fresh tar generator', it was designed to minimize the occurrence of secondary reactions of coal volatiles. The typical charge to this reactor of 1 gm coal/12 gm SiC formed a bed of about 3.8 cm depth.

After the entire reactor system was assembled and leak-checked, Reactor-1 was heated from room temperature, at a constant (5°C/min) heating rate, up to 700°C where the evolution of tar was almost completed. The volatiles generated
### Table 4.1-1 Typical Experimental Conditions

<table>
<thead>
<tr>
<th></th>
<th><strong>REACTOR-1</strong></th>
<th><strong>REACTOR-2</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Purpose</strong></td>
<td>Tar Generation</td>
<td>Tar Cracking</td>
</tr>
<tr>
<td><strong>Sample</strong></td>
<td>1 gm coal/12 gm SiC</td>
<td>None (in mode-3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 gm CaO (in mode-2 and mode-4)</td>
</tr>
<tr>
<td><strong>Particle Size</strong></td>
<td>300-350 micron</td>
<td>300-350 micron</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>25-700°C</td>
<td>First 500°C, then final cracking temp. (in mode-2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>400-800°C (in mode-3 &amp; -4)</td>
</tr>
<tr>
<td><strong>Heating Rate</strong></td>
<td>3°C/min</td>
<td>3°C/min (in mode-2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0 (in mode-3 and -4)</td>
</tr>
<tr>
<td><strong>Holding Time</strong></td>
<td>0</td>
<td>90 min (in mode-2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 200 min (in mode-3 &amp; -4)</td>
</tr>
<tr>
<td><strong>Carrier Gas</strong></td>
<td>He (2% Ar)</td>
<td>He (2% Ar)</td>
</tr>
<tr>
<td><strong>Pressure</strong></td>
<td>1.2-1.3 atm</td>
<td>1.2-1.3 atm</td>
</tr>
<tr>
<td><strong>Volatiles</strong></td>
<td>0.04-0.12 sec</td>
<td>2.0-6.0 sec (Homo.)</td>
</tr>
<tr>
<td><strong>Residence Time</strong></td>
<td></td>
<td>0.06-0.25 sec (Hetero.)</td>
</tr>
</tbody>
</table>
were rapidly swept downstream by a superimposed, constant mass flow of preheated carrier gas. The volatiles residence time (calculated by the equation given in Appendix A) in the first bed, normally very short (about 0.04 - 0.12 sec), could be varied by adjusting the flow rate, ranging from 500 - 1500 scc/min, of the helium (with 2 percent Ar as tracer) carrier gas.

As discussed previously, in typical runs the fresh volatiles, which remained in the vapor phase, were introduced directly into a downstream reactor (Reactor-2) as reactants, and underwent secondary reactions either homogeneously in the vapor phase (mode-3 experiments where Reactor-2 was unpacked), or heterogeneously (as well as homogeneously) in the presence of a 0.5 g calcium oxide packed bed (mode-4 experiments) at a constant volatiles cracking temperature between 400 and 800°C.

The pressure of the system was typically kept at about 1.2 - 1.3 atm by a downstream pressure regulator. The flow rate of helium carrier gas was adjusted to maintain the volatiles residence time in the homogeneous phase to be about 2.0 sec, and the contact time with the active solid to be about 0.12 sec. The conditions in Reactor-2 were such that cracking of light hydrocarbon gases and light oils were relatively unimportant. The major reactions studied were therefore the secondary cracking of coal tars.

Tars (room temperature condensable volatiles) were generally collected as seven fractions over seven predetermined
intervals of temperature in Reactor-1, in the tar traps maintained at ambient conditions. The tars were then recovered for various means of characterization (see Section 4.3.1). The tars trapped on the teflon wool of each cartridge were extracted with methylene chloride/methanol—67/33 (v/v) and stored in narrow-mouth amber bottles. Care was taken to minimize exposure of the tars to light, air, and heat before and during subsequent analyses.

Gas samples were taken both by a syringe (for \( \text{H}_2 \) detection) and by the 16-loop sampling valve (for analyzing hydrocarbon gases, \( \text{CO}_2 \) and \( \text{CO} \)), at fifteen predetermined temperatures in the volatiles generation bed. Conversely, the water and in selective runs, light oil were each collected continuously in separate traps.

Yields of coal tar and water were measured gravimetrically. The yields and compositions of product gases and light oils were determined by GC analysis. Yields of primary char remaining in Reactor-1 and secondary coke formed on the surface of the \( \text{CaO} \) (and diluent — quartz) were also determined gravimetrically by difference. Yields of secondary coke formed on the reactor wall were measured in selected runs by oxygen burnoff followed by catalytic conversion of \( \text{CO} \) to \( \text{CO}_2 \), and then quantitative determination of \( \text{CO}_2 \) in the product gases by precipitation as \( \text{BaCO}_3 \) powder.
4.1.4 Sample Preparation

Coal Sample

Pittsburgh Seam (No. 8) Bituminous coal with a particle size range from 300 to 350 micron was used in this program. The coal, which came from the Ireland Mine of the Consolidation Coal company, is representative of a strongly caking eastern U.S. bituminous coal. Many M.I.T. researchers (Anthony, 1974; Suuberg, 1977; Franklin, 1981; Serio, 1984) used coal samples from this same mine. The characteristics of these coal samples are shown in Table 4.1.2. The coal particles used in this study were prepared by grinding coal lumps larger than 5 mm in size for 15 minutes in a stainless steel rod mill under a nitrogen environment to minimize oxidation. The ground coal was then mechanically dry-sieved for 1 hour per batch of about 50 gm. The collected fraction of 300-350 micron particles was further subjected to wet sieving to remove electrostatically adhered fine powder and other impurities. The resulting 'clean' coal particles were dried in a desiccator and stored under nitrogen atmosphere.

The typical amount of coal charged to Reactor-1 was about 1 gm per run. Reactor plugging was experienced when only coal was used as the packed bed. This was due to coal particle softening and agglomeration at temperatures around 390-420°C (heating rates were 0.05°C/sec). Stable operation was attained
Table 4.1-2 Characteristics of Coal Sample Studied\(^{(a)}\)

Coal Type: Pittsburgh Seam No. 8 Bituminous Coal

<table>
<thead>
<tr>
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<tbody>
<tr>
<td><strong>Ultimate Analysis</strong> (Wt%, dry)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>68.8</td>
<td>73.59</td>
<td>71.5</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.2(^{(b)})</td>
<td>5.16</td>
<td>5.1</td>
</tr>
<tr>
<td>Oxygen</td>
<td>8.2(^{(b)})</td>
<td>7.07</td>
<td>8.2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.3</td>
<td>1.29</td>
<td>1.2</td>
</tr>
<tr>
<td>Sulfur</td>
<td>5.4</td>
<td>5.32</td>
<td>4.4</td>
</tr>
<tr>
<td>Ash</td>
<td>11.5</td>
<td>10.26</td>
<td>9.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Proximate Analysis</strong> (Wt%, dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile Matter</td>
</tr>
<tr>
<td>Fixed Carbon</td>
</tr>
<tr>
<td>Ash</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Moisture</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4(^{(d)})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Heating Value</strong> (Btu/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N.A.(^{(e)})</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Analyzed by Huffman Laboratories, Inc., Wheat Ridge, CO.

\(^{(b)}\) Determined by difference.

\(^{(c)}\) Based on partially dried basis.

\(^{(d)}\) As-received basis.

\(^{(e)}\) Data not available.
however, when diluent such as silicon carbide or washed sand in the 300-350 micron size range was mixed with the 1 gm charge of coal in a ratio of about 4:1 by volume. (This corresponds to 8:1 sand/coal and 12:1 SiC/coal weight ratios, respectively.) Preliminary testing showed that SiC, being less active for tar cracking was a better choice as a diluent. Therefore, a charge of 1 gm coal/12 gm SiC was typically used in Reactor-1 in this study.

Stone Preparation

The origin of the starting material and preparation methods can significantly influence the reactivity of CaO (see Sections 3.1 and 3.2.1). Previous work (Ellig, 1981) has shown that use of CaO prepared by (further) calcination of quicklime (essentially pure CaO) gave scattered results in pure compound cracking studies. Acceptable repeatability was achieved by using CaO prepared by calcination of reagent grade Ca(OH)$_2$.

Use of calcium hydroxide, which is a fine powder, demanded some special handling procedures. Initially it was mixed with sieved quartz particles to prevent crystal agglomeration, ensure uniform gas flow and to reduce pressure drop (Ellig, 1981). However, at the higher carrier gas superficial velocities (> 5 cm/sec) used in this study, sedimentation of the Ca(OH)$_2$ powder from the packed-bed mixture occurred. This caused a non-uniform axial concentration profile of Ca(OH)$_2$ in the bed and a sharp
increase in the bed pressure drop at flows of operating interest. A new technique for better dispersion of the Ca(OH)$_2$ powder among the inert solid diluent was therefore developed.

Quartz chips, obtained from Thermal American Fused Quartz Co., (Montville, NJ), were ground in a rod mill and sieved to obtain a particle size fraction of 300-350 micron. This fraction was then thoroughly mixed with a carefully prepared Ca(OH)$_2$ slurry (e.g., 5.5 ml of distilled water for each gram of Ca(OH)$_2$) and dried. It was found that, to minimize formation of the undesirable impurity CaCO$_3$ (from interaction with atmospheric CO$_2$), the slurry should be dried under vacuum. More than 99.5 percent of the added water was removed through this process. The resulting Ca(OH)$_2$-coated-quartz (C.C.Q.) was stored in a moisture-and-CO$_2$-free desiccator for later use. The samples used in this study normally contained about 6 Wt. percent of Ca(OH)$_2$. Some C.C.Q. samples containing 12.6 Wt. percent or 16.8 Wt. percent Ca(OH)$_2$ were also prepared for the uniformity tests of CaO coating on the quartz particles.

**Preparation of Ca(OH)$_2$ Crystals**

As is discussed in a later section (5.3.2), tar cracking experiments were performed in this study over different sizes of CaO particle, to determine the relative importance of pore diffusion limitations in the heterogeneous tar cracking reactions.

The commercially available calcium hydroxide, the starting
material for preparing the C.C.Q. used in this study, is prepared by precipitation and obtained only in powder form (approximately 1-5 microns in size). A special procedure was therefore utilized to grow calcium hydroxide crystals of 10-300 microns in size (Dave and Chopra, 1966). A modified set-up was used which consisted of a 100 ml pyrex flat-topped beaker placed in a 600 ml beaker.

Fifty ml of potassium hydroxide (reagent grade) saturated solution was prepared in CO₂-free distilled water and delivered to the inner beaker. Forty ml of a similarly prepared solution of the saturated calcium chloride was added to the larger outside beaker. The CO₂-free distilled water was added very carefully along the inside walls into both beakers, respectively, with little mixing occurring, to a depth just 2-3 mm above the rim of the inner beaker. Finally, the 600-ml beaker was covered with an inverted watch glass dish and immersed in a 50°C water bath.

In this arrangement, the ions of the reagents were allowed to slowly diffuse through the aqueous media toward each other. The nucleation rates of Ca(OH)₂ which were controlled by the rates of diffusion, were significantly slower and thus larger crystals could be formed. The first calcium hydroxide crystals appeared on the outside of the smaller beaker within about 24 hours and then on the inner wall of the 600-ml beaker. The crystals were collected after 36-48 hours and washed with distilled water and then with acetone, and finally dried and stored
in a CO$_2$ and H$_2$O-free desiccator.

A sufficient amount of crystal samples were prepared by this procedure to allow studies on the effects of CaO dimension on coal volatiles cracking reactions. The crystals were sieved to yield particles of narrow size distribution (i.e., 38-45 microns, 90-106 microns and 180-250 microns, respectively). The results of the cracking experiments are discussed in Section 5.3.2.
4.2 Characterization of Calcium Oxide

4.2.1 Physical Properties

The preparation of Ca(OH)$_2$-coated-Quartz (C.C.Q.) is discussed in Section 4.1.4. An important question to be addressed was whether the coating (or mixing) of the Ca(OH)$_2$ in C.C.Q. thus prepared was uniform. The thermogravimetric analysis (TGA) system in our laboratory was used for this purpose.

The system includes a Dupont 951 Thermogravimetric Analyzer and a Dupont 990 Thermal Analyzer Controller and Recorder. The TGA was typically designed to study gas-solid reactions, solid decomposition reactions, etc., by continuously monitoring changes in the weight of a solid sample as a function of time, temperature, and environment. The high sensitivity of the TGA for weight determination was capitalized on in this study. The uniformity of C.C.Q. coating was tested by measuring the weight losses due to calcination of samples containing as little as 0.3 to 1.8 mg of Ca(OH)$_2$. The results of this test are given in Section 5.1.1.

B.E.T. Measurement

Surface area and pore size distribution which are important physical properties for CaO characterization, were deter-
mined by nitrogen adsorption and B.E.T. analysis. The surface area measurement was done on a dynamic adsorption/desorption apparatus called Quantasorb Quantachrome located in our laboratory at M.I.T.

The procedure includes first introducing a calcined C.C.Q. sample (see Section 5.1.2 for details) into a U-shaped quartz sample holder, weighing the sample, and degassing the adsorbed gases. The latter was achieved by heating the sample at about 150 - 180° C under vacuum for one hour. The quartz tube was then connected to the apparatus, and a steady flow of 30% nitrogen in helium was passed over the sample. The nitrogen adsorption and desorption was performed by alternately immersing the sample holder in liquid N₂ or hot glycerol (about 140° C) bath.

It was experimentally determined that equilibrium N₂ adsorption could be achieved within 30 min. The total volume of adsorbed nitrogen was then estimated by integrating the desorption signal (which was sharper and gave a more reliable measurement). The response of the hot wire detector was calibrated by injection of known quantities of pure N₂ into the apparatus.

This volume was related to the total surface area of the sample by using the (single point) B.E.T. analysis (Brunauer et al., 1938) which calculated the number of N₂ molecules which would have covered the surface in a monolayer. This value was then converted to the total surface area by using an approximate value of the area equivalent to the coverage of one N₂ molecule.
A more detailed description of the B.E.T. calculation can be found in the thesis of Snow (1985).

The pore size distribution of one selected CaO sample prepared from a mode-2 experiment was determined by Porous Materials, Inc. (Ithaca, NY). The measurement of $N_2$ adsorption/desorption was done over a relative pressure range of about 0.1 to 0.96. The data analysis was done by considering the shape of the pores in CaO (from calcining Ca(OH)$_2$) to be slit-like (Beruto et al., 1980). The result is given in Section 5.1.3.

4.2.2 Electrical Resistance Measurement

The surface of CaO is well known to be basic (electron donating) in nature when titrated at room temperatures (Take et al., 1971; Lai, 1986). However, as discussed in Section 5.9.2, we postulate that the surface actually becomes acidic (electron accepting) at high temperatures, perhaps above 400°C.

To test this hypothesis, one must identify a method which can 'titrate' the CaO surface in-situ at high temperatures. Obviously, the conventional, wet chemistry titration techniques could not achieve this. The method we proposed was to measure the effects of chemisorption (at temperatures above 400°C) of various gases or vapors (such as $H_2$, $O_2$, $C_2H_4$, toluene, heptane, etc.) on CaO surfaces, on the electrical resistance of the calcine.
A block of polycrystalline calcium oxide was prepared \textit{in-situ} from an Iceland spar (CaCO$_3$) single crystal (about 2.5 cm x 2 cm x 1.2 cm in dimension), instead of from the powdered Ca(OH)$_2$ (or occasionally CaCO$_3$) typically used for pyrolysis studies. It was gently sandwiched between two stainless-steel metal leads so that reasonably good electrical contacts between the fragile oxide and the leads could be achieved. The calcination of Iceland spar was carried out at 800$^\circ$C for 30 min. under a constant (750 sccm) purge of helium gas.

The resulting CaO, presumably containing an excess but small amount of O$^-$ ions (see Section 5.9.2), was then cooled to a lower temperature (between 400 - 500$^\circ$C) for chemisorption studies. Under these conditions, only the effect due to adsorption and not cracking of the various reagents on CaO was investigated. The resistance of the stone was monitored by a high impedance digital electrometer (Keithley, Model #616). The constant helium purge was maintained throughout all the measurements.

The existence and extent of chemisorption of a reagent over CaO was indicated by a reasonably fast change (typically a reduction) in the measured electrical resistance of the stone. The effect of hydrogen partial pressure on the electrical resistance of the CaO sample was investigated at 402$^\circ$C. Chemisorption reactions of oxygen and various hydrocarbon gases over CaO (at 501$^\circ$C) were also studied individually. The partial
pressures of these reagents were typically maintained at about 2 torr in the mainstream helium carrier gas (at a total pressure of about 1 atm). The results and discussion of these chemisorption studies are given in Section 5.9.
4.3 Characterization of Pyrolysis Products

4.3.1 Coal Tar Characterization

To assist in the characterization of properties of coal tar, both primary (mode-1) and secondary (mode-3 and -4) tars were analyzed by a variety of techniques. These included gel permeation chromatography (GPC), which determines the molecular weight distribution, non-Aqueous thermometric titration (Vaughan and Swithenbank, 1965; 1970), which measures the concentration of phenolic (or acidic) functional groups, $^1$H-NMR which gives average structural parameters, and elemental (C,H,O,N,S) analysis. Selected tar samples were also subjected to bacterial cell forward mutation bio-assay (Skopek et al., 1978a; b), which shed light on the mutagenic potency of tars.

NMR Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique useful in tar analysis. On a molecular level the tars are complex organic mixtures containing several hundred distinct compounds spanning a molecular weight range from $< 200$ to as much as 2000 or 3000. NMR is useful since it probes the average contributions of important structural features in these mixtures. For example, proton-NMR measurements which were used in this work gave information on the average fractions of aromatic and aliphatic hydrogen in the tars.
The solvent used for preparing proton-NMR samples was deuterated chloroform (CDCl₃ with 99.8 atom percent D, Aldrich Chemical Company, Inc., 'Gold Label') which contained 2500 ppm of tetramethysilane (Merck Sharp & Dohme Canada Ltd.) as an internal NMR reference standard. Typically, enough CDCl₃ was added to dissolve the dried pyrolysis coal tars to make a 5-10 mg/ml solution. This solution then filtered (to remove a small amount of undissolved tars) through a Kimwipe-packed disposable pipette into a 5 mm dia. NMR tube.

To enhance the solubility of coal tars, a solvent mixture prepared by adding a small amount (<10 percent in volume) of deuterated pyridine-d₅ (99.5 atom percent D, Merck Sharp & Dohme Canada Ltd.) or methanol (methyl-d₃ alcohol-d, CD₃OD, 99.5 atom percent D, Aldrich Chemical Company, Inc., 'Gold Label') was tested. The improvement of coal tar solution concentration which increased the S/N (signal to noise) ratio accordingly, was more than counterbalanced by the appearance within the spectral range of interest, of impurity peaks which interfere with the desired NMR spectra. Deuterated chloroform was therefore used as the only solvent for sample preparation.

The NMR spectra of tar samples were obtained on a JOEL FX90Q Fourier Transform NMR Spectrometer. The sample tube was kept spinning at 25 Hz to minimize the possible inhomogeneity in the tar solution. The observation frequency was 89.54 MHz and the offset frequency 44.35 KHz (for CDCl₃). About 256 accumulations were required for spectra acquisition with the
observation amplitude set at 26-27 dB for the solution concentrations used. To achieve sensitivity enhancement and better S/N ratio, with some loss of resolution, the exponential window decay constant was chosen to be 1.0. Acquisition and workup (i.e., phasing the peaks, performing integrations, plotting, etc.) of one complete proton-NMR spectrum generally took approximately 1-1.5 hours. Analysis and discussion of the NMR spectra are given in Section 5.8.1.

Gel Permeation Chromatography

A Waters Associates' ALC/GPC 201 chromatography system was used in this study for determination of molecular weight distribution (MWD) of coal tars. This system was equipped with a high performance M-45 solvent delivery pump for precise control of solvent flow rates, two Waters microstyrigel 30 cm columns connected in series, and an ultraviolet (UV) and a refractive index (RI) detector.

The columns were packed with 500 Å microstyrigel and 100 Å microstyrigel (up-stream and downstream, respectively). These were selected to cover the molecular weight range of approximately 200-3000 gm/mol expected for the coal tars, and to minimize polar interactions with the tars. Only the UV detector was employed in this study for measurement of the weight concentration of the tar sample being eluted at a given retention time (or equivalently, elution volume). It has been
shown (Suuberg and Unger, 1981) that the response of the UV detector is essentially linear in sample concentration. Calibration runs in this study again confirmed that this was true for the coal tars in the molecular weight range of interest.

Pyridine (reagent grade) was chosen as the mobile phase (solvent) in the GPC system. It has been found that the GPC separation is improved by using pyridine as the eluent (Ouchi et al., 1980). It is the best solvent for coal derivatives and even dissolves constituents of very polar functionalities and higher molecular weights (Schanne and Haenel, 1981). Pyridine has a UV absorbance cutoff at 330 nm, therefore requiring monitoring the UV absorbance of coal tar molecules at longer wavelengths (e.g., 405 nm in this study). The pyridine employed in the system was degassed for 10 min. and filtered through a 0.2 micrometer Nylon-66 membrane filter before use.

Part of the samples was prepared by re-dissolving the dried tar (which was also used for other analyses such as NMR and elemental analysis) in pyridine. However, in the later part of this research, conversion behavior of different tar fractions with narrow MWD was studied for the kinetic modeling of tar cracking over CaO (see Section 5.10.1). Inevitable changes in the MWD of tars due to drying were therefore not desirable. Instead the tar collected in the traps was extracted by pyridine as soon as possible, brought up to a known volume, and stored under N₂. A small, known volume of the resulting solu-
tion of tar in pyridine was removed and dried at approximately 60°C under a nitrogen purge to determine the weight of tars and thus the weight concentration of tar sample in the stored solution.

The solution was then filtered through a 0.45 micron disposable filter to remove any fine particles that might otherwise block the porous packing material and in-line filters used in the GPC system. This was done in a glove box to minimize moisture absorption by pyridine. Finally, an appropriate amount of tar sample was loaded into the GPC system injector through a 100 (or 250) microliter syringe. The signal output from the UV detector was monitored and stored by a Bascom-Turner data recorder (Model No. 4120) for later data manipulation. A detailed description of the use of vapor pressure osmometry for calibrating the GPC performance was given in the thesis of Oh (1985), and will not be discussed here.

**Preparative-Scale GPC**

Determination of the extent to which functional groups (such as phenolics) and hetero-atoms are uniformly distributed throughout the entire molecular weight range of the tar mixture, was of interest in assessing the validity of using MW range alone as a measure of the reactivity of tar lumps. These measurements required preparation of about 0.1 g samples of tar in more narrow molecular weight ranges (see also Section 5.10.1). A preparative scale GPC (prep-GPC) was set up for this purpose.

The column was made of heat-exchanger type, concentric
double jacket glassware (400 ml volume, 80 cm length) which was filled with Sephadex LH 60-pyridine gel (Pharmacia Fine Chemicals, Code #17-0890-01). Ideally, fractionation in a GPC column is induced by differences in the molecular size of the mixture constituents. In practice, column performance can also be influenced by adsorption of polar components on the gel, in particular when less polar solvents, such as the commonly used benzene, toluene, chloroform, and tetrahydrofuran are employed (Ignasiak et al., 1978).

The situation could also be improved by using pyridine as the eluent. The prep-GPC column was heated to 60°C by circulating hot water. This reduced tar adsorption on the gel and increased tar dissolution in the pyridine. It also decreased the pyridine viscosity, thus increased the elution rate.

About 1 g of total tar sample was prepared by pyrolyzing Pittsburgh No. 8 Seam Bituminous coal under a constant helium purge. The tar sample was dissolved in 3 ml of pyridine under a nitrogen environment and was filtered through kim-wipes packed filter. The solution was then introduced to the top of the prep-GPC column which was then eluted with pyridine for 3.5-4 hrs at 60°C under a nitrogen blanket. The eluting rate of pyridine was 2.2-2.3 ml/min.

Samples of narrower MWD were collected in six 11 ml fractions between the cumulative elution times of 1 2/3 to 2 1/6 hrs. After 500 ml pyridine had passed through the column,
the Sephadex LH 60-pyridine-gel was almost colorless and translucent again, and could be re-used for repeated separations.

Non-Aqueous Thermometric Titration

A relatively simple but accurate technique, the non-aqueous thermometric titration (Vaughan and Swithenbank, 1965; 1970), for determining the concentration of phenolic (or acidic) hydroxyl groups in coal tars was employed in the study. The titration equipment is sketched in Figure 4.3-1. The titration vessel consisted of a 2.9 cm I.D. x 7.6 cm L. round bottom glass test tube of 40 ml total volume. The vessel was sealed by a rubber cap through which were introduced

(A) an acetone inlet from a pipettor;
(B) an inlet for purge gas which was CO₂- and H₂O-free nitrogen;
(C) a thermistor, Omega type ON-410-pp;
(D) a capillary tube for introducing titrant; and
(E) an outlet for the nitrogen purge gas.

The test tube was surrounded by glass fiber contained in a large beaker to act as a thermal insulator.

Acetone was used as a solvent as well as an end point 'indicator' for the thermometric titration. It was found that at the end point of titrating acidic compounds, dissolved in
A: inlet for acetone (dry) from the pipettor
B: inlet for the purge gas (dry and CO₂-free nitrogen)
C: thermistor (Omega type ON-410-PP)
D: inlet for introducing titrant
E: outlet for purge gas
F: magnetic stirrer
G: Galvanometer (Kintel, model 204A)

Fig. 4.3-1. Schematic of Enthalpimetric Titration System
the acetone, with an alcoholic alkali, a large amount of heat evolves which causes a sharp rise in the solution temperature (Vaughan and Switchenbank, 1965). This was due to the formation of diacetone alcohol from dimerization of acetone in the presence of small excess amount of alkali:

$$2 \text{CH}_3\text{CO-CH}_3 \xrightarrow{\text{OH}^-} \text{CH}_3\text{CO-CH}_2\text{-C(OH)(CH}_3\text{)}_2 \quad \text{Eq.} \,(4.3-1)$$

Trace amounts of water in the acetone have been shown to greatly suppress the dimerization rate and thus have detrimental effect on the determination of titration end point. The water concentration should be much less than 0.2 volume percent to ensure fast and accurate detection of the titration end point.

A distillation setup was used to prepare 'dry' acetone by distilling as-received, reagent grade acetone (OmniSolv, order code AX0116-1, MCB reagents) over a mild drying agent, boric anhydride (Fisher Scientific, Cat. No. A-76, purified). The 'dried' acetone was then stored in a 2-liter automatic pipettor (VWR Scientific, Cat. No. 53518-084) which was open to the atmosphere via a silica gel-Ascarite II guard tube to keep the acetone from contacting H$_2$O and CO$_2$.

The fact that coal tars were much more readily dissolved in pyridine required the employment of this special reagent as co-solvent. A typical combination was first the introduction of 1 ml dry pyridine into the titration vessel, followed by addition of 5 ml dry acetone. The effect of adding pyridine
to the acetone has been shown (Vaughan and Switchenbank, 1965) to be only a reduction in temperature rise of the solution. It did not affect the rate of acetone dimerization and therefore the titration end point could be detected with the same accuracy. During titration, the solution of coal tars in acetone/pyridine was constantly agitated by a magnetic stirrer (F) to ensure well-mixing and fast monitoring of the temperature increase.

The titrant which was chosen to be a 1 normal solution of potassium hydroxide in dry isopropanol was introduced into the titration vessel at a constant rate by a 1.0 ml Hamilton gas-tight syringe (No. 1001) which in turn was driven by a syringe pump (Sage Instruments, model 341). To make the quantitative admission of titrant (normally at a very slow rate of 13 microliter/min) as precise as possible, a capillary tubing of 0.13 mm I.D. was used as the syringe needle.

The thermistor (whose resistance measures 2252 ohm at 25°C) used to detect the titration end point formed one side of a Wheatstone bridge powered by a 6V dry battery. The other sides of the bridge were two 1000 ohm resistor, R₃, in series with a variable 1500 ohm resistor, R₄, for zero adjustment. The output (in terms of current generated due to the voltage difference between junctions X and Y as shown in Figure 4.3-1) of the bridge was measured by a galvanometer (Kintel, Model 204A). The voltage output of the galvanometer was continuously monitored by a 10V potentiometric strip chart recorder (VWR
Scientific, Cat. No. 55423-251).

The calibration and detailed experimental procedure of the titration system is described in Appendix D. The results of acidic group concentration of the tars which correspond to the titration end points, are discussed in Section 5.8.3.

Other Analysis Technique

A special procedure was required for preparing tar samples used in the mutation bio-assay studies. Since some of the more volatile, lower molecular weight tar molecules which are suspected to be potentially mutagenic could be lost during the conventional drying process, the tar which was typically extracted from the tar trap with methylene chloride/methanol—67/33 (v/v), needed to be transferred to the test solvent (DMSO) used in the bio-assay without being dried completely.

The 'solvent exchange' technique was carried out by first concentrating the original solution of (about 10-30 mg) tar at 40°C in a 8 ml vial under a N₂ purge. About 1-2 ml of DMSO was added when the volume of the tar solution was reduced down to about 1 ml. The remaining methylene chloride and methanol could then be completely removed by continued N₂ purging for about 30 min. The loss of more volatile tar fraction was therefore minimized through this process.

The bacterial cell forward mutation bio-assay was performed by Dr. A.G. Braun and his co-workers of the Department of Applied
Biological Sciences at MIT. A description of the technique can be found in the literature (Skopek et al., 1978a; b).

The elemental analysis of the tar samples was performed in two separate places. The analysis for C, H, and N was done on a Perkin-Elmer (model 240B) Elemental Analyzer, a facility of the Chemical Engineering Department at MIT. The O and S analysis was done by Huffman Laboratories, Inc., (Wheat Ridge, CO).

The sample was prepared by first transferring the CH₂Cl₂/CH₃OH/tar solution to a 3 ml micro-vial with a cone-shaped bottom. This geometry allowed the tar to be collected in a small area. The solvent was evaporated under a N₂ purge in a 40°C water bath. The sample was then equilibrated in a dessicator and weighed.

The minimum amount of tar sample required for C, H, N, O, and S analyses was about 40-60 mg, mainly because that larger sample sizes were needed for both S (about 30 mg) and O (at least 10 mg) determination. Since most of the tar samples were used destructively when subjected to analysis such as titration and mutation bio-assay, there was in some cases not enough tar sample available, and therefore the result of O and S elemental analysis was not complete (see Section 5.8.5).
4.3.2 Gas and Light Oil Analysis

Gas Analysis

A Perkin-Elmer Model 3920 gas chromatograph was used for analyzing light hydrocarbon gases, CO and CO₂. Two columns, each 0.32 cm in outer diameter, were installed in series in the GC to improve the gas separation. The first was packed with Porapak QS (80/100), a porous polymer, and the second with 5 Å molecular sieve. These columns were respectively 3 m and 1.8 m long. The helium carrier gas flow rate was 30 ml/min.

The sequence for column utilization (including column reversal), advancement of the multiposition gas sampling valve, and operation of the GC were automated using a Spectra-Physics minigrator, a Hewlett-Packard 3390A reporting integrator, a Valco multiposition control module (MCM), and a Valco digital valve sequence programmer (DVSP) (see Figure 4.3-2).

The chromatograph was equipped with hot wire (HWD), flame ionization (FID), and flame photometric (FPD) detectors. A 2 cc sample from each loop of the multiposition gas sampling valve was analyzed first by HWD and then by FID. The 2 percent argon tracer in the helium carrier gas was used to quantitatively determine the rates of evolution of various gases and was detected by the HWD. The FID was used to detect hydrocarbon gases due to its high sensitivity and high degree of accuracy.
Fig. 4.3-2. Block diagram of automatic gas analysis

- = 1/8 SS tubing for gas connection

Spectra-Physics

INTEGRATOR START/RESET

GC START

TCO/FID SIGNAL

VALCO 10-PORT VALVE FOR COLUMN REVERSAL

VALCO 16-LOOP MULTIPosition VALVE FOR GAS SAMPLING (AND INJECTION)

VALCO 8-LOOP MULTIPosition VALVE FOR GAS SAMPLING (AND INJECTION)

VALCO MULTIPosition CONTROL Module (MCM)

VALCO DIGITAL VALVE SEQUENCE PROGRAMMER (DVSP)

VALCO MULTIPosition CONTROL Module (MCM)
in quantitation of these compounds.

Carbon dioxide, as well as carbon monoxide, could not be accurately quantified directly by HWD due to their very low concentrations in the carrier gas. This problem was resolved by first converting each of these gases to a compound (methane) detectable on the much more sensitive flame ionization detector (FID).

This was accomplished by installing a methanizer immediately upstream of the FID. It consisted of a 0.16 cm I.D. x 6.4 cm L. stainless steel tube packed with 60/80 mesh Zirconium/Nickel catalyst. The catalyst was typically heated to 350°C and was operated in the presence of H₂. In operation the CO and CO₂ were separated on the GC columns before each was passed through the methanizer where it was reduced to CH₄ with essentially 100 percent conversion efficiency. The higher sensitivity of the FID made it possible to detect these fixed gases at concentrations down to about 5 ppm range. The yield of water, which was detected by the HWD, could not be accurately quantified. Water molecules are polar, and interact strongly with Porapak QS, the column packing commonly used for separation of fixed gases and hydrocarbon gases. The result was that when the water was released by the column it evolved in such a broadened and skewed peak that accurate integration was impossible.

Moisture from the GC carrier gas, although very low in concentration, might also be condensed and accumulated during
the cool-down stage of the GC temperature programming. It eluted later when the columns were heated up, as indicated by repeated appearance of a H₂O peak from blank (control) runs when no sample was introduced to the GC. This made H₂O quantitation by GC even more difficult. Instead, the water yield was determined gravimetrically after collecting it on the packed Drierite (anhydrous CaSO₄) trap.

The thermal conductivity of H₂ is similar to that of He which was the carrier gas for the above-mentioned GC. As a result, hydrogen yield could not be quantitatively measured in the He carrier gas and was determined by a separate GC using argon as the carrier.

The evolution rate of a gas component at each sampling time was calculated by the formula given in Appendix B. The total yield of each gas was determined by numerical integration (using the trapezoidal rule) of the component evolution rate over the time of the experiment. The computer program used for this purpose is given in Appendix E.

**Light Oil Analysis**

The light oils extracted from the glass wool packing of the trap with methylene chloride, were analyzed by a capillary column GC in several selected runs. The fused silica capillary column was 30 meters long and 0.4 mm in I.D. The helium carrier gas flow rate was 25 ml/min. The oven temperature was
programmed at 40°C for 5 min., then heated up at 5°C/min rate to a final temperature of 250°C. Major components, such as benzene, toluene, xylene, m-cresol, and naphthalene were determined quantitatively.

As discussed in Section 5.4.3., the absolute light oil yields for selected mode-3 and -4 runs were found to be about 1 wt% of parent coal. On a basis of total tar fed, the yields and changes in yields of individual light oil components for different modes of experiments were also insignificant. As a result, no further light oil analyses were performed in this study.
5. Results and Discussion

5.1 Characterization of the CaO Packed Bed

As discussed in Section 4.1.4, reagent grade Ca(OH)$_2$ (or occasionally CaCO$_3$) was used for preparation of active CaO packed bed with acceptable experimental repeatability. The calcium hydroxide, which is a micron size powder, was mixed with 300 - 350 micron quartz particles to ensure uniform gas flow and to reduce pressure drop.

To minimize the problem of sedimentation of the Ca(OH)$_2$ powder due to the drag caused by the high superficial velocities of carrier gas used in this work (> 5 cm/sec at room temperature), a special technique was developed to prepare Ca(OH)$_2$—coated—quartz (C.C.Q.) (Longwell et al., 1983) as the starting material for bed packing (also see Section 4.1.4).

5.1.1 Uniformity of CaO Distribution in the Bed

An important question which must be addressed in this program, was whether the coating of C.C.Q. thus prepared, and therefore the distribution of Ca(OH)$_2$ was uniform. Since there is only limited quartz surface (about 0.16 m$^2$/g quartz) for Ca(OH)$_2$ coating, too high a ratio of Ca(OH)$_2$/quartz used for C.C.Q. preparation will result in a mixture of fluffy Ca(OH)$_2$ powder and C.C.Q.

The uniformity of C.C.Q. coating can be more stringently tested by comparing the experimentally observed sample weight
loss, when calcined in-situ in a T.G.A., to the theoretical value. Due to the high sensitivity of the T.G.A., sample size as small as 5 - 15 mg of C.C.Q. (containing 0.3 to 1.8 mg of Ca(OH)$_2$) could be used in the T.G.A. experiment.

Results of the actual % weight loss of C.C.Q. during calcination, each an average value of the results of at least five randomly chosen samples, as well as those of theoretically expected values are given in Table 5.1-1.

Good agreement between the two indicated homogeneous distribution of Ca(OH)$_2$ over the C.C.Q. down to the milligram range. It was also observed that C.C.Q. thus prepared contained less than 2 Wt% of calcium carbonate which might have formed by reaction of the Ca(OH)$_2$ slurry with atmospheric CO$_2$ during C.C.Q. preparation.

5.1.2 Uniformity of CaO Surface Area in the Bed

One of the major objectives of this research was to investigate the global kinetics of coal tar cracking in the presence of a CaO packed-bed. It is therefore desirable to characterize the surface properties of CaO which was typically derived from Ca(OH)$_2$ in this study. Various researchers have related the reactivity of CaO to its surface area, porosity, pore size distribution, crystallinity, basicity, etc. (see background discussion in Section 3.2.1). In this study, surface area was determined by the B.E.T. method, using molecular nitrogen as
Table 5.1-1  Percentage weight Loss of C.C.Q. During Calcination\(^{(a)}\)

<table>
<thead>
<tr>
<th>Percent Ca(OH)(_2) in C.C.Q.</th>
<th>Theoretical Percent weight Loss of C.C.Q.</th>
<th>Actual Percent Weight Loss of C.C.Q.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.66</td>
<td>1.62</td>
<td>1.58 ± 0.09(^{(b)})</td>
</tr>
<tr>
<td>12.5</td>
<td>3.05</td>
<td>2.86 ± 0.17</td>
</tr>
<tr>
<td>100 (pure Ca(OH)(_2))</td>
<td>24.3</td>
<td>22.7 ± 0.12</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Determined by T.G.A. experiments.

\(^{(b)}\) Average value of results of at least five randomly chosen samples.
the adsorbate.

**In-situ Calcination of C.C.Q. Packed-Bed**

During the mode-2 and -4 experiments, C.C.Q. was packed in a fixed bed and calcined *in-situ* to generate active CaO. A constant downward flow of helium as a carrier gas was imposed on the tandem packed-beds during both the calcination step as well as the coal volatiles generation/cracking processes. The superficial gas velocity (at room temperature) ranged from 5 to 20 cm/sec.

If the mechanical strength of the C.C.Q. coating is inadequate to withstand the shear force exerted by helium gas, Ca(OH)$_2$ would be carried downstream and accumulate toward the bottom of the packed bed. This would result in increasing total effective surface area per cross-section of the packed-bed (due to increased amount of Ca(OH)$_2$) with increasing bed depth.

To test whether this effect was important, simulated runs were made using sample sizes of about 9 g C.C.Q. (containing 12.5 Wt% Ca(OH)$_2$) which form packed beds of about 4.75 cm depth. The C.C.Q. was heated, at 3°C/min linear rate, to the desired final reaction temperature (here = 700°C) in one step, and then held at 700°C for 90 min. in the presence of flowing helium gas.

After calcination was complete, the reactor was cooled to
room temperature, and then moved quickly into a glove-box which was \( \text{H}_2\text{O}^- \) and \( \text{CO}_2^- \) free. Layers of calcined C.C.Q., each of about 0.6 - 1.0 cm thickness, were removed successively from the packed bed to give 5 to 7 fractions.

Each fraction was transferred to a U-shaped quartz tube, which was sealed gas-tight with quick-connectors, inside the glove-box. The quartz tube was then connected directly to the dynamic Quantasorb Quantachrome sorption apparatus for B.E.T. measurement of the CaO surface area. The results, plotted as circles in Figure 5.1-1, showed that, contrary to expectation, the reverse trend was observed. C.C.Q. surface area per cross-section of packed bed actually decreased with increasing bed depth.

The results of another stone preparation experiment, shown in cross symbols, where C.C.Q. was first calcined at a lower (550\(^\circ\)C) temperature for 30 min. before the temperature was raised finally to 700\(^\circ\)C for another 60 min., also suggest a somewhat similar trend.

Reasons for Non-uniform CaO Surface Area in the Packed-Bed

This behavior is believed to be a direct result from an increase in moisture concentration with increasing bed depth during the calcination process. If Ca(OH)\(_2\) -derived moisture can not be removed promptly, it will progressively reduce the driving force for Ca(OH)\(_2\) decomposition.
Figure 5.1-1 The Surface Areas of Calcined C.C.Q. in a Packed Bed.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Bed Height (cm)</th>
<th>Heating Rate (°C/min)</th>
<th>Calcination History</th>
<th>He Flow Rate (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>2.8</td>
<td>3</td>
<td>700°C for 90 min</td>
<td>750</td>
</tr>
<tr>
<td>×</td>
<td>4.3</td>
<td>3</td>
<td>1) 550°C for 30 min 2) 700°C for 60 min</td>
<td>750</td>
</tr>
<tr>
<td>□</td>
<td>4.8</td>
<td>3</td>
<td>700°C for 90 min</td>
<td>No He flow between 250 to 700°C</td>
</tr>
<tr>
<td>△</td>
<td>3.8</td>
<td>3</td>
<td>1) 500°C for 90 min 2) 700°C for 90 min</td>
<td>750</td>
</tr>
<tr>
<td>+</td>
<td>4.0</td>
<td>3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It has been shown that high reactivity, high surface area CaO is formed by calcining CaCO$_3$ or Ca(OH)$_2$ in vacuum where the product gas (CO$_2$ or H$_2$O) is quickly removed from the decomposing stone (Glasson, 1956; Beruto and Searcy, 1976; Beruto et al., 1980). The high specific surface area (about 100 m$^2$/g) CaO thus produced is not due to any basic structural difference since electron diffraction measurements confirmed that this fine CaO is crystallographically identical to CaO formed in air (Towe, 1978). Rather, X-ray data showed that CaO produced in vacuum has much finer crystallite size and higher porosity.

Glassen (1956) proposed that higher nucleation rates enable the CaO newly formed under vacuum to recrystallize from a pseudo-lattice of Ca(OH)$_2$ to very fine individual crystals having a more stable lattice and higher specific surface area. Nucleation would be inhibited in air (and in helium as well) since the removal of water vapor from the Ca(OH)$_2$-CaO reaction interface would be limited by the rate of internal and external diffusion of water vapor.

This results in fewer nucleation sites for CaO recrystallization and larger-size crystallites therefore form. The resulting CaO, having larger grains, possesses lower specific surface area (SSA). Calcination of C.C.Q. packed bed in flowing helium produced CaO with lower SSA (about 25 - 50 m$^2$/g) than that of CaO generated in vacuum, further confirmed the above picture.
Ewing et al. (1979) also found that the surface area of CaO prepared from calcite powder decreases when CO$_2$ background pressure exceeds 10% of the equilibrium decomposition pressure of CaCO$_3$. By reasoning similar to Glasson's, they suggest that this is due to the increased CaO crystallite sizes and pore diameters at the reaction front as the local partial pressure of CO$_2$ approaches its equilibrium value inside the calcite/CaO crystal.

In this research, we also demonstrated that higher partial pressure of moisture lowered the resulting CaO surface area. This was done by deliberately stopping the helium flow during calcination of the C.C.Q. bed from 250$^\circ$C to 700$^\circ$C, to increase the local partial pressure of moisture. The specific surface area of the resulting CaO was, as predicted, drastically reduced (see Figure 5.1-1, square symbols).

**Two-Step Calcination Procedure**

Since a packed bed with uniform surface area over its entire bed length is desired for well-defined tar cracking experiments, it is important to keep the content of H$_2$O in the C.C.Q. bed as low as possible throughout the calcination process. Such conditions can be approximated by a properly designed 2-step C.C.Q. calcination protocol.

It involves first calcining C.C.Q. at a low temperature, when the rate of Ca(OH)$_2$ dissociation is relatively slow and
the local H₂O concentration is low enough that no significant increases in crystal size and pore diameter will occur. The sample is held at that temperature for a period long enough for complete calcination, then brought to the desired final temperature for pyrolysis reactions.

Selection of a temperature that will minimize the H₂O partial pressure in the bed while allowing Ca(OH)₂ dissociation to proceed to completion within a reasonable period of time, requires a knowledge of the kinetics of Ca(OH)₂ dissociation. Unfortunately, to date our literature survey has not produced enough information on the effect of H₂O pressure on the rate of Ca(OH)₂ decomposition. On the other hand, the effect of CO₂ background pressure on calcite decomposition rate has been studied by many researchers, such as Hyatt et al. (1958), Cremer and Nitsch (1962), Darroudi and Searcy (1981), etc.

It is therefore not possible at present, to decide whether Ca(OH)₂ decomposition is controlled thermodynamically or kinetically under various conditions. Similarly, the optimal temperature history for complete calcination of the C.C.Q. packed-bed, within a preset calcination period, also can not be predicted a priori.

In this study, a 2-step calcination protocol was tested by first heating up the packed bed at 3°C/min to 500°C, and there holding for 90 min to slowly achieve complete C.C.Q. calcination, then heating up or cooling down to the desired
cracking temperature.

The results of two such duplicate tests for 700°C cracking temperature (shown in Figure 5.1-1 in triangle and plus symbols) indicated that calcined C.C.Q. of relatively high and uniform surface areas (about 40 m²/g) throughout the bed could be achieved under a constant helium purge flow of 750 scc/min. This calcination protocol was therefore adopted as the standard procedure for preparing active CaO packed bed when C.C.Q. was used as the starting material.

5.1.3 Physical Properties of CaO

The various CaO samples prepared from Ca(OH)₂ by the proposed 2-step calcination protocol (see Section 5.1.2), experienced similar calcination history (i.e., at 500°C for 90 min), but quite different heating up or cooling down temperature-time history from each other.

For example, it took about half an hour to bring an already calcined CaO sample (at 500°C originally) to 600°C tar cracking temperature and about another 2 hrs at 600°C before the introduction of coal volatiles from coal pyrolys's performed in Reactor-1. For 800°C tar cracking runs, the same calcined CaO (at 500°C initially) would experience first a 100 min heating up period, then a 2 hrs soaking period at 800°C before coal volatiles were cracked over the CaO.

The specific surface areas of CaO samples thus prepared
for different tar cracking temperature runs, were characterized
with the BET surface area analyzer using nitrogen as the adsor-
bate. Figure 5.1-2 shows the change of specific surface area
of CaO (just before introducing the coal volatiles) as a func-
tion of the tar cracking temperature.

The reproducibility of the BET measurements and the CaO
sample preparation (mode-2) experiments, is demonstrated by
the data shown at 700°C. The lower two symbols represented
duplicate measurements of samples from the same batch of cal-
cined CaO. The measurements were done in our laboratory at
M.I.T.. The upper one, on the other hand, was the surface
area of a duplicate CaO sample prepared by calcining a diffe-
rent batch of C.C.Q. under the similar conditions. The BET
analysis was performed by Porous Materials, Inc. (Ithaca, NY).
The agreement among these data was quite good.

The results indicated that significant stone sintering
occurred at temperatures above 700°C, over the extended (more
than 2 hrs) soaking period. The pore size distribution of a
selective CaO sample prepared for 700°C cracking experiments,
was also determined by the BET technique (performed by Porous
Materials, Inc., Ithaca, NY), where the relative pressure
(P/P₀) of nitrogen (the adsorbate) was varied between about
0.1 to 1. The shape of the pores in the CaO crystal prepared
from Ca(OH)₂ was determined to be slit-like (Beruto et al.,
1980).

The relationship between P/P₀ and the corresponding size
Figure 5.1-2  Specific Surface Area of CaO, Prior to the Introduction of Coal Volatiles, as a Function of Temperature. (CaO from Calcining Ca(OH)$_2$ at 500°C for 90 min, then Held at the Desired Cracking Temperatures for about 90 min.)
of slit-shape pore that would be filled with nitrogen in the absence of capillary condensation, was estimated from the value of the constant C derived from BET measurements (Beruto et al., 1980). The results of pore distributions are shown in Figure 5.1-3, both as a function of relative pressure of N₂ (P/P₀) and of slit width (d) of pores in CaO sample calcined from Ca(OH)₂. The sizes of slit range from about 2 to 14 nm, with the most common slit width being about 4 - 6 nm.
Figure 5.1.3 Pore-size Distributions in CaO Calcined from Ca(OH)$_2$. (Sample prepared for a 700°C Mode-4 experiment)
5.2 Characterization of Feed (Primary Coal Tar)

The feed to mode-3 (vapor phase cracking) and mode-4 (heterogeneous cracking over CaO) experiments was the primary coal tar generated in the mode-1 runs. As described in Section 4.1.3, this was typically achieved by heating up 1 g of coal (mixed with 12 g of SiC to prevent coal caking) in Reactor-1 at 3°C/min rate from room temperature to 700°C for essentially complete evolution of primary coal tar.

The primary tar as well as other coal pyrolysis products (such as light gases and light oils) were immediately quenched upon exiting Reactor-1, and were characterized accordingly to determine the quantity and nature of the 'reactant' which was cracked in the mode-3 and mode-4 experiments.

5.2.1 Product Distribution

A series of six replicate mode-1 runs were performed to give the information concerning product evolution rates and product distributions. The results of these runs indicated that good reproducibility could be achieved. The average results of cumulative yield of tar and the evolution rates of major light hydrocarbon gases and H₂, are all given in Figure 5.2-1, as a function of volatiles formation temperature (i.e., temperature of Reactor-1). Since the reactor was heated at 3°C/min constant rate, the abscissa can also be considered as
Fig. 5.2-1  Volatiles From Coal Pyrolysis (Mode-1 Experiment).
a time scale. The evolution curve for C₃H₈ was similar to that of C₃H₆ and was not plotted.

The CO and CO₂ yields were determined by first converting the carbon oxides (after passing through the GC column and were separated from one another) to CH₄ through a methanizer, which was then detected by the flame ionization detector (FID) of the GC. The evolution rates of CO and CO₂ are given in Figure 5.2-2.

The time resolved water evolution from coal pyrolysis could not be achieved because of the instrument sensitivity limitations that made difficult the quantitative determination of water which existed in very low concentrations (being greatly diluted by the helium carrier gas) in the pyrolysis product gases. The overall yield of water was, instead, determined gravimetrically by using the water trap described in Section 4.1.2.

As would be expected for coal pyrolysis reactions at these operating conditions, char which remained in the packed bed of Reactor-1, was the major coal decomposition product, accounting for about 61 - 62 Wt% of the parent coal (see Table 5.2-1).

The yield of primary tar was typically 25 - 26 Wt% of the parent coal. The data in Figure 5.2-1 also indicated that over 95% of the tar was formed below 550°C and that the maximum rate of tar formation occurred at about 420 - 430°C.

The evolutions of C₂H₄, C₂H₆, C₃H₆, and C₃H₈ were essen-
Figure 5.2-2 CO and CO₂ Evolution Rates as a Function of Reactor-1 Temperature for Mode-1 Experiments.
Table 5.2-1  Comparison of Product Distributions for Pyrolysis of Pittsburgh No. 8 Seam Bituminous Coal

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Diluent</td>
<td>SiC</td>
<td>Sand</td>
<td>None</td>
</tr>
<tr>
<td>Reactor type</td>
<td>Packed bed (1.6x3.8 cm)</td>
<td>Packed bed (1.1x6.5 cm)</td>
<td>Screen Heater</td>
</tr>
<tr>
<td>Pretreatment</td>
<td>Wet-sieved Partially dry</td>
<td>Wet-sieved Partially dry</td>
<td>As-received</td>
</tr>
<tr>
<td>Particle size</td>
<td>300-355 micron</td>
<td>250-350 micron</td>
<td>53-88 micron</td>
</tr>
<tr>
<td>Sample size</td>
<td>1 gm</td>
<td>1 gm</td>
<td>10-15 mg</td>
</tr>
<tr>
<td>Temperature</td>
<td>700°C</td>
<td>550°C</td>
<td>850-1000°C</td>
</tr>
<tr>
<td>Heating rate</td>
<td>0.05°C/s</td>
<td>0.05°C/s</td>
<td>1000°C/s</td>
</tr>
<tr>
<td>Holding time</td>
<td>0</td>
<td>30 min</td>
<td>2 - 10 sec</td>
</tr>
<tr>
<td>Pressure</td>
<td>1 atm</td>
<td>1 atm</td>
<td>1 atm</td>
</tr>
<tr>
<td>Environment</td>
<td>Helium</td>
<td>Helium</td>
<td>Helium</td>
</tr>
</tbody>
</table>

Product Yield (Wt percent of sample coal)

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Tar</td>
<td>25.47</td>
<td>24.21</td>
<td>23.0</td>
</tr>
<tr>
<td>Light oil</td>
<td>(1.0)a</td>
<td>4.30-5.57</td>
<td>2.4</td>
</tr>
<tr>
<td>Gas (total)</td>
<td>13.10</td>
<td>9.34</td>
<td>18.8</td>
</tr>
<tr>
<td>CH₄</td>
<td>2.34</td>
<td>1.84</td>
<td>2.5</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.21</td>
<td>0.12</td>
<td>0.8</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.64</td>
<td>0.57</td>
<td>0.5</td>
</tr>
<tr>
<td>C₃H₆</td>
<td>0.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.23</td>
<td>0.14</td>
<td>1.3</td>
</tr>
<tr>
<td>Other HC gas</td>
<td>NDb</td>
<td>0.04</td>
<td>1.3</td>
</tr>
<tr>
<td>H₂O</td>
<td>7.24</td>
<td>3.54</td>
<td>7.8</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.16</td>
<td>2.68</td>
<td>1.2</td>
</tr>
<tr>
<td>CO</td>
<td>0.68</td>
<td>0.40</td>
<td>2.4</td>
</tr>
<tr>
<td>H₂</td>
<td>0.41</td>
<td>0.055</td>
<td>1.0</td>
</tr>
<tr>
<td>Char</td>
<td>61.63</td>
<td>62.2</td>
<td>53.0</td>
</tr>
<tr>
<td>Total</td>
<td>101.20</td>
<td>100-101.3</td>
<td>97.2</td>
</tr>
</tbody>
</table>

a. estimated value.

b. not determined.
tially complete by the time tar formation was essentially over. The methane evolution, which peaked at about 510°C (a temperature slightly higher than those of other HC gases, i.e., 450 - 480°C), decreased to almost zero, while production of H₂, CO, and CO₂ appeared to persist, at the end of the coal pyrolysis run (i.e., at 700°C, no holding period). The total yield of each gas was determined by numerical integration (using the trapezoidal rule) of the component evolution rate over the time of the experiment. The results are also given in Table 5.2-1.

The total yield of light oils was estimated to be about 1 Wt% of the parent coal. The major, identified, components were BTX, m-cresol and naphthalene. However, detailed analysis of light oils by capillary column GC was not done routinely because it was found, in the test runs, that the yield of light oils was not significantly affected by the presence of CaO, even when over 75 (relative) % of the primary tar was cracked. The time-consuming analysis of light oils was therefore not justified. Overall material balance was found to be quite good (see Table 5.2-1).

5.2.2 Comparison with Other Works

The product yields for primary coal pyrolysis are compared with the results of Serio (1984) and Suuberg (1977), who also used coal samples similar (in source) to those of
this work (see Table 5.2-1).

The ultimate yield of primary tar (about 25.5 Wt% of parent coal) is very similar to those obtained by Serio (1984) and by Suuberg (1977). The latter studied the pyrolysis of a very thin layer (approaching the limit of monolayer) of 53 - 88 micron size coal at 1000°C/sec heating rate to 850 - 1000°C (1 atm, in helium) in a screen-heater reactor, which was designed to minimize the extraparticle secondary reactions of coal tar.

The agreement between the results of these two different reactor systems indicated that these secondary reactions were largely minimized in the tar generation reactor of this study, at least to the extent that could be accomplished at 1 atm pressure. This was presumably due to the combination of (a) using a thin packed bed of coal, (b) diluting the caking coal particles with an inert (SiC), (c) use of a lower heating rate which caused most of the tars to be formed and be evolved at relatively low temperatures (≤ 550°C) where secondary cracking would not be significant (Serio, 1984), and (d) rapid dilution and removal of coal volatiles from the pyrolyzing coal by a superimposed helium carrier gas flow. The average residence time of tar in the formation bed was typically kept below 0.1 second.

The fact that lower yields of gases, which are characteristic of high temperature coal pyrolysis, i.e., CO, C₂H₄, C₃⁺ gases, and H₂, were observed in this study, suggested the
coal (and tar) pyrolysis process in the tar generation bed was less severe than that of Suuberg's. The yields of C\textsubscript{2}H\textsubscript{4} and C\textsubscript{3}\textsuperscript{+} gases (which were closely related to the formation of primary tar, see Figure 5.2-1) were probably the best indicator of the severity of side chain cracking experienced by the tar (and tar precursors) during coal pyrolysis.

There were results in Suuberg's work that indicated some tar cracking was occurring to produce C\textsubscript{2}H\textsubscript{4} in his base case experiments (1000\degree C/sec to 1000\degree C in 1 atm helium) shown in Table 5.2-1. The ethylene yields were decreased by about 50% under either of the following conditions: (a) the coal was heated under a vacuum, (b) the coal was heated at a lower heating rate (350 - 450\degree C/sec), and (c) the coal was heated to a lower peak temperature (about 600\degree C) and held for longer times.

The results shown in Table 5.2-1, clearly indicated that functional-group and side-chain cracking of primary tar was occurring more severely in the base case studies of Suuberg than in Serio's work (1984) or in this study. This was presumably due to the use of a low heating rate (3\degree C/min) in this study which generated tars at lower temperatures (mostly between 430 - 490\degree C), when compared to the screen-heater experiments where more tar evolved from the coal particles and through the heating screen at higher temperatures due to rapid heating. The result suggested that the low heating rate technique used in this study was more appropriate for primary tar
generation at atmospheric pressure conditions since the side chain cracking reactions were not significant under these conditions.
5.3 Importance of External and Internal Mass Transfer

Study of the global kinetics of heterogeneous reactions of coal volatiles with the CaO active sites, was one of the major objectives of this research. To achieve this goal, it is important to perform experiments under conditions such that limitations due to the internal (intra-particle) and the external (extra-particle or boundary layer) mass transfer processes are absent (or at least minimized).

5.3.1 Effect of Carrier Gas Flow Rate

If a differential reactor was used in the study, then to show that a mass transfer limitation exists between the fluid (carrier gas) and the catalyst particle surface, it is necessary and sufficient only to demonstrate that reaction rate increases with increase in carrier gas velocity at constant temperature.

However, such a test is inconclusive in most cases when a packed-bed (an intergral reactor) of catalyst is involved. If the reactant conversion is appreciable (such is usually the case in this study) over the packed bed, then a change in gas flow rate will change the global (overall) reaction rate simply by changing the average reactant concentration, an effect totally independent of that of mass transfer.

To overcome this difficulty, test experiments to see if
the mass transfer limitation between the fluid and the CaO surface is negligible, were performed using packed beds of depths differing by a factor of up to 4, i.e., 2.5 cm, 5 cm, and 10 cm of packed C.C.Q., respectively (see Table 5.3-1). The volatiles contacting times were kept the same (0.12 sec) by varying the carrier gas flow rates appropriately, i.e., by a factor of up to approximately 4. The coal/CaO ratio and the input concentration of tar was also kept constant by varying the amount of coal employed accordingly.

Traditionally, external mass transfer coefficients are correlated as a function of Reynold's number, as suggested by Chilton and Colburn (1934):

$$J_D = \frac{K_c \rho}{G} N_{Sc}^{2/3} = f(N_{Re}) \quad \text{Eq. (5.3-1)}$$

where $K_c$ is the mass transfer coefficient, $\rho$ the gas density, $G$ the mass velocity of the gas, $N_{Sc}$ the Schmidt number, and $N_{Re}$ the Reynolds number for the gas.

The carrier gas linear velocity is chosen to be less than about 45 cm/sec in this study. This corresponded to a Reynold's number, based on the C.C.Q. particle size, of order $10^{-1}$ or less. Wilson and Geankoplis (1966) have reported data on fluids-solids mass transfer in packed beds and suggested

$$J_D = \frac{1.09}{\varepsilon N_{Re}^{2/3}} \quad \text{Eq. (5.3-2)}$$
Table 5.3-1  Effect of Space Velocity of Carrier Gas/Feed Mixture on the Extents of Coal Volatiles Conversion Over CaO. (Cracking Temperature = 600°C, contact time 0.12 sec)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>M4-44</th>
<th>M4-45</th>
<th>M4-47</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO/Coal (g/g)</td>
<td>0.25/0.5</td>
<td>0.5/1.0</td>
<td>1.0/2.0</td>
</tr>
<tr>
<td>C.C.Q. Bed Depth (cm)</td>
<td>2.5</td>
<td>5.0</td>
<td>10.1</td>
</tr>
<tr>
<td>Space Velocity (cm/sec)</td>
<td>10.5</td>
<td>21.5</td>
<td>44.0</td>
</tr>
<tr>
<td>Tar(^{(a)}) (trap)</td>
<td>6.92</td>
<td>7.52</td>
<td>6.78</td>
</tr>
<tr>
<td>(extra)</td>
<td>5.90</td>
<td>6.45</td>
<td>6.11</td>
</tr>
<tr>
<td>Gas(^{(a)}) (total)</td>
<td>15.83</td>
<td>15.69</td>
<td>15.70</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>3.25</td>
<td>3.33</td>
<td>3.29</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>(0.28)(b)</td>
<td>(0.32)(b)</td>
<td>0.49</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>0.71</td>
<td>0.74</td>
<td>0.76</td>
</tr>
<tr>
<td>C(_3)H(_6)</td>
<td>(0.60)(b)</td>
<td>(0.75)(b)</td>
<td>(0.65)(b)</td>
</tr>
<tr>
<td>C(_3)H(_8)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H(_2)O</td>
<td>6.00</td>
<td>6.03</td>
<td>5.73</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>2.44</td>
<td>2.31</td>
<td>2.38</td>
</tr>
<tr>
<td>CO</td>
<td>1.70</td>
<td>1.40</td>
<td>1.58</td>
</tr>
<tr>
<td>H(_2)</td>
<td>0.85</td>
<td>0.81</td>
<td>0.82</td>
</tr>
<tr>
<td>Char(^{(a)}) (R1)</td>
<td>60.32</td>
<td>61.04</td>
<td>59.62</td>
</tr>
<tr>
<td>Coke(^{(a)}) (C.C.Q.)</td>
<td>9.92</td>
<td>9.99</td>
<td>9.36</td>
</tr>
<tr>
<td>Material Balance</td>
<td>98.89</td>
<td>100.69</td>
<td>97.57</td>
</tr>
<tr>
<td>% Tar Conversion</td>
<td>48.7</td>
<td>44.2</td>
<td>48.4</td>
</tr>
</tbody>
</table>

(a) Product yields reported were in terms of Wt% of the parent coal.

(b) Unreliable data.
for values of $\varepsilon$, the void fraction of the packed bed, from 0.35 - 0.75 and $0.0016 < N_{Re} < 55$.

At the same contact time, the mass velocity will be greater in the deeper bed. The mass transfer coefficient, $K_c$, would increase by about 60 percent (based on Eq.(5.3-1) and (5.3-2)) when the gas space velocity was increased to 4 times its initial value. If external mass transfer was the rate limiting step, the extent of reaction would also increase by approximately 60 percent.

The results given in Table 5.3-1 indicated that the degrees of coal tar conversion and various gas yields were, within the experimental accuracy, essentially unchanged. Thus external mass transfer limitations were found to be not significant in this study under the above stated conditions.

5.3.2 Effect of Crystal Size of CaO

A classical way of determining the importance of pore (intra-particle) diffusion limitations is to perform experiments with two (or more) sizes of catalyst (Froment and Bischoff, 1979). If it is assumed that external mass transfer is not the rate limiting step and that the reaction rate coefficient and the effective diffusivity are the same for the different size catalysts, then it can be shown that

$$\frac{R_{obs1}}{R_{obs2}} = \frac{L_2}{L_1}$$

Eq.(5.3-3)
for the case of strong pore diffusion limitation, and

\[
\frac{(R_{\text{obs}})_1}{(R_{\text{obs}})_2} = 1 \quad \text{Eq.}(5.3-4)
\]

for the case where the global rate is controlled by chemical kinetics. In the above expression, \(L_1\) and \(L_2\) are the characteristic sizes of the catalysts, and \((R_{\text{obs}})_1\) and \((R_{\text{obs}})_2\) are the observed rates for the different size catalysts.

The commercially available calcium hydroxide, the typical starting material for preparing the calcium oxide used in this study, is prepared by precipitation and obtained only in powder form (i.e., \(L\) is approximately \(1 - 5\) microns). A special procedure was therefore utilized to grow calcium hydroxide crystals of \(10 - 300\) microns in size (Dave and Chopra, 1966). A brief description of the simple set-up used for crystal growth is given in Section 4.1.4.

The crystals thus prepared were sieved to yield particles of narrow size distribution (e.g., \(38 - 45\), \(90 - 106\), and \(180 - 250\) microns, respectively). About \(0.66\) gm of each of the sieved Ca(OH)\(_2\) crystal samples was employed in each of a series of test runs where all other experimental parameters were kept the same. The weight of coal and in-situ prepared CaO stone from calcining Ca(OH)\(_2\), was \(1.0\) and \(0.5\) gm respectively. The prompt coal tar from coal pyrolysis, underwent cracking reactions at \(700^\circ\text{C}\), over a \(0.12\) sec volatiles contact time in the presence of a packed
bed of different crystal size CaO.

Results of the effects of crystal size on the thermal cracking behavior of prompt coal tars over CaO are given in Figure 5.3-1. The overall percentage of tar conversion caused by CaO packed-bed, was essentially unaffected when CaO of crystal size less than about 40 microns was employed.

In a later section (Section 5.6.2) where the effect of CaO pore size distribution on the molecular weight (M.W.) distribution of surviving tars is discussed, we will see that the higher M.W. tar constituents (M.W. heavier than 500 - 550) actually experienced certain intraparticle transport limitations when cracked over CaO prepared from Ca(OH)_2 powder. Fortunately more than 70 percent of the prompt tar molecules are lighter than 500 gm/mole. It can therefore be concluded that pore (internal) diffusion limitations were not significant for most of the prompt coal tar constituents in this study, where powdered Ca(OH)_2 (of size less than 5 microns) was typically employed in the packed bed for generating active CaO stone.
Figure 5.3-1 Effect of Ca(OH)$_2$ (CaO) Crystal Size on the Overall Conversion of Coal Tar.
5.4 Effect of Cracking Temperature on Coal Volatiles Pyrolysis

The effects of cracking temperature on the pyrolysis reactions of freshly formed tars both in the vapor phase and heterogeneously in the presence of CaO generated \textit{in-situ} were systematically studied in the 400 - 800°C range. All the other experimental parameters, i.e., amounts of coal (1 gm) and CaO (0.5 gm) used, the volatiles residence time in the homogeneous phase (about 2 sec), and contact time with the CaO bed (about 0.12 sec), were maintained constant in this set of experiments.

Figures 5.4-1 to 5.4-3 display product distributions for these pyrolysis reactions as a function of volatiles cracking temperature. The product yields are calculated based on the amount of parent coal used. To characterize the input to the thermal treatment reactor, each figure also displays the yields of char, tar and light gases evolved by the 'generation' reactor (i.e., by pyrolysis of coal in Reactor-1). As would be expected for packed bed carbonization at these operating conditions, char which remained in the first reactor, was the major coal decomposition product, accounting for about 60 - 62 Wt percent of the parent coal.

The tar yields decreased with increasing volatiles cracking temperature, and to a much greater extent in the presence of calcium oxide. The rate of cracking reactions of coal tar over CaO was found to be typically one to two orders of magnitude higher than the rate of a duplicate vapor phase cracking run.
Fig. 5.4-1 Product Distributions for Mode-3 and Mode-4 Experiments, as a Function of Cracking Temperature.

\[ t_{\text{homo}} = 2. \text{ s}; \ t_{\text{hetero}} = 0.12 \text{ s}; \ \text{coal/CaO} = 2. \ (\text{w/w}). \]
Fig. 5.4-2  Yields of Light Hydrocarbon Gases for Mode-3 and Mode-4 Experiments, as a Function of Cracking Temperature.

* $t_{\text{homo}} = 2.0$ s; $t_{\text{hetero}} = 0.12$ s; coal/CaO = 2. (w/w).
Symbol △ is for Mode-1, ○ for Mode-3, and × for Mode-4.
Fig. 5.4-3 Yields of CO$_2$, CO, H$_2$O, and H$_2$ for Mode-3 and Mode-4 Experiments, as a Function of Cracking Temperature.

* $t_{\text{homo}} = 2.2$ s; $t_{\text{hetero}} = 0.12$ s; coal/CaO = 2. (w/w).

Symbol △ is for Mode-1, ○ for Mode-3, × for Mode-4.
The major components of mode-3, secondary tar cracking products were light hydrocarbon gases (mainly as CH₄, C₂H₄, and C₃H₆), CO and CO₂, for temperatures below 700°C. At 800°C, effects of reactor surface became important, resulting in the formation of 5 - 8 Wt% (of parent coal) of secondary coke formed on the reactor wall, along with the increased evolution of CH₄, C₂H₄, CO, CO₂ as well as H₂.

In the presence of CaO, the additional tar pyrolysis products (excluding the contributions from concurrent, vapor phase cracking reactions) were mainly secondary coke formed on the CaO surface (accounted for 80 - 85 Wt% of total cracked tar), a significant amount of hydrogen gas, and (below 700°C) small amounts of CH₄ and C₂H₄.

The total light oil yield was found to be little affected by the presence of CaO (see Section 5.4.3), and was estimated to be 1 - 2 Wt percent of parent coal from results of capillary column GC analyses of selected samples. The overall material balances for all modes of experiments fell in the range of 93 - 108 Wt percent of parent coal.

5.4.1 Tar Yields

Tar yields were determined gravimetrically by measuring the weights of tars exiting the reactor for duplicate experiments carried out in the absence and presence of the CaO bed. Although most of the tar was collected in the teflon wool traps, a significant amount (about 20 - 30 percent) was deposited at the lower
portion of the reactor tubes and particularly in the three-way valve whose temperature was kept below 240°C because of limitations on its sealing material.

After disassembling the reactor system, these adsorbed tars were extracted by sequential washings with the following three solvents: methylene chloride/methanol—67/33 (v/v), tetrahydrofuran/methanol—90/10 (v/v), and pyridine. The solvent was removed from the solution of tar extract by heating to 50°C in a heated water bath (90°C for the pyridine fraction) under a constant nitrogen purge. The latter was used to accelerate evaporation and minimize tar oxidation. After drying in a desiccator, the total amount of extracted tars was determined gravimetrically.

All the solvent handling and evaporation steps were done inside a ventilated hood. The problem of possible formations of peroxide (which is explosive upon heating) from tetrahydrofuran was minimized by using the stabilized reagent and, when not in use, by keeping the fresh reagent under a nitrogen blanket while stored in a refrigerator.

If it is assumed that the deposition rate of tars on the reactor (and valve) walls was directly proportional to their true evolution rate, then the latter could be determined by adding the proportionately redistributed extra amount of tars to each trapped fraction obtained from the corresponding tar trap over a certain temperature interval. (A more detailed description of this data manipulation is given in Appendix C.)
Following this procedure, the cumulative yields of coal tar collected from both mode-3 and mode-4 experiments were determined, and are shown in Figures 5.4-4 and 5.4-5 respectively. The data for the base case, mode-1 run, are also plotted for reference. It is recalled that the prompt tar samples for thermal treatment studies were generated by linearly heating a thin packed bed of coal in the mode-1 reactor. Thus the temperature of this reactor was also a convenient measure of the run time. The ultimate yield of primary tars, i.e., the feed introduced into Reactor-2 in mode-3 and -4 experiments, accounted for 25 - 26 Wt percent of the parent coal. Thus since the initial loading of Ca0 in a typical run was 0.5 gm and since about 1 gm of coal was employed in Reactor-1, the typical stone to cumulative tar feed ratio was 2.

The fractional yields and corresponding conversions of tar evolved from coal over a narrow range of tar generation temperature, could be determined directly from data given in Figures 5.4-4 and 5.4-5. The fractional conversions were shown in Figures 5.4-6 and 5.4-7 for homogeneous and heterogeneous cracking experiments, respectively. Here, the data given in Figure 5.4-7 were based on the conversion of the corresponding mode-3 tar fraction, i.e., the contributions of the concurrent vapor phase cracking to overall tar conversion were subtracted and only the effect of Ca0 on tar cracking was considered.

Those tars evolved at temperatures below 460°C exhibited modest reactivity as indicated by results of mode-3 runs (Figure 5.4-6) where volatiles undergo vapor phase thermal cracking
Fig. 5.4-4 Cumulative Tar Yields for Mode-3 Experiments* Performed at Different Cracking Temperatures, as a Function of Tar Formation Temperature.

* $t_{hom0} = 2.0$ sec; coal/CaO = 2. (w/w).
Fig. 5.4-5 Cumulative Tar Yields for Mode-4 Experiments* Performed at Different Cracking Temperatures, as a Function of Tar Formation Temperature.

* $t_{\text{homo}} = 2$ sec; $t_{\text{hetero}} = 0.12$ sec; coal/CaO = 2. (w/w).
Fig. 5.4-8 Fractional Tar Conversion for Vapor Phase Cracking (mode-3) Experiments at Different Cracking Temperatures, as a Function of Average Tar Formation Temperature.

Symbol | Cracking Temp (°C)
-------|------------------
△      | 500
□      | 600
○      | 700
+      | 800
Fig. 5.4-7  Fractional Tar Conversion for Heterogeneous Cracking Reactions Over CaO at Different Cracking Temperatures, as a Function of Average Tar Formation Temperature.

* % Conversion of Corresponding Fractions of Mode-3 Tar
reactions with about 2.0 sec residence time. Generally, the tars produced at higher temperatures appeared to be less reactive, as suggested by the decreasing extents of fractional tar conversions for any given volatiles cracking temperature (see Figure 5.4-6).

This was probably because the low temperature tar typically had higher ratio of aliphatic to aromatic hydrogen, as suggested by the $^1$H-NMR results both from this work and from Serio's experiments (1984). The higher content of aliphatics led to higher conversion in the mode-3 runs, since aliphatic bonds are generally more susceptible to thermal scission (for more details see Section 5.8.1).

In the presence of calcium oxide (0.12 sec contacting time), the overall extent of tar removal was typically more than double that from homogeneous phase cracking at a residence time of 2.0 sec. Furthermore, above a cracking temperature of 700°C, as shown in Figure 5.4-7, tars evolved at higher temperatures could be removed with a consistently high efficiency, an additional improvement when compared with the mode-3 results.

The results also showed that under the given conditions for cracking temperatures above 700°C, and a ratio of CaO/cumulative tar fed of 2, the bed of coked calcium oxide remained active for tar removal throughout the entire experiment. This was somewhat unexpected since high tar conversions were accompanied by extensive deposition of coke on the stone surface. Evidence for this was found in increase in weights of CaO and
the eventual change in the color of the entire bed of C.C.Q. from white to black with the increasing stone utilization.

At the same cracking temperature, CaO exhibits much greater capacity for cracking freshly formed pyrolysis tar than for a representative pure polycyclic aromatic compound (Lai, 1986; Ellig et al., 1985). This may reflect different chemical behavior, i.e., cracking reactivity, of tar which contained aromatics with more condensed rings and of some of the compounds, such as heteroatom-containing polycyclic aromatics, and phenolics, expected to be present in significant concentrations in the fresh coal tars (see also Section 5.8.3). Partial regeneration of CaO reactivity by regasification of fresh coke deposits by coal-derived CO₂ and/or steam might also be a factor.

5.4.2 Gas Yield

Figures 5.4-2 and 5.4-3 display yields of hydrocarbon gases, CO₂, CO, water, and hydrogen as a function of volatiles cracking temperature, both for mode-3 and mode-4 experiments. The yields of methane, which was the major hydrocarbon gas product of coal and homogeneous phase volatiles pyrolysis reactions, amounted to 2 – 4 percent (by Wt of parent coal). The yields from mode-4 runs were slightly but consistently higher than those of mode-3 cases below 700°C. In all the cases, methane yields increased steadily with increasing volatiles
cracking temperatures.

There were typically two major sources for methane production, as shown in Figure 5.4-8 for results of mode-4 runs, which presents the rate of gas evolution as a function of temperature in Reactor-1. The first of the two methane peaks which are partially overlapped, is located around 360 - 460°C, and is apparently related to the tar cracking process. The second peak around 400 - 700°C is due to the generation of 'primary' gas from coal pyrolysis alone, and gives rise to a primary methane yield of 2.1 - 2.3 Wt%. It was also found that methane was not cracked to a significant extent either in mode-3 or in mode-4 runs (at 400 - 800°C pyrolysis temperatures) (see Figure 5.4-8).

Above 600°C vapor phase thermal treatment of tar gave major increases in the yields of the olefinic gases C₂H₄ and C₃H₆ (factors of about 10 and 4 times, respectively). The absolute yields, and the changes in the yields, of the light alkanes C₂H₆ and C₃H₈ were not significant.

The ratios of increased methane yields (as well as C₂H₄ and C₃H₆ yields) to amounts of tars cracked in the presence of CaO were typically much lower than those from mode-3 runs (see Figure 5.4-9). This phenomenon of lower relative methane yield in the presence of CaO has also been observed in a series of studies in this laboratory on the pyrolysis of methyl-substituted pure aromatic compounds over CaO (Ellig, 1981; Lai, 1986). These effects are therefore considered to be a general feature of the pyrolysis behavior of aromatic systems in the presence
Fig. 5.4-8  CH₄ Evolution for Mode-4 Runs at Different Cracking Temperatures, as a Function of Reactor-1 (Volatile Generation) Temperature.

* \( t_{\text{homo}} = 2.8 \) s; \( t_{\text{hetero}} = 0.12 \) s; coal/CaO = 2. (w/w)
Fig. 5.4-9  Effect of CaO and Cracking Temperature on Relative CH₄ Yield.
of calcium oxide (Ellig et al., 1985).

Figure 5.4-10 shows the hydrogen evolution rate of mode-4 runs versus temperature of volatiles generation in Reactor-1. These curves have similar characteristics to those of methane. Therefore, similar conclusions about their origin can be drawn.

The changes in yields of \( \text{H}_2 \) and oxygenated light gases (CO, \( \text{CO}_2 \), and \( \text{H}_2\text{O} \)) were greatly complicated by the presence of CaO. In the absence of other reactions, the CO yields should increase with increasing cracking temperature for vapor phase tar pyrolysis reactions. This is supposedly due mainly to the thermal cracking of ethers and phenolics in the tar mixture, with CO as the major oxygenated gaseous product (Schlosberg et al., 1983; Cyprés and Bettens, 1975).

The CO yields should be higher from mode-4 runs when compared with duplicate mode-3 experiments, as a result of enhanced cracking of phenolics over CaO (which is discussed in Section 5.8.3). The experimentally observed CO yields were actually lower for the runs with CaO present. The same trend was also observed for \( \text{H}_2\text{O} \) yields. These suggest the presence of water gas shift reaction catalyzed by CaO.

The \( \text{H}_2 \) produced from this reaction as well as from steam gasification of coke deposited on the CaO surface, would at most account for about 30 - 50 relative percent of the difference in \( \text{H}_2 \) yields between mode-4 and mode-3 runs at temperatures above 600°C. The additional \( \text{H}_2 \) production must have resulted primarily from dehydrogenation of tar molecules, which was
Fig. 5.4-10 H₂ Evolution for Mode-4 Runs at Different Cracking Temperatures, as a Function of Reactor-1 (Volatile Generation) Temperature.

* t_{homo} = 2. s; t_{hetero} = 0.12 s; coal/CaO = 2. (w/w).
enhanced in the presence of CaO.

Below 500°C, about half or more of the CO₂ was apparently removed by CaO through recarbonation reactions over a relatively short contact time, 0.12 sec. Above 600°C, however, little recarbonation reaction would have occurred, since the typical partial pressure of CO₂ (<10⁻³ atm) in the gas stream of the pyrolysis products was lower than its equilibrium-allowed value in the presence of CaO at these temperatures.

The relative significance of water gas shift reaction and steam-carbon reaction could not be quantitatively addressed here, due to the lack of information on the instantaneous water concentration in the pyrolysis gases.

5.4.3 Light Oil Yields

At some point many of the light aromatic hydrocarbons, such as benzene, toluene, xyylene (BTX), and ethylene that are derived from petroleum currently and used as feedstocks for chemical industry, will probably have to be produced from coal, once again. It is therefore of interest also to investigate the roles of CaO in the production of these potential chemical feedstocks from coal gasification and pyrolysis processes.

The effect of CaO on the yield of ethylene from coal tar pyrolysis is discussed in the previous section. The yields of light oils for a selective set of mode-3 and mode-4 runs (at 700°C cracking temperatures) were determined by the capillary
column GC analysis, (the procedure for light oil analysis is given in Section 4.3.2).

The results, both of yields of identified compounds such as benzene, toluene, p-xylene, o-xylene, m-cresol, and naphthalene, as well as estimated yields of unknowns (presumably compounds with less than three rings), are given in Table 5.4-1. It was observed that the yields of various light oils were generally reduced in the presence of CaO over a 0.12 sec contact time, when compared to the mode-3 run (with a 2 sec vapor phase residence time), with possibly benzene and toluene as the exceptions.

The overall conversion of light oils (based on the yield of the mode-3 run) cracked over CaO at 700°C was estimated to be about 30 Wt%, which was considerably lower than the corresponding conversion of tar (about 70 Wt%, see Figure 5.4-1) which contained much heavier polycyclic aromatics with more condensed rings per molecule. This observation is in line with the results of pure compound studies (e.g., Ellig et al., 1985; Lai, 1986), and also agreed well with the GPC result of this study (see Section 5.8.2).

The fact that benzene yield actually increased and toluene yield remained relatively unchanged for the mode-4 run, might be due to the following reasons. Firstly, they were major volatile aromatic products from the cracking reactions of toluene and m-cresol respectively (Lai, 1986), and presumably also from cracking xylenes and related compounds, although their absolute
Table 5.4-1 Yield of Light Oils for Mode-3 and Mode-4 Experiments, at 700°C Cracking Temperature<sup>(a)</sup>

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mode-3</th>
<th>Mode-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.19</td>
<td>0.15</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>0.07</td>
<td>0.12</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>0.09</td>
<td>0.11</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.07</td>
<td>0.10</td>
</tr>
<tr>
<td>Unknowns</td>
<td>0.20&lt;sup&gt;(b)&lt;/sup&gt;</td>
<td>0.52&lt;sup&gt;(b)&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>0.88</td>
<td>1.28</td>
</tr>
</tbody>
</table>

<sup>(a)</sup> Coal/CaO weight ratio = 2, vapor phase residence time \( \geq 2 \) sec, and contact time over CaO \( \approx 0.12 \) sec.

<sup>(b)</sup> Estimated value.
yields were typically low (Lai, 1986). Furthermore, no significant conversion of benzene was observed over CaO (calcined from Ca(OH)$_2$) at 700$^\circ$C for a contact time of about 1 sec. (Ellig, 1981).

The general conclusion was that the effects of cracking reactions over CaO on the yield of light oils from tar pyrolysis under the given (inert gas environment) conditions, were small when normalized to a basis of total amount of tar plus light oils fed. However, in situations where more light oils are present these effects could be important. Routine analysis of the light oils, which was time consuming, was therefore not undertaken in this work.
5.5 **Effect of Cumulative Feed to CaO Ratio on Coal Tar Pyrolysis**

Catalyst deactivation in the presence of coke formation is an important problem in any heterogeneous catalysis study involving reactions of hydrocarbons (or other types of coke precursors). This is even more so in this case, since coke formation is found to be the major reaction in the study of coal tar-CaO thermal interactions.

There have been many papers over the years on the subject of catalyst deactivation (to name a few: Levenspiel, 1972; Butt and Billimoria, 1978; Wolf and Alfani, 1982; Jossens and Petersen, 1982; Beeckman and Froment, 1979; Hatcher, 1985). Most of these approached the problem by relating coke contents of the catalyst with the change in catalyst activity.

Ideally, the studies on catalyst fouling should be undertaken with a differential reactor, operating under conditions of constant temperature and (essentially) constant reaction mixture composition in both the time and space domains (Jossens and Petersen, 1982). This would allow direct determination of the deactivation kinetics for the catalyst and a better value for the initial reaction rate. A differential reactor can be approximated by proper operation of a thermogravimetric analyzer (TGA), where the coke content and reaction rate could be continuously monitored.

However, this approach was not realizable since the study of interactions of CaO with prompt coal tar (directly from coal
pyrolysis reaction) was the desired goal in this work. In order to be able to introduce coal pyrolysis tar continuously into the TGA, the tar must be first collected by condensation from coal pyrolysis, then vaporized as reactants. During both processes, the chemical and physical properties of the tar molecules are expected to be changed significantly, therefore may not be representative of those of prompt coal tar.

Furthermore, the difficulties associated with quantitative analysis of tar, which can not be easily achieved by such technique as chromatographic determination (applicable for characterizing a simple compound, or mixture), make the use of TGA even more formidable.

The alternative was to use the existing intergral reactor (fixed-bed reactor) of this research, to study the stone (CaO) deactivation and its relationship to coke content. The price paid was that data were much more difficult to analyze and interpret, since they were taken under conditions wherein the reaction mixture composition varied with both time and space.

A series of experiments were performed at constant cracking temperatures, to study the changes of extent of conversion of overall tar, which cracked over a C.C.Q. packed-bed containing 0.5 g of CaO, with the change in cumulative feed to CaO weight ratio. The carrier gas flow rate was adjusted at different cracking temperatures, to maintain a constant volatiles vapor phase residence time (about 3 sec) and contact time with the packed-bed (about 0.12 sec). All other experimental conditions
were as described in Section 4.1.3.

The study of the effect of cumulative feed (i.e., coal tar) to CaO weight ratio, on the pyrolysis of coal tar, was performed over 500 - 700°C temperature range. The yields of coal tar samples, undergoing various degree of heterogeneous phase cracking, were determined by the gravimetric measurements as discussed in Section 4.1.3. In order to obtain a good measurement of the tar yield, a minimum amount of 0.1 g of coal, used for generating about 0.025 g primary tar, was therefore required for the tar cracking study.

The results of overall conversion of mode-3 tar (which survived thermal treatment and actually reached the CaO packed bed as the reactant) are plotted in Figure 5.5-1 as a function of cumulative tar/CaO ratio (W/W) (which was varied from about 0.05 to 0.5).

The general trend observed was that the cracking activity of CaO typically decreased at a faster rate with increasing tar/CaO ratio (or equivalently, coke content of CaO) initially, then at a much slower rate at higher ratios. This picture was qualitatively in agreement with the results of corresponding pure compound studies where the effect of cumulative feed of pure compound (instead of coal tar) on CaO activity was examined (Lai, 1986).

The tar conversion information obtained from this set of experiments (i.e., at cracking temperatures between 500 and 600°C, and cumulative tar/CaO weight ratios between 0.05 and 0.5) was used to derive kinetics for modelling tar pyrolysis.
Figure 5.5-1  Effect of Cumulative Tar/CaO Ratio on Tar Cracking Activity of CaO.

* Tar cracking temperature; $t_{\text{hetero}} = 0.12$ s.
reactions over CaO, which will be discussed in detail in Section 5.10.
5.6 Effects of Other Parameters on Coal Tar Pyrolysis

5.6.1 Primary Tar Concentration

It has been demonstrated in this study that neither internal diffusion nor external mass transfer of the coal volatiles (with the possible exception of a small fraction of the most heavy tar constituents), is the rate limiting step for the complex cracking reactions of coal tars over powder-sized (less than 5 microns) calcium oxide. (See Section 5.3 for details).

A study of the effect of feed (i.e., primary coal tar) concentration was undertaken to address the relative importance of adsorption, surface reaction, and desorption, and to justify the use of a relatively simple kinetic model to describe the global kinetics of these complex interactions between CaO and coal volatiles. Ultimate extension to provide quantitative predictions of tar reaction behavior under different conditions is also a motivation.

It is important to keep in mind that experiments must be performed under otherwise identical reaction conditions, in order to study only the effect of feed concentration on overall extents of tar conversion over calcium oxide. Increasing only the amount of coal used in Reactor-1 (tar generation reactor) also changes the reaction conditions by increasing the coal/CaO ratio. Changing the helium carrier gas flow rate (to change
the tar concentration in the feed) also affects the volatiles contact time with the CaO packed bed.

One technique for studying only the tar concentration effects is to increase the temperature of the packed coal bed (for volatiles generation) in Reactor-1 at different heating rates, while studying the pyrolysis reactions under otherwise identical reaction conditions. The heating rate for Reactor-1 was chosen to be at 1, 3 and 6°C/min respectively, mainly due to the physical limitations (i.e., the bulkiness of the furnace, and the existence of a relatively thick packed-bed when compared with that of the screen-heater technique (Anthony, 1974) associated with the existing experimental system.

The primary tar concentration in the helium carrier gas was varied by a factor of about six in these experiments, since the rate of coal devolutilization was found to increase approximately linearly with heating rate over a small range of coal heating rate (Van Krevelen et al., 1956). The pyrolysis of coal volatiles were undertaken at 700°C. The homogeneous (vapor phase) residence time of coal volatiles was about 6 seconds in all cases. The volatiles contact time with the CaO bed was maintained at 0.24 - 0.25 seconds.

The results of coal volatiles cracking over CaO derived from Ca(OH)₂ are given in Table 5.6-1 for the three different volatiles concentrations studied. Here the tar conversion in the presence of CaO is expressed as the percentage conversion of the tar that survived thermal cracking — i.e., the separate
Table 5.6-1  Effect of Coal Tar Concentration on Tar Conversion(a) over CaO

<table>
<thead>
<tr>
<th>Run No.</th>
<th>M3-100</th>
<th>M4-89</th>
<th>M4-85</th>
<th>M4-76</th>
<th>M4-90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of Cracking</td>
<td>Vapor Phase</td>
<td>Ca0</td>
<td>Ca0</td>
<td>Ca0</td>
<td>Ca0</td>
</tr>
<tr>
<td>Coal Heating Rate (°C/min)</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Tar Yield (Wt% of total coal)</td>
<td>14.02</td>
<td>1.33</td>
<td>1.75</td>
<td>1.43</td>
<td>1.45</td>
</tr>
<tr>
<td>% Conversion (base case)</td>
<td>0</td>
<td>90.5</td>
<td>87.5</td>
<td>89.8</td>
<td>89.6</td>
</tr>
</tbody>
</table>

(a) Pyrolysis temperature = 700°C  
(b) Volatiles vapor phase residence time ≲ 6 sec.  
(c) Volatiles heterogeneous contact time with CaO = 0.24 - 0.25 s.
contribution of vapor phase tar cracking, determined from a
duplicate run without CaO was accounted for.

The data show that a high extent of volatiles conversion
(about 90 Wt%) was consistently achieved under the given con-
ditions. The results further show that, to within the expe-
rimental accuracy, there is no significant effect of feed
concentration on the overall conversion of coal tars over CaO.

This indicates that the global kinetics of coal volatiles
-cracking over CaO can be approximated as first order with re-
spect to the coal volatiles concentration. This would be the
expected result since the cracking experiments were typically
done under conditions where tar concentration was kept very low,
i.e., less than $10^{-7}$ mole/cm$^3$. Under these conditions, the
Langmuir-Hinshelwood types of kinetics, which may best describe
the chemisorption reactions of tars over the CaO active sites,
could be approximated as first order kinetics.

The true picture for the pyrolysis of a very complex
mixture such as coal tars, over an non-homogeneous solid
surface such as that of the polycrystalline CaO, is obviously
not as simple as just described. However, in the absence of
a suitable technique to probe the true reaction mechanism for
individual coal tar molecules, it is appropriate at present to
assume (based on experimental observations just discussed) first
order dependency on tar concentration, of global kinetics, of
tar pyrolysis over CaO.
5.6.2 **Origin of Calcium Oxide**

Calcium oxide can be prepared from many different stone sources. It can be obtained by calcining calcium hydroxide (which gives out water), calcium carbonate (with CO₂ evolution), as well as calcium oxalate (with CO and CO₂ evolution). The chemical composition of the lime derived from different stone origins is expected to be CaO (or more likely, as will be discussed in Section 5.9, CaO with a small but non-trivial excess amount of oxygen as O⁻ anion present in the calcium oxide ionic structure). The resulting crystalline conglomerates, however, may vary greatly in size and spacing in their matrices.

The above variations are partly due to the different crystal structure of different starting material, from which individual CaO crystallite starts its rearrangement and recrystallizes into its face-centered cubic system during and/or after the calcination step. The difference may also be due to different preparation methods and procedures required for calcining stones of various origin.

The CaO is industrially derived mainly from the calcination of limestone, which is the most abundantly available stone containing this alkaline earth element. It is therefore desirable to compare the coal tar cracking ability of calcium oxide generated from lime stone, i.e., calcium carbonate, to that from calcium hydroxide, under otherwise identical pyrolysis conditions.

Two duplicate mode-4 runs (M4-52 and M4-63) were performed
using calcium oxide obtained by calcining calcium carbonate. The decomposition temperature of calcium carbonate is much higher than that for the hydroxide, when equilibrated with the same equilibrium partial pressure of CO₂ or H₂O, respectively. A higher calcination temperature (700°C) and longer period (2 hrs) was required for completion of stone decomposition. All other experimental condition were kept the same as those of the M4-14 and -43 runs, duplicate standard experiments where Ca(OH)₂ was employed as the starting material for generating active CaO. The results of the absolute yields of surviving coal tars as well as the % tar conversion are summarized in Table 5.6-2.

The calcium oxide generated from carbonate (for simplicity, we will call it C-CaO from now on,) was found to be slightly more reactive (or effective) for tar removal reactions. About 83 ± 1% of the original tars were removed by reacting over C-CaO at a contact time of about 0.12 sec, as compared to 76.5 ± 4% when H-CaO (i.e., calcium oxide prepared by calcining calcium hydroxide) was employed instead.

The specific surface areas of both C-CaO and H-CaO were determined from B.E.T. surface area measurements using nitrogen as the adsorbate. The results shown in Table 5.6-2, indicate that the surface areas of both CaO samples were essentially the same, with the possibility that C-CaO might have a little less surface probably due to the higher calcination temperature employed. However, the results of Gel Permeation Chromatography
Table 5.6-2  Effect of CaO Source on Overall Yields of Coal Pyrolysis Tar

<table>
<thead>
<tr>
<th>Run No.</th>
<th>M4-14</th>
<th>M4-43</th>
<th>M4-52</th>
<th>M4-63</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source of CaO$^{(d)}$</td>
<td>Ca(OH)$_2$</td>
<td>Ca(OH)$_2$</td>
<td>CaCO$_3$</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td>Shape of Pores</td>
<td>Slit</td>
<td>Slit</td>
<td>Cylindrical</td>
<td>Cylindrical</td>
</tr>
<tr>
<td>Critical Dimensions of Pores, Å</td>
<td>40-50</td>
<td>40-50</td>
<td>&gt;100</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Specific Surface Area$^{(c)}$ (m$^2$/g CaO)</td>
<td>38-42</td>
<td>38-42</td>
<td>34-36</td>
<td>34-36</td>
</tr>
<tr>
<td>Total Tar Yield (Wt% of Parent Coal)</td>
<td>7.0</td>
<td>4.97</td>
<td>4.59</td>
<td>4.16</td>
</tr>
<tr>
<td>% Tar Conversion$^{(b)}$</td>
<td>72.5</td>
<td>80.5</td>
<td>82.0</td>
<td>83.7</td>
</tr>
</tbody>
</table>

(a) Volatiles cracking temperature = 700°C; heterogeneous contacting time = 0.12-0.13 sec; and the CaO/Coal (g/g) ratio = 0.5/1.0.

(b) Assuming a cumulative tar feed of 25.5 Wt% of parent coal.

(c) Values from 2-4 B.E.T. surface area measurements using nitrogen as the adsorbate (see Figure 5.1-2).

(d) Ca(OH)$_2$ calcination was performed by first decomposing the stone at 500°C for 90 min, then heating up to 700°C; CaCO$_3$ was calcined at 700°C for 120 min instead.
(which are discussed in detail in Section 5.8.2) for the two tar samples surviving pyrolysis reactions over C-CaO and H-CaO, respectively, can shed some light on why C-CaO is more effective in coal tar removal.

The yield of higher molecular weight (M.W. heavier than about 500 gm/mole) tar fractions from the M4-52 run (involving C-CaO) is found to be significantly lower than it is in the M4-43 run (where H-CaO was employed) (see Figure 5.6-1). This difference is believed to be mainly due to the difference in critical dimensions of pores in these two CaO samples.

Beruto et al. (1981) reported that the average width of slit-shaped pores of H-CaO is about 20 - 30 angstroms, and that the size of cylindrical shaped pores of C-CaO is about 100 Å when stone is prepared under vacuum. The actual average slit width of the H-CaO prepared in 1 atm helium purge gas was experimentally determined to be 40 - 50 Å (see Section 5.1.3).

The results shown in Figure 5.6-1 are to be expected since the larger diameter pores of the C-CaO obviously reduced the intraparticle transport limitations supposedly experienced by the heavier (and larger) tar molecules, and allowed more of the higher M.W. tar constituents (which are also expected to exhibit higher intrinsic thermal reactivity over CaO than the lower M.W. ones) to contact the stone surface and be chemisorbed and cracked.

Also in line with this hypothesis is the observation (Figure 5.6-1) that for the C-CaO, the intermediate M.W. tar
Fig. 5.6-1 Effect of CaO Source on the Molecular Weight Distribution of Coal Tars Subjected to Thermal Cracking Over CaO.
fractions actually underwent less conversion. Apparently this is because of the higher CaO affinity towards the higher M.W. tar components which were competing for the same and limited numbers of active sites on the CaO surface with other, smaller tar molecules. Results of the model compound work (Lai, 1986) similarly suggest that the larger the tar molecules, the stronger the interaction of π-bonding system with active sites on CaO, assuming pore diffusion limitations are unimportant.

This result also suggests that the tar cracking reactions over CaO would presumably be best described by Langmuir-Hinshelwood types of kinetics under these conditions (i.e., coal/CaO weight ratio = 2). However, as discussed in Section 5.6.1, first order kinetics could be treated as good approximations, especially in the set of experiments (Section 5.5) performed for kinetic studies where the weight ratios of coal/CaO were typically lower than two (i.e., between 0.2 to 1.2), and the concentrations of coal tar, competing for the same numbers of active sites, were accordingly lower.

5.6.3 Gaseous Environment

Coal Tar Cracking in the Presence of Steam

There is always a significant amount of moisture within most coal combustors, gasifiers, or pyrolyzers. It is therefore of practical importance to study the effect, if any, of
steam on the activity of CaO in tar conversion reactions.

A series of mode-4 experiments have been performed at 650°C where steam was deliberately introduced into the system just upstream of Reactor-2. It was done either before the process of calcining Ca(OH)$_2$ began (Run No. M4-37) or after the stone calcination was complete and Reactor-2 had reached the volatiles cracking temperature (Run No. M4-35). The steam generation system used in these studies has been described in Section 4.1.2.

Except for the existence of approximately 25 vol% steam mixed in the preheated helium carrier gas, all other reaction conditions were kept the same as those described before for the runs without steam injection. The system pressure was kept at approximately 1.25 - 1.30 atm. At 650°C volatiles cracking temperature, approximately 710 standard cm$^3$/min (vapor) of steam (equivalent to 10.4 cm$^3$/hr of liquid water) was introduced into the system just upstream of Reactor-2 and mixed with 2080 cm$^3$/min of main stream helium from Reactor-1, to maintain a 0.12 sec volatiles contacting time with the CaO packed bed and to keep the steam partial pressure at approximately 0.3 atm.

The tars together with some moisture were retained in the tar traps. The remaining steam was condensed from the carrier gas (downstream of the tar traps) using a water separator immersed in an ice bath. A Drierite (CaSO$_4$) trap was installed upstream of the multiposition gas sampling valves, to remove residual moisture from the carrier gas, to avoid excessive damage
to the molecular sieve column used in the GC. Tar traps were
dried overnight in the desiccator under a helium environment
until steady weight measurements were obtained.

The results of these prompt tar conversion reactions over
CaO are summarized in Table 5.6-3. Also listed for comparison
are data of a mode-1 (base) run, a mode-3 run, and a mode-4
control (i.e., no steam) experiment (at 650°C cracking tempe-
rature).

The specific surface areas of CaO, both prepared in 1 atm
helium and in the presence of additional 0.3 atm steam which
was introduced either before or after the Ca(OH)₂ calcination
step, were determined by nitrogen BET measurements to be about
48, 25, and 31 m²/g respectively. The values corresponded to
CaO surface areas just prior to the introduction of coal vola-
tiles to the CaO packed-bed. The difference in the CaO surface
area was mainly due to the difference in product (water) removal
rate during C.C.Q. calcination (which was hindered in the M4-37
run), and the difference in the period of exposing CaO to the
steam (which was about 0, 2.5 and 1.5 hrs, respectively).

The presence of 0.3 atm steam was found to lower slightly
the cracking activity of CaO presumably mainly due to reduction
in the surface area. The total amount of tar cracked in mode-4
runs (heterogeneous contact time = 0.12 sec) declined from about
15 Wt% (of parent coal) to about 12 Wt% with the addition of
steam. The yields of light hydrocarbon gases also decreased,
presumably as a consequence of lower tar conversion.
Table 5.6-3 Effects of Steam\(^{(a)}\) on Tar Conversion\(^{(b)}\) Over CaO

<table>
<thead>
<tr>
<th>Effects</th>
<th>None (Tar Generation)</th>
<th>Thermal (No CaO, No Steam)</th>
<th>Thermal (CaO+He)</th>
<th>Thermal (CaO+Steam)(^{c}) M(^{4-35})</th>
<th>Thermal (CaO+Steam)(^{d}) M(^{4-37})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tar Conversion (%)</td>
<td>—</td>
<td>17</td>
<td>58</td>
<td>46</td>
<td>45</td>
</tr>
<tr>
<td>CaO Specific Surface Area (m(^2/g))</td>
<td>—</td>
<td>—</td>
<td>48</td>
<td>31</td>
<td>25</td>
</tr>
<tr>
<td>Yields (% of Coal)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tar</td>
<td>25.5</td>
<td>21.1</td>
<td>10.6</td>
<td>13.6</td>
<td>13.7</td>
</tr>
<tr>
<td>H(_2)</td>
<td>0.42</td>
<td>0.45</td>
<td>0.97</td>
<td>1.32</td>
<td>1.49</td>
</tr>
<tr>
<td>Coke (on CaO)</td>
<td>—</td>
<td>—</td>
<td>9.5</td>
<td>6.1</td>
<td>(0.19)(^{e})</td>
</tr>
<tr>
<td>Material Balance (%)</td>
<td>101.2</td>
<td>102.3</td>
<td>—</td>
<td>100.2</td>
<td>95.1(^{e})</td>
</tr>
</tbody>
</table>

\(^{(a)}\) 0.3 atm of steam in 1 atm of He.

\(^{(b)}\) Cracking temp. = 650\(^{0}\)C, CaO/Coal = 0.5, contact time = 0.12 sec.

\(^{(c)}\) Steam was introduced into Reactor-2 after the calcination step was completed and volatiles cracking temperature achieved.

\(^{(d)}\) Steam was fed prior to and during the Ca(OH)\(_2\) calcination.

\(^{(e)}\) Unreliable data due to loss of C.C.Q. sample.
Hydrogen yield increased significantly by as much as 30 - 50% (relative) in the presence of steam. The steam-carbon reaction and water-gas shift reaction, both catalyzed by CaO, were considered to contribute to this. The relative yields of coke (based on weight of tar cracked) formed on the C.C.Q. were accordingly lower. The changes in the evolution rates and yields of CO and CO₂, both of which were involved in these reactions, were not available due to the much lower sensitivity of the thermal conductivity detector used before the methanizer was installed on the GC.

It is interesting to notice that no significant difference was observed in the cracking activity of CaO in either M₄-35 or M₄-37 run, despite the fact that the former initially had a packed bed of CaO with higher surface area than the latter. This might be because of two reasons. The CaO of M₄-35 run with higher initial surface area, would further sinter at a higher rate than that of M₄-37 run (Ito et al., 1981) in the presence of steam. Also, the difference in total nitrogen BET surface area may not be a good measure of the difference in stone reactivity.

The results of these experiments also have practical implications. They suggest that the inevitable presence of moisture within coal conversion processes will not severely reduce the activity of CaO in tar conversion reactions (at least under the conditions described above).

An advantage of the steam-CaO combination is the signifi-
cant increase in the yield of hydrogen mainly as a product from steam gasification of coke, which results in product gas of higher heating value. Another possible benefit could be longer stone lifetime for tar cracking due to lower net coke deposition and continuous regeneration of CaO active sites through the CaO-enhanced steam gasification of coke (Table 5.6-3).

Coal Tar Cracking in The Presence of A Reactive Gaseous Mixture

The effect of a reactive gaseous environment (i.e., CO₂, CO, CH₄, and H₂) on the extent of overall conversion of freshly formed coal pyrolysis tars over CaO, was also studied in this period. The experiment was undertaken by introducing a mixture of reactive gases (i.e., 5% CO₂ + 22% CO + 1% CH₄ + 22% H₂, all in volume percent, with the balance being the helium carrier gas), into the system just upstream of Reactor-2 (the cracking reactor). The total flow rate was adjusted to give the coal tar mixture a 3 sec residence time in the vapor phase, and 0.12 sec in contact with the CaO bed. All the other experimental conditions are the same as those given in Section 4.1.3.

Carbon dioxide gas has been shown to catalyze a reduction in calcium oxide surface area at temperatures as low as 900 K and pressures as low as 0.2 Pa (Ewing et al., 1979). This pressure is only 0.5% of the equilibrium allowed pressure of CO₂ over CaCO₃ at 900 K. Thus the surface area reduction can not be attributed to CaCO₃ formation and most probably arises
from sintering of the CaO.

The tar cracking temperature was chosen to be 800°C, to ensure that CaO remained the dominant calcium salt in the thermal treatment reactor (Reactor-2), since the formation of calcite (CaCO$_3$) is precluded (Beruto et al., 1984), if the CO$_2$ partial pressure is always kept below 20% of its equilibrium allowed value over CaCO$_3$. To reduce CO$_2$-promoted sintering of CaO in the present work, feeding of the reactive gaseous mixture (5% CO$_2$) was delayed until the temperature of the tar generation reactor reached 260°C.

The nitrogen BET surface area of CaO was found to decrease from about 20 m$^2$/g in the helium environment, to about 10 m$^2$/g in the presence of 5% CO$_2$, at 800°C cracking temperature prior to volatiles introduction. The CaO was exposed to CO$_2$ for a period of about 45 min in the latter case.

Table 5.6-4 summarizes the effect of this reactive gaseous environment on CaO cracking activity. For comparison, results of two mode-3 runs (homogeneous, vapor phase tar cracking experiments) performed under similar conditions in the absence of CaO, and also of a mode-4 'control' run, heterogeneous tar cracking over CaO using inert (helium) rather than reactive carrier, are also tabulated.

The overall tar conversion was reduced from 64 to 54 Wt% in the reactive gaseous atmosphere runs. At least two factors, i.e., decrease of CaO surface area due to CO$_2$, and possible adverse effects of reactive gases (e.g., H$_2$) on tar cracking
Table 5.6-4 Effect of a Reactive Gaseous Environment on Tar Conversion\(^{(a)}\) over CaO

<table>
<thead>
<tr>
<th>Run No.</th>
<th>M3-70</th>
<th>M3-98(^{(c)})</th>
<th>M4-102</th>
<th>M4-93(^{(d)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaseous Environment</td>
<td>He</td>
<td>He</td>
<td>He</td>
<td>Reactive(^{(e)})</td>
</tr>
<tr>
<td>Tar Yield (Wt% of Coal)</td>
<td>15.02</td>
<td>15.20</td>
<td>5.44</td>
<td>6.90</td>
</tr>
<tr>
<td>% Conversion(^{(b)})</td>
<td>—</td>
<td>—</td>
<td>64</td>
<td>54</td>
</tr>
<tr>
<td>CaO Present</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>CaO Specific Surface Area (m(^2/g))</td>
<td>—</td>
<td>—</td>
<td>~20</td>
<td>~10</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Cracking temp. = 800\(^0\)C, CaO/Coal = 0.5, Contact time = 0.12 s.

\(^{(b)}\) Tar conversion in the presence of CaO is defined as the percentage removal of the tar that survived thermal cracking. The latter was determined from control runs under similar conditions but in the absence of CaO (see runs M3-70 and M3-98).

\(^{(c)}\) Weight of coal used in M3-98 run was 0.1 g.

\(^{(d)}\) The CaO had been exposed to CO\(_2\) for 55 min when coal tar evolution reached its peak value.

\(^{(e)}\) The reactive gaseous mixture contained 5% CO\(_2\), 22% CO, 1% CH\(_4\), 22% H\(_2\), and the balance was helium.
over CaO, can contribute to this lowered stone activity. The
detail gas analysis was made impossible due to the presence of
excess, externally introduced CO, CO₂, and CH₄ in quantities
that greatly exceed those for the corresponding gases from
coal/tar pyrolysis.

5.6.4 Other Alkaline Earth Metal Oxides

As discussed in more detail in the background Section 3.2.1,
alkaline earth metal oxides, i.e., MgO, CaO, SrO, and BaO are
found to be catalytically active for reactions such as the hydro-
genation as well as the isomerization of olefins at moderate to
low temperatures, when these oxides were evacuated and activated
at specific ranges of high temperatures (Tanaka et al., 1976;
Hattori et al., 1975; 1976). In the study of esterification of
benzaldehyde to benzyl benzoate at 120 - 200°C, the alkaline
earth metal oxides are also found to be active with the catalytic
activity increasing in the order of MgO < CaO < SrO < BaO (Tanabe and
Saito, 1974).

In our present research, we focus on the catalytic activity
of calcium oxide in coal tar heterogeneous pyrolysis reactions.
However, it would be interesting to perform similar comparison
studies involving other alkaline earth metal oxide. This is so,
not only for practical reasons (since naturally and commercially
available dolomitic compounds such as dolomite, contain MgCO₃ as
well as CaCO₃), but also for the interest of mechanistic study.
It is hoped that this type of observation, e.g., investigating the effect of a different alkaline earth oxide—MgO vs. CaO—on coal tar cracking would help to elucidate the mechanism responsible for these special CaO (or MgO)—aromatics interactions.

The MgO was prepared by calcining MgCO₃ (Fisher Scientific Company, Cerfitied, powder form) at 400°C instead of the 500°C used for calcining Ca(OH)₂, because of the much lower MgCO₃ decomposition temperature. The experimental conditions were chosen such that the coal to oxide weight ratio was about 2, the volatiles contact time with the oxide packed bed was about 0.25 sec, and the cracking temperature was 700°C. The specific surface area of MgO sample thus prepared was determined by the B.E.T. technique using nitrogen as the adsorbate.

It was found that magnesium oxide thus prepared was active in catalyzing coal tar cracking (see Table 5.6-5). About 86% overall conversion of coal tars was achieved in the presence of MgO, while about 90% tar conversion over CaO was observed under otherwise identical experimental conditions. The specific surface area (surface area per unit weight of material) of MgO and CaO was measured to be 93 and 40 m²/g respectively. The specific tar cracking reactivity (based on unit surface area) of MgO was therefore about half that of CaO.

This observation is qualitatively in line with our proposed mechanism (Longwell, et al., 1984) (also see Section 5.9), in which we suggest that (at least one of) the active sites of
Table 5.6-5 Comparison of Coal Tar Cracking Over CaO and MgO\(^{(a)}\)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>M3-100</th>
<th>M4-76</th>
<th>M4-85</th>
<th>M4-89</th>
<th>M4-91</th>
<th>M4-92</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source of Stone</td>
<td>none</td>
<td>Ca(OH)(_2)</td>
<td>Ca(OH)(_2)</td>
<td>Ca(OH)(_2)</td>
<td>MgCO(_3)</td>
<td>MgCO(_3)</td>
</tr>
<tr>
<td>Specific Surface Area (m(^2)/g)</td>
<td>—</td>
<td>40</td>
<td>40</td>
<td>40</td>
<td>93</td>
<td>93</td>
</tr>
<tr>
<td>Tar Yield (Wt% of Parent Coal)</td>
<td>14.02</td>
<td>1.43</td>
<td>1.75</td>
<td>1.33</td>
<td>2.02</td>
<td>1.98</td>
</tr>
<tr>
<td>% Conversion</td>
<td>0 (base case)</td>
<td>89.8</td>
<td>87.5</td>
<td>90.5</td>
<td>85.6</td>
<td>85.9</td>
</tr>
</tbody>
</table>

\(a\) Tar cracking temperature = 700\(^{\circ}\)C, vapor phase residence time = 6 sec, volatiles contact time with CaO bed = 0.24-0.25 sec, and coal/CaO weight ratio = 2.
these oxides for cracking coal tars may be crystal defects or combinations of $O^-$ (or $OH^-$) and extrinsic cation vacancies induced by a small amount of peroxide anion inevitably present in oxide calcined from hydroxide (Inoue and Yasumori, 1981) or carbonate.

The concentration of $O^-$ anions described above is likely to be higher on CaO surface, since the formation of peroxide is more favored in calcium oxide than in magnesium oxide (Inoue and Yasumori, 1981). However, quantitative assessment can not be attempted here for lack of more detailed information for the surface properties of stone. A more detailed description of the probable mechanism for CaO (as well as MgO) surface to be active for thermal conversion of aromatics will be given in Section 5.9.
5.7. **Deactivation/Regeneration of CaO Activity**

The CaO deactivation/regeneration studies were done under high tar conversion conditions at 700°C cracking temperature. The volatiles contact time over CaO was chosen to be 0.24 - 0.25 sec. All the other experimental conditions are as described in Section 4.1.3. The initial, overall tar conversion (based on the yield of mode-3 tar which is the 'reactant' for heterogeneous reactions) over the fresh CaO packed bed, was as high as 89 - 91%. About 80 - 85 Wt% of the resulting product was coke, formed on the CaO surface, which eventually reduced the stone surface area by as much as 50% (see Section 5.10).

The surface area reduction is presumably achieved through a mechanism of pore filling due to the occurrence of multi-layer coke formation (which will be discussed in more detail in Section 5.10) within the pore structure. The intrinsic surface area of CaO would also decrease (in addition to coke formation) due to stone sintering at the high temperature (> 700°C), and in the presence of water vapor and CO₂ from the coal/tar pyrolysis.

After the pyrolysis reaction, the coked CaO was then baked in inert helium atmosphere at 700°C overnight before the coke on CaO surface was removed by oxygen burnoff. This was achieved by passing 250 ml/min of pure oxygen for 20 min over the packed bed at 700°C. The system was then purged with helium at 750 scc/min for half an hour to ensure an inert environment before another cycle of volatiles cracking was begun. This cycle of
baking — O\textsubscript{2} burnoff — volatiles cracking was repeated four times to give information on the change of CaO activity with extent of utilization and regeneration.

It was found that the cracking activity of CaO could only be recovered by about 85 - 90 (relative) \% after each regeneration. The overall tar conversion was decreased from approximately 90\% initially, to approximately 63\% after the fourth regeneration cycle, as shown in Figure 5.7-1.

This decreasing trend could be the result of several different causes. It may be due to the decreasing intrinsic surface area of CaO. The stone sintered when it was either exposed to CO\textsubscript{2} and H\textsubscript{2}O from the coal pyrolysis, or kept at 700\textdegree C overnight (as discussed above). The contribution from the former process was expected to be more important since the presence of these gases was shown to catalyzed significantly, the CaO sintering process (Beruto et al., 1984).

The CO\textsubscript{2} generated within the CaO pore structure during coke burnoff process could also affect the stone sintering. This picture is supported by the fact that the CaO surface area was found to decrease by about 20\% after one cycle of cracking/regeneration experiment, in a pure compound study (Lai, 1986) also performed in this laboratory. The reduction in overall CaO activity may also be due to the progressive destruction of (O\textsuperscript{-} ion) active sites, by the deposited coke or the formation of sulfate (discussed later). The nature of the active sites of CaO is discussed in Section 5.9.
Fig. 5.7-1 Effect of Burnoff and Hydration/Recalcination on the Percentage Tar Conversion Over CaO.

* Fresh CaO was employed in Run #0 for tar cracking. In between Run #0 to #8, coked CaO was kept at 700°C overnight before regenerated by O₂ burnoff. After Run #4, the regenerated CaO was first hydrated, then recalcined in-situ before Run #5. After Run #7, ~0.25 atm of steam was passed over CaO bed after burnoff for 20 min.
Since the process of coke burnoff alone can not completely recover the initial surface area and the activity of CaO, an alternative regeneration technique is therefore desirable. The coke-free CaO sample after the fourth burnoff cycle was first cooled to room temperature, then hydrated by adding stoichiometrically sufficient distilled water to the packed bed, and finally recalcined as usual to produce CaO in-situ.

Because this CaO sample had been exposed to coal derived sulfur-containing gases such as \( \text{H}_2\text{S} \), it was also partially sulfated. The result of elemental analysis of a coked C.C.Q. sample, after one cycle of tar cracking, suggested that the sulfur content of CaO was about 2 - 3 Wt\%, presumably in the form of sulfate (or sulfide). The cracking study of fresh coal tars over this CaO was then undertaken to shed light on the extent of regenerability of the stone activity.

The effect of hydration and recalcination on the stone activity was dramatic. It appeared that similar amounts of active sites (to those on the original, fresh CaO) were reintroduced into the partially sulfated crystal lattice, and that a high extent of coal tar conversion (approximately 89\%) was once again achieved (see Figure 5.7-1). Also shown in Figure 5.7-1 are the results of three additional cycles of repetitive pyrolysis/O\(_2\)-burnoff experiments (Run numbers 6 - 8), performed after the hydration/recalcination step.

The stone's activity was shown to decrease more rapidly than that of the freshly generated CaO. This may be due to the
adverse effect of the higher content of sulfate arising from sulfur pickup in earlier cycles. The sulfate may either enhance crystal sintering (due to its much lower melting point), or enhance active site poisoning/pore plugging. After Run #7, steam at a partial pressure of about 0.25 atm was passed over the CaO packed bed at 700°C (total pressure was about 1.3 atm) for 20 min after the coke burnoff step. This presence of steam at (2% of its saturation pressure above CaO) had little significant effect on regenerating the stone's activity.
5.8 Coal Tar Characterization

Based on the knowledge accumulated in our laboratory regarding both pure compound cracking studies (Lai, 1986; Ellig, 1981; Mead, 1979) and fluidized bed pyrolysis of coal (Yeboah, 1979) in the presence of CaO (and related dolomitic compounds), we expect not only reduction in total yields of coal tars when they are pyrolyzed over CaO, but also significant modification of the physical, chemical, and biological properties of the surviving tars.

A great deal of the experimental effort was devoted to the characterization of the collected tar samples in this study. The tars are expected to be very complex mixtures, probably containing hundreds of compounds distinguishable by modern analytical instruments. However, complete molecular characterization of the tars is much too time-consuming and would generate more information than is practically usable for the main goals of the proposed research.

Instead, the tars were analyzed by NMR spectroscopy, GPC size separation technique, non-aqueous enthalpimetric titration, as well as elemental analysis to provide global, both structural and chemical, information that is of interest in studying the effects of CaO on tar cracking reactions. These analyses typically were done both for low temperature tars (A-tar, which evolved from coal pyrolysis below 430°C and survived secondary thermal cracking), and for high temperature tars (B-tar, evolved
between 430 - 700°C).

Selected tar samples were also subjected to bacterial cell forward mutation bio-assay (Skopek et al., 1978a; 1978b), to shed light on changes in the mutagenic potency of tars caused by secondary reactions with or without CaO.

The technique of gradient elution (column) chromatography can be used to separate tars into fractions containing similar chemical functionalities (Farcasiu, 1977; Schiller and Mathiason, 1977). Serio (1984) in his work applied this technique extensively to separate samples, both primary coal tar from pyrolysis of Pittsburgh Seam No. 8 bituminous coal similar (in source) to the ones used in this study, and tars that had undergone secondary cracking reactions.

Serio's tar mixtures were separated into saturates, aromatics, ethers, nitro-heteroatom compounds, and hydroxyls. His results suggested that there is almost always a significant amount (typically between 20 to 50 Wt% of total introduced tar sample) of unrecovered tar fraction remained on the packing material (neutral alumina) of the column chromatography even after the column was eluted with a polar solvent (methanol). This, therefore, makes the interpretation of column chromatography data less conclusive.

Since the coal samples used in this study are similar to those used in Serio's work, it was expected that the global properties of the pyrolysis tars generated from pyrolyzing the coal and therefore the amount of unrecovered tars would be similar to
each other. In addition to this drawback of lack of material balance, this separation technique is also time-consuming and requires relatively large amount of sample for desired experimental accuracy. It was therefore not adopted in this research as a standard technique for coal tar characterization.

5.8.1 NMR Analysis

Nuclear magnetic resonance (NMR) spectroscopy has been a powerful tool useful in tar analysis. Many investigators (Collin et al., 1980; Retcofsky et al., 1977; Yamada et al., 1976; Iwata et al., 1980) have used or modified the Brown and Ladner (1960) equations to estimate several important global structural parameters of tar liquids, such as carbon aromaticity (fa), the degree of substitution of aromatic rings, and the H/C ratio for the hypothetical unsubstituted aromatic nucleus — an index of degree of ring condensation.

In general, these estimations can be derived from information on: (a) $^1$H NMR spectra, of the tar sample, where the hydrogen distributions on the aromatic nucleus and aliphatic side chains are directly determined, (b) results of tar elemental analysis (O, C/H ratio, N,S), and for certain modified calculation schemes (Iwata et al., 1980), the following information: (c) tar average molecular weight, and (d) specific assumptions regarding heteroatom (e.g., O,N. and S) functionalities of the average tar molecules. The thesis of Lennox (1983) is a good
reference for the background and more detailed description on the derivation of average coal tar structural parameters from the NMR spectra.

One of the major assumptions concerning the Brown and Ladner equation for aromaticity calculation is that the atomic hydrogen-to-carbon ratio of the aliphatic structure is assumed to be equal to 2 for aliphatic hydrogen at alpha and beta position, and 3 for gamma position relative to an aromatic ring. The assumption has found broad application in the characterization of such diverse mixtures as coal pyrolysis products (Collin et al., 1980), oils and asphaltenes from coal hydrogenation (Maekawa et al., 1975), and coal extracts (Retrofsky and Friedel, 1970). Obviously the validity of this choice of values for aliphatic H/C ratios has been a major concern.

The carbon aromaticity ($fa$), i.e., the fraction of aromatic carbon can also be determined directly and unambiguously from $^{13}C$ NMR spectra provided that suitable precautions are taken to ensure that the NMR measurement is quantitative (Thiault and Mersseman, 1976; Joseph and Wong, 1980).

Retrofsky et al. (1977) compared the aromaticity ($fa$) determined from proton coupled $^{13}C$ NMR spectra of materials derived from coal, with the estimated values based on $^{1}H$ NMR data. The 29 samples investigated were chosen to cover a broad range of $fa$ values, the actual range was determined by $^{13}C$ NMR to be 0 - 0.95.

The results suggest that at least for materials similar to
those chosen in the study, reasonably good estimates of carbon aromaticities can be derived from $^1$H NMR data with the preassumed aliphatic H/C ratios. This good correlation is probably a direct consequence of the fact that the aliphatic structures of most materials derived from coal are predominantly methylene in nature (H/C = 2), with the exception of less abundant, remote CH$_3$ groups where H/C equals to 3. It is believed that a modified set of equations proposed by Lennox for calculating carbon aromaticity would give the best estimate in the absence of a direct $^{13}$C NMR analysis, because the proposed calculation procedure is more rigorous than other approaches (Lennox, 1983).

The quantitative reliability of $^{13}$C-NMR measurements have been tested in this study (Longwell et al., 1982) using a model mixture. The aromaticity calculated from NMR agreed with the actual values to within 3.5%. The major drawback of the quantitative $^{13}$C NMR technique is the long times required for Fourier Transform data accumulations. Typically it takes more than three hours per sample, due to the low natural abundance of the $^{13}$C nucleus and its low magnetic moment, both of which result in very weak signals.

Because of the time-constraint and the fact that aromaticity data obtained from $^1$H NMR analysis of coal tars from this study can be viewed with a considerable degree of confidence (Retcofsky et al., 1977), only the proton NMR technique was applied for coal tar characterization in this work.
**1H-NMR Analysis**

A representative \(^1\text{H}-\text{NMR}\) spectrum for a primary tar sample is shown in Figure 5.8-1. The \(^1\text{H}-\text{NMR}\) spectrum can be divided into several parts according to the chemical shift, a measure of the degree of shielding of the proton nucleus, and assigned to protons of different chemical environments. A comprehensive compilation of chemical shift regions corresponding to different types of protons in solutions of coal extracts and derivatives, can be found in the literature (Bartle and Jones, 1972; Collin et al., 1980; Speight, 1970).

The scheme adopted here was proposed by Lennox (1983) based on a survey of the above mentioned literature. The proton peak of tetramethyrsilane (TMS), an internal standard which has highly shielded nuclei, is found at the right hand side or upfield of the spectrum and the corresponding chemical shift is defined as zero. The assignment of various chemical shift regions is as follows: 6.2 - 9.2 ppm to aromatic and phenolic protons which give NMR resonance in the downfield region; 0.5 - 4.4 ppm to aliphatic protons.

The aliphatics band can further be divided into four types of proton as follows: methyl hydrogen gamma or further from an aromatic ring (0.5 - 1.0 ppm); alkyl methylene hydrogen beta or more remote from a ring, plus methyl groups beta to a ring (1.0 - 1.4 ppm); naphthenic methylene hydrogen other than alpha to a ring (1.4 - 2.0 ppm); and hydrogen on carbon alpha to a ring
Fig. 5.8-1 A Typical $^1$H-NMR Spectrum of a Tar Sample (from Mode-1 Runs).
(2.0 - 4.4 ppm).

The aromatics band can also be divided into regions corresponding to resonance of protons from monoaromatics, diaromatics, and polyaromatics (Bartle and Smith, 1965; Heredy et al., 1966), although no such further attempts were made in this work. No distinctive phenolic proton signal was observed in any of the spectra collected in this study. It is believed to be present in the upfield region of the aromatics envelope (Heredy et al., 1966). The determination of phenolic contents of the coal tar samples was instead achieved by a separate technique — non-aqueous thermometric titration which is described in Sections 4.3.1 and 5.8.3.

The $^1$H-NMR measurement was carefully performed (with suitably chosen experimental parameters such as pulse width and pulse delay) so that quantitative determination of various hydrogen distributions for a sample could be achieved. To demonstrate this, a simple, simulated coal liquid was prepared as a test sample for NMR study. A mixture of naphthalene, 1-methylnaphthalene, m-cresol, and 2,4-dimethylphenol of known composition was chosen both because these compounds are among the major components of a coal gasifier tar (Schiller and Mathiason, 1977), and because these are readily available chemical from M.I.T. laboratory supply.

In theory, the area under a given peak is directly proportional to the total amount of the type of proton contributing to the peak. The NMR spectrometer provides an integration
routine that permits the determination of various hydrogen distributions in the sample. Both the experimentally determined and actual (expected) values of aromatic and aliphatic (all at the alpha position) hydrogen fractions, and fa of the simulated liquid are given in Table 5.8-1. Generally the agreement is satisfactory within 2.5%.

Hydrogen Fractions

Pyrolysis coal tar samples were generally grouped into two fractions (i.e., A-fraction, tar generated at lower temperatures (less than 430°C), and B-fraction, tar generated at higher, 430 - 700°C, temperatures) for separate NMR analyses. Results of hydrogen distribution obtained from $^1$H-NMR measurement of mode-3 and mode-4 coal pyrolysis tars, both for A-fraction and B-fraction, are presented together for comparison.

Figures 5.8-2 to 5.8-6 present various hydrogen fractions as a function of volatiles cracking temperature. Figures 5.8-7 to 5.8-11 present the hydrogen fractions as a function of overall tar conversion. The reproducibility of the measured NMR spectra of duplicate tar samples was found to be generally within 5 - 10% for repeated experiments.

The effect of tar formation temperature (Reactor-1 temperature) on the hydrogen distribution of tar samples is found to be relatively minor. The A-fraction mode-1 tar is likely to be a little richer in aliphatic hydrogen. This observation is
Table 5.8-1 Results of NMR Analyses of a Simulated Coal Liquid Sample\(^{(a)}\) and the Experimental % Errors

<table>
<thead>
<tr>
<th></th>
<th>$H^*_\text{ar}$</th>
<th>$H^*_\text{al}$</th>
<th>$f_a$ (^{(d)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
<td>0.591</td>
<td>0.352</td>
<td>0.881</td>
</tr>
<tr>
<td>Experimental</td>
<td>0.579</td>
<td>0.360</td>
<td>0.878</td>
</tr>
<tr>
<td>% Error</td>
<td>2.0</td>
<td>2.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

(a) Mixture contained naphthalene, 1-methylnaphthalene, m-cresol, 2,4-dimethylphenol.

(b) This represents the aromatic hydrogen fraction.

(c) All of the aliphatic hydrogens are at the alpha positions.

(d) $f_a$, the carbon aromaticity, was determined from the $^1$H-NMR spectrum with the assumption that $H_{\text{ali}}/C_{\text{ali}} = 3.$
Figure 5.8-2  Alpha Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Cracking Temperature.

* $t_{\text{homo}} = 2.0$ s, $t_{\text{hetero}} = 0.12$ s, Coal/CaO (w/w) = 2.
Figure 5.8-3 Beta Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Cracking Temperature.

* \( t_{\text{homo}} = 2.0 \, \text{s} \), \( t_{\text{hetero}} = 0.12 \, \text{s} \), Coal/CaO (w/w) = 2.
Figure 5.8-4  Gamma Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Cracking Temperature.

* $t_{homo} = 2.0 \text{ s}$, $t_{hetero} = 0.12 \text{ s}$, Coal/Cao (w/w) = 2.
Figure 5.8-5  Naphthenic Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Cracking Temperature.

* $t_{\text{homo}} = 2.0 \text{ s}$, $t_{\text{hetero}} = 0.12 \text{ s}$, Coal/CaO (w/w) = 2.
Figure 5.8-6  Aromatic and Phenolic Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Cracking Temperature.

\[ t_{\text{homo}} = 2.0 \text{ s}, \ t_{\text{hetero}} = 0.12 \text{ s}, \ Coa1/CaO (w/w) = 2. \]
Figure 5.8-7  Alpha Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Tar Conversion.

* $t_{homo} = 2.0\ s$, $t_{hetero} = 0.12\ s$, Coal/CaO (w/w) = 2.
Figure 5.8-8 Beta Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Tar Conversion.

* $t_{homo} = 2.0$ s, $t_{hetero} = 0.12$ s, Coal/CaO (w/w) = 2.
Figure 5.8-9  Gamma Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Tar Conversion.

* $t_{\text{homo}} = 2.0 \text{ s}$, $t_{\text{hetero}} = 0.12 \text{ s}$, Coal/CaO (w/w) = 2.
Figure 5.8-10  Naphthenic Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Tar Conversion.

* $t_{homo} = 2.0 \text{ s}$, $t_{hetero} = 0.12 \text{ s}$, Coal/CaO (w/w) = 2.
Figure 5.8-11 Aromatic and Phenolic Hydrogen Fraction of Mode-3 and Mode-4 Tars as a Function of Tar Conversion.

* $t_{homo} = 2.0$ s, $t_{hetero} = 0.12$ s, Coal/CaO (w/w) = 2.
in agreement with the results from Serio's work (1984), in which the tar generated below temperature 350°C was found to have a greater content of saturates with significantly longer alkyl chain length.

The hydrogen fraction data must be interpreted with care. An apparent increase in one fraction (e.g., aromatic hydrogen fraction) may be due to the formation reactions (e.g., dehydrogenation of the naphthenic ring) and/or due to selective removal of other (i.e., aliphatic) fractions. On the other hand, if a fraction decreases, it is being lost at a greater than the overall tar conversion rate.

The hydrogen distributions of mode-3 tar which survived thermal cracking reactions at 500°C or lower, appear to be relatively unchanged from those of mode-1 tar. This would be expected since little tar cracking and light gas yield increases were observed under these conditions (See Figure 5.4-2). The beta and gamma hydrogen fractions (see Figures 5.8-3 and 5.8-4) decrease at cracking temperatures above 600°C, while the naphthenic hydrogen fraction (Figure 5.8-5) remains relatively constant below 700°C cracking temperature.

A major reduction of the aliphatic hydrogen fractions, with the exception of alpha hydrogen fraction, is observed when tar was pyrolyzed at 800°C. The alpha hydrogen fraction (see Figure 5.8-2) is found to be relatively insensitive to the cracking temperature up to 800°C. The aromatic plus phenolic fraction (Figure 5.8-6) increases monotonically with tar cracking tempe-
rature, with the more significant changes occurring above 600°C. The absolute phenolic fraction is actually found, by enthalpimetric titration, to be decreasing with increasing cracking temperature (discussed in Section 5.8.3). However, the phenolic hydrogen constitutes only a small portion (about 5% or less) of the total aromatic plus phenolic fraction. Therefore, the changes of this fraction, in effect, are reflecting mainly the behavior of the aromatic hydrogen.

The absolute yield of a specific hydrogen fraction ($Y_f$, g/100g coal) can be calculated as follows:

$$Y_f = (H_f^*)(H)(Y_T)$$  \hspace{1cm} Eq.(5.8-1)

where

- $H_f^*$ = hydrogen fraction determined from NMR analysis
- $H$ = hydrogen content of tar (g/g tar)
- $Y_T$ = tar yield (g/100g coal)

The absolute amount of aromatic hydrogen in prompt tars and in secondary mode-3 tars that had undergone various degrees of conversions, is found to be relatively unchanged (at about 0.5 Wt% of parent coal) with cracking temperature (Figure 5.8-12). This implies that the aromatic rings of coal tar are largely intact in the mode-3 reactions, and that the observed increase in aromatic fraction is primarily due to the cracking of aliphatic
Fig. 5.8-12 Comparison of Absolute Yield of Aromatic Hydrogen (g/100g Coal) for Primary and Secondary Tars.
hydrogen, especially the beta and gamma fractions.

The above observation can be explained based on the free radical initiated cracking of coal tar constituents supposedly prevalent in the homogeneous phase (mode-3) tar pyrolysis reactions. The energetically preferred initiation step is the breakage of the alkyl aliphatic side chains of the aromatics that exist in the tar. This bond breakage is then followed by beta-bond scission of the resulting radical chain with the major products being ethylene and methane. This is in good agreement with the experimental result of significant increases in methane and ethylene gas yields for mode-3 tar cracking runs at temperatures above 600°C (see Figure 5.4-2).

Bond breakage is generally easier for bonds at a distance greater than one carbon atom from the aromatic ring. For example, the bond dissociation energies for molecules to form benzyl radical and alkyl radicals (e.g., CH₃, C₂H₅, i-C₃H₇, or t-C₄H₉) are about 92 to 100 Kcal/mole (Benson, 1976). The dissociation energies are significantly lower for the formation of phenyl radical and corresponding alkyl radicals, i.e., about 65 to 72 Kcal/mole (Benson, 1976).

The energy needed for opening up an alkyl bond that is at the beta position or further away from the aromatic ring is therefore at least 20 Kcal/mole less than that for an alpha bond. This explains the apparent greater stability of the alpha hydrogen fraction relative to the beta (and gamma) alkyl protons. The naphthenic hydrogen is found to be slightly more stable and
decreases at a slower relative rate when compared with the beta and gamma fractions. A similar trend was also observed by Serio (1984).

Tar samples for mode-4 experiments show interesting differences from those of mode-3 runs. These are clearly indicated by the spectra in Figure 5.8-13. The NMR spectra show significant changes in the relative amounts of aromatic and various aliphatic hydrogen fractions for tars pyrolyzed at the same temperature in the absence (mode-3) or presence (mode-4) of CaO. The effect of CaO on coal tar hydrogen distribution is shown in Figures 5.8-2 to 5.8-6 as a function of cracking temperature. However it can be best demonstrated in Figures 5.8-7 to 5.8-11 where hydrogen fractions are presented as a function of overall tar conversion. At the same tar conversion level, mode-4 secondary tars contained significantly lower aromatic hydrogen fraction and retained higher aliphatic hydrogen contents.

This is good evidence that pyrolysis of coal tar over CaO was taken place via a totally different pathway from that of vapor phase cracking reactions. Instead of through the free radical, dealkylation mechanism that was responsible for mode-3 tar cracking, CaO achieved the same tar conversion by selectively catalyzing the removal of aromatic fraction of coal tar. The picture is also supported by the decrease in absolute yields of aromatic hydrogen for mode-4 tars, shown in Figure 5.8-12. This observation is in good agreement with the results of pure com-
pound studies (Mead, 1979; Ellig, 1981; Lai, 1986) where CaO was shown to be very active in pyrolytic destruction of aromatic compounds in contrast to its moderate activity for paraffin pyrolysis.

**Carbon Aromaticity**

Carbon aromaticity (fa) is defined as the fraction of the total number of carbon atoms that are aromatic in nature. Only this average structural parameter will be discussed in this work. Others, such as the degree of ring substitution, number of aromatic rings per unit tar molecule, etc., can not be calculated due to the lack of complete information for O and S elemental contents. This is mainly because that the amounts of recoverable tar samples for high temperature (greater than 600°C) mode-4 experiments were typically small, and that samples were usually used destructively by other analyses such as titration, bio-assay, etc. It is also important to note that there are limitations in considering these average parameters as representative of true properties. In fact, these are only properties of a mathematically derived, hypothetical tar model which possesses the average characteristics of the real tar system.

Based on the discussion made in the first part of this section, the carbon aromaticity of tar samples in this work can best be estimated by the set of equations proposed by Lennox
(1983), which are described in detail in his thesis. The additional information, i.e., the carbon to hydrogen atom ratio was determined from the elemental analysis (given in Section 5.8.5).

The calculated carbon aromaticities for mode-3 and mode-4 secondary tars are presented in Figure 5.8-14a as a function of tar cracking temperature and in Figure 5.8-14b as a function of overall tar conversion. The aromaticity of mode-3 tar increases with cracking temperature, suggesting the higher pure thermal stability of the aromatic relative to the aliphatic fractions of coal tar. The increase in aromaticity, as discussed previously, is actually a result primarily of dealkylation reactions.

The CaO catalyzes tar cracking by globally promoting the selective removal of aromatic-rich components of the tar mixture. As a result, the product tar of a mode-4 run usually has lower aromaticity than its reactant, i.e., the duplicate mode-3 secondary tar (see Figure 5.8-14a). The aromaticity of mode-4 tar for lower temperature (below 600°C) experiments, where there is minimum vapor phase tar cracking, appears to be lower than that of the primary coal tar.

The same tar conversion level can be achieved by tar cracking over CaO without as high an increase in tar aromaticity as compared to that of a duplicate mode-3 run (see Figure 5.8-14b). The important implication here is that upgrading of coal tar mixtures (to yield products of higher aliphatic contents) could potentially be achieved by this special CaO-aromatics chemistry
Figure 5.8-14a. Carbon Aromaticity for Mode-3 and Mode-4 Tars as a Function of Cracking Temperature.
Figure 5.8-14b. Carbon Aromaticity for Mode-3 and Mode-4 Tars as a Function of Tar Conversion.
under the appropriate conditions (e.g., below 600°C) without additional and expensive hydrogenation processes. This would be most effective for those tar mixtures where most aliphatic components exist as separate compounds, and not as side chains on the aromatic constituents of tar.

5.8.2 GPC Separation and Analysis

Both the preparative-scale GPC (Prep-GPC) and the analytical GPC were used in this study. A description of the apparatus, procedure and sample preparation for GPC analysis is given in Section 4.3.1. The Prep-GPC can handle large amounts (greater than 1 gm) of tar sample and was used mainly to prepare enough separated tar fractions with narrower molecular weight distribution (MWD) for further analyses. The analytical GPC was used to study the changes in the MWD and the average molecular weights of various coal tar samples.

The average molecular weights calculated are number-average (Mn) and weight-average (Mw) values. Mn is the first moment of the MWD and is more sensitive to the changes of lower molecular weight tars. Mw is the second moment of the MWD and is weighed more heavily by the higher molecular weight fraction. The ratio (Mw/Mn) is a measure of the spread of the MWD, and is called polydispersity index (PI). For a monomer or a single compound, Mw and Mn are the same and PI equals one.

The formulas used to determine the Mn and Mw values can be
found in the thesis of Oh (1985). The peak position method was
chosen to calibrate the performance of the GPC column for
separating the particular tars in this study. All of the MWD
data generated by GPC were collected by and stored in a digital
data acquisition instrument (Bascom-Turner 4120T). These data
were subsequently transferred to a personal computer for calcu-
lation of the average molecular weights. The calculation was
done using a version of the computer program written by Lennox
(1983).

The tar samples which were collected from pyrolysis experi-
ments and prepared in pyridine solution in this study, were
analyzed by the analytical GPC as soon as possible to minimize
changes in the MWD of the tar mixtures due to storage effects
(Braun and Hilfman, 1984; Finseth et al., 1984). The sensor
used to detect the elution of solute (tar species) was an ultra-
violet (UV) detector. This was chosen over a refractive index
detector mainly because UV data were more reproducible and not
affected by the presence of water impurity in the sample.

Effect of Tar Generation Temperature

The GPC results for five tar samples which were collected
from a typical mode-1 run over predetermined intervals of evo-
lution temperature are plotted as solute concentration (as
measured by the UV detector of the GPC) (arbitrary units) vs.
elution volume (ml) of pyridine, the eluant (see Figure 5.2).
The results are normalized to give GPC curves of approximately identical, total integration areas, i.e., same total amounts of tars detected, to allow for direct comparison.

It is clearly seen that, with the exception of tars evolved below 400°C which account for about 25 Wt% of total prompt tars, the majority of mode-1 coal tar samples (generated between 400-700°C) gives quite similar MWD curves. The Mn and Mw date, given in Figures 5.8-16 and 5.8-17, indicate quantitatively a slightly increasing trend of average molecular weight with increasing tar generation temperature, with the effect being less significant for tars formed above 400°C.

Similar results were observed by Serio (1984) and by Unger and Suuberg (1983). It was suggested that the trend of slight increases in the tar MW could be explained based on chemical reaction control mechanism. Since larger tar molecules are likely to have more linkages to be broken from the coal matrix during coal pyrolysis, their formation would be enhanced at higher generation temperature that would increase the decomposition rate of the coal metaplast.

Comparison of Mode-3 and Mode-4 Tars

The number-average and weight-average MW of tars from mode-3 and mode-4 experiments are plotted in Figures 5.8-18 and 5.8-19 respectively, as a function of tar cracking temperature. The secondary tar that underwent vapor phase pyrolysis reactions
Fig. 5.8-18 Effect of Evolution Temperature on the Number-average Molecular Weight of Mode-1 Tars.

Fig. 5.8-17 Effect of Evolution Temperature on the Weight-average Molecular Weight of Mode-1 Tars.
Fig. 5.8-18 Effect of Cracking Temperature on the Number-Average Molecular Weight of Mode-3 and Mode-4 Tars.
Fig. 5.8-19  Effect of Cracking Temperature on the Weight-Average Molecular Weight of Mode-3 and Mode-4 Tars.
generally had a decreasing trend for average MW with increasing cracking temperature (i.e., increasing extent of tar conversion). The NMR results of mode-3 tars given in the last section, indicated that the vapor phase thermal cracking of tar was mainly achieved through the breakage of aliphatic linkages rather than the aromatic ring systems.

A comparison of the GPC chromatogram for primary and secondary tars suggested that while the cracking of tar molecules to form lighter products were dominant, there were some heavier tars formed presumably through recombination reactions of lighter tars. This redistribution of molecular weight of tar through pyrolysis was also reflected by the increasing trend of polydispersity index (i.e., ratio of weight average MW to number average MW) of coal tar with increasing temperature.

Thermal cracking reactions over CaO reduced the average MW of secondary tars further at the same cracking temperature. The results together with the NMR information for mode-4 tar, i.e., increased aliphatic to aromatic hydrogen ratios and reduction in absolute aromatic hydrogen yields when compared to those of mode-3 tar, indicate that, in the absence of pore diffusion limitations, higher MW tars (generally with higher number of condensed aromatic rings) have a higher affinity for the CaO active sites, and are cracked preferentially. Results of pure compound work performed in this laboratory (Lai, 1986; Ellig et al., 1985) also support this picture.
It was also supported by the finding that heavier tar molecules (e.g., with MW > 500 g/mole) were removed more efficiently when CaO prepared from CaCO$_3$ (instead of Ca(OH)$_2$) was used, based on the same level of overall tar conversion, i.e., about 75% at 700°C cracking temperature (see Section 5.6.2 for more details).

This was because the larger diameter pores (>10 nm) of the CaCO$_3$-derived CaO, reduced the intra-particle transport limitations for the heavier tar, and allowed more of the higher MW tar constituents (which were also expected to be thermally more reactive over CaO) to contact the CaO active sites and be converted.

5.8.3 Thermometric Titration

The acidic content of coal tar was determined by the non-aqueous thermometric titration technique (Vaughan and Switchenbank, 1965; 1970) which has been shown to be applicable to the determination of monohydric and polyhydric phenols and particularly useful for detecting sterically hindered phenols which were probably present in coal tar mixtures. The detailed description of the titration apparatus and procedures are given in Section 4.3.1 and Appendix D.

Since the acidic functional groups in Pittsburgh Seam No. 8 bituminous coal were suggested to be mostly (>90%) phenolic (Whitehurst et al., 1981; Attar and Hendrickson, 1982),
and the carboxylic, carbonyl, and ester functional groups were considered to be so reactive that they would not survive even mild thermal processing (Ruberto and Cronauer, 1978), the acidity change of the tars in this study can be considered mainly as the change in the phenolic content.

The effect of thermal treatment, with or without CaO, on the phenolic content of coal pyrolysis tar was of great interest for practical purposes. Phenolic compounds, which typically exist in significant concentrations (Fleming and Talbot, 1982) in the tars are suspected to contribute several problems associated with lower tar quality, including liquid instability, high viscosity (Brown and Karn, 1980), toxicity, and incompatibility with petroleum feedstocks (Gould and Long, 1982). A process that can minimize or eliminate phenols in coal-derived liquids efficiently and economically, is thus desirable.

The titration results, presented as phenolic oxygen content (Wt% of tar) in Figure 5.8 - 20, indicated that the phenolic fraction of tar became susceptible to vapor phase thermal treatment at temperatures above 700°C. This was also in agreement with a corresponding increase in the yields of carbon oxide gases, especially the carbon monoxide, since it was found to be the major oxygenated gas product for vapor phase thermal cracking of phenols (Jones and Neuwirth, 1952; 1953).

The phenolic contents of mode-4 tars were consistently lower than those for mode-3 tars at the same cracking temperature, suggesting the existence of special CaO-phenolics
Fig. 5.8-20 Phenolic Content of Mode-3 and Mode-4 Tars as a Function of Cracking Temperature.
interactions. In a pure compound study performed in this laboratory (Lai, et al., 1986), the conversion of m-cresol was found to be greatly enhanced over CaO. Below 500°C temperature, the formation of a calcium half-salt through the base-acid interaction was proposed (Schlosberg and Scouten, 1983). At higher temperatures, conversion of m-cresol over CaO resulted in the formation of toluene and carbon monoxide suggesting reversion of the mechanism to direct pyrolysis or that the calcium half salt was formed but then pyrolyzed. Similar reactions are expected for the removal of phenolic fractions from coal tar mixture through thermal treatment with CaO.

However, the results of pure compound studies would suggest a much higher selectivity for phenolics removal from the coal tar mixture than actually observed in this study. At 600°C, for example, thermal cracking over CaO resulted in about 45% overall conversion of coal tar and only about 60% removal of total phenolic functional groups from the primary tar. At 700°C, it was about 75% tar conversion, and 85 - 90% phenolic group conversion, respectively. This apparent reduced selectivity for phenolics cracking over CaO was presumably due to the existence of certain phenolics, in coal tar, with sterically hindered functional groups. This therefore would not allow effective acid-base interactions between certain tar phenolic constituents and the CaO surface.
5.8.4 Mutation Bio-Assay

The mutagenicity of the tars was measured by the forward mutation of *Salmonella typhimurium* using 8-azaquanine resistance as a genetic end point marker (Skopek et al., 1978a; 1978b). The tests were performed by Dr. A.G. Braun and co-workers in the Department of Applied Biological Sciences at M.I.T.

The results for metabolic activated (indirect) bacterial cell mutagenicity of coal tar are shown in Figure 5.8-21. The unit for specific mutagenicity is the concentration of tar in μg/ml (of DMSO test solvent) where a plot of number of induced mutations vs concentration of test material crosses the 99% upper confidence limit of historical backgrounds. Thus the higher the value of this unit the lower the mutagenic potency of test material (see Figures 5.8-21 and 5.8-22).

Thermal treatment without CaO at high temperatures (700 - 800°C) destroyed from 20 - 40% of the tar (see Figure 5.4-1). However as seen in Figure 5.8-21 the tar which survived thermal treatment was significantly more mutagenic than the mode-1 control tar.

Additional treatment over CaO at the above conditions resulted in a cumulatative tar destruction of about 75 - 80% (see Figure 5.4-1). The effects of CaO on surviving tar mutagenicity were strongly temperature dependent, with 700°C treatment markedly reducing the tar mutagenicity almost to that of the control. However 800°C treatment caused only a modest
FIG. 5.8-21 Effect of Cracking Temperature and CaO on Coal Tar Mutagenicity. (With Metabolic Activation)
reduction in mutagenicity compared to that for the tar surviving thermal treatment alone.

Results for direct bacterial cell mutagenicity tests (without the metabolic activation) are given in Figure 5.8-22. Because of the typical problem of rather low survival rate of the bacteria used in the test, presumably as a result of tar toxicity, this set of data was considered statistically less reliable. The results exhibited significant high temperature scatter, but potentiation of specific mutagenicity reduction by CaO at 700°C seemed to be indicated.

Figures 5.8-23 and 5.8-24 respectively recast the data of Figures 5.8-21 and 5.8-22 in terms of the total amount of mutagenicity evolved from the coal as tar, i.e., they weight the specific mutagenicity of the surviving tar by the mass of that tar. In these two figures, the higher the value on the ordinate the greater the total mutagenicity of the coal evolved as surviving tar.

At 700 and 800°C, (mode-3) thermal treatment produced secondary tar of significantly higher indirect mutagenic impact than the control value (Figure 5.8-23). At these temperatures, CaO was effective in reducing the total indirect mutagenic activity engendered by mode-3 treatment, to levels comparable to the control (Figure 5.8-23). However for direct activity (Figure 5.8-24) a clear advantage of CaO treatment over thermal treatment as a pathway to tar mutagenicity control seemed to be limited to a more narrow temperature window about 700°C.
FIG. 5.8-22 Effect of Cracking Temperature and CaO on Coal Tar Mutagenic Impact. (With Metabolic Activation)
FIG. 5.8-23 Effect of Cracking Temperature and CaO on Coal Tar Mutagenicity.
(Without Metabolic Activation)
FIG. 5.8-24 Effect of Cracking Temperature and CaO on Coal Tar Mutagenic Impact. (Without Metabolic Activation)
The absence of this effect at 800°C reflected the compensating action of: (a) greater tar destruction by Ca0 (vs mode-3 thermal treatment) (see Figure 5.4-1), and (b) higher specific direct mutagenicity of the tar surviving mode-4 runs (vs. mode-3 thermal treatment) (see Figure 5.8-22). It is to be recalled that data given in Figure 5.8-24 are also considered less reliable statistically.

The data in general suggested opportunities for detoxification of coal tars subjected to high temperature (above 700°C) thermal treatment, i.e., by controlled thermal treatment over Ca0 at appropriate conditions (e.g., 700°C).

5.8.5 Elemental Analysis

The elemental composition of both primary and secondary tars is summarized in Table 5.8-2. Although the results were obtained from two different laboratories (i.e., C, H, and N from the Chemical Engineering Department of M.I.T., while O and S from Huffman Laboratories, Inc., (Wheat Ridge, CO)), the overall C, H, N, O, and S elemental balances were typically better than 95%.

The H/C atomic ratio showed decreasing trend with increasing cracking temperatures for tars which survived thermal (mode-3) treatment. This observation was in agreement with the NMR results where loss of aliphatic side chains (with higher H/C ratio), by dealkylation reactions, from the surviving aromatic ring core (which has lower H/C ratio) was suggested to
Table 5.8-2. Elemental Analysis of Primary Tar and Secondary Tars from Runs at Cracking Temperatures Between 400 and 800°C

<table>
<thead>
<tr>
<th>tar</th>
<th>thermal treatment</th>
<th>crack temp. °C</th>
<th>Wt%</th>
<th>H/C at ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>primary</td>
<td>none</td>
<td>81.6</td>
<td>6.97</td>
<td></td>
</tr>
<tr>
<td>secondary</td>
<td>vapor phase</td>
<td>80.7</td>
<td>7.16</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>81.5</td>
<td>6.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>82.3</td>
<td>5.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>86.4</td>
<td>5.49</td>
<td></td>
</tr>
<tr>
<td>secondary</td>
<td>over CaO</td>
<td>83.2</td>
<td>7.11</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>81.2</td>
<td>6.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>83.2</td>
<td>7.42</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>76.6</td>
<td>6.14</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>84.5</td>
<td>6.22</td>
<td></td>
</tr>
</tbody>
</table>

\( ^a \) Determined by difference.
have occurred in the mode-3 thermal cracking reactions of coal tar (see Section 5.8.1).

The value of H/C atomic ratio of the tar was typically higher for mode-4 runs with CaO present when compared to the duplicate mode-3 runs at the same cracking temperature. This also agreed well with the NMR analysis of mode-4 tar which suggested the occurrence of enhanced cracking of aromatic-rich tar constituents (with lower H/C ratio) through special interactions with the CaO surface.

The difference in H/C atomic ratio between mode-3 and mode-4 tars was even more dramatic when it was compared on the basis of equal tar conversion level. For example, at 35% overall tar conversion (the highest level achieved in mode-3 runs at 800°C), the H/C ratio for mode-3 tars (about 0.76) was about 25% lower than that for mode-4 tars (H/C atomic ratio about 1.0). This was additional evidence of the selectivity of CaO chemistry for aromatics removal from coal tar, to achieve a given conversion level through thermal treatment over CaO.

The results of nitrogen analysis were somewhat scattered. This was presumably due to a small amount of residue pyridine (used as one of the extracting solvent for tar recovery) which remained in the tar sample even after the solvent removal process which included about half an hour vacuum drying at 50 - 60°C.

The nitrogen and sulfur contents of mode-3 tars appeared to be insensitive to the cracking temperature (Table 5.8-2). Oxygen content showed a decreasing trend with temperature which
reflected the occurrence of cracking of ethers and phenolics in coal tar mixture under these thermal conditions (see Section 5.8.3). A corresponding increase in CO yield was also observed (Section 5.4.2).

Tar cracked in the presence of CaO typically had lower contents of nitrogen, oxygen and sulfur than those of mode-3 runs at the same temperature. The oxygen and sulfur content appeared to be declining with increasing cracking temperatures. The former could be related to the enhanced cracking of phenolics over CaO (see Section 5.8.3). The analysis of nitrogen and sulfur containing hetero-atom compounds (such as pyridines, carbazoles, thiophenes, and diaryl sulfides) of coal tar, however, was not attempted in this work.
5.9 Chemisorption Study via Measurement of the Electrical Resistance of CaO

Both the aromatics and calcium oxide (when titrated at low temperatures) are well known to be basic (electron donating) in nature. Given that many conventional cracking catalysts are acidic, it was therefore unexpected and interesting to find out that calcium oxide exhibits a strong activity for enhanced thermal cracking of both pure polycyclic aromatic hydrocarbons (Ellig et al., 1985; Longwell et al., 1985a), and freshly formed, highly aromatic coal pyrolysis tars (Longwell et al., 1985b) (also see Section 5.4.1).

Another interesting and surprising phenomenon also deserves special attention. It has been repeatedly observed that there was always a limited but finite amount of CO (as well as CO$_2$, whose absolute yield was typically one to two orders of magnitude smaller than that of CO) evolved during pyrolysis of oxygen-free, pure aromatic hydrocarbons over calcium oxide (obtained by calcining calcium hydroxide or calcium carbonate) in an inert (helium) environment (Lai, 1986; Longwell et al., 1985a). A similar finding was also reported for the pyrolysis of ethane over lime between 600 and 980$^\circ$C (Elliott, 1963). It is, therefore, highly desirable to identify the source of these mysterious oxygen species, and to explain the unusual ability of the calcium oxide surface to enhance cracking of aromatics.
5.9.1 Chemisorption Studies Over Calcium Oxide

The fact that Longwell et al. (1985a) observed that the CO yield dropped rapidly with pyrolysis of successive aliquots of 1-methylnaphthalene over the same packed-bed of calcium oxide, indicates that the oxygen was primarily from a limited, internal source, and not due to leakage of atmospheric air. It was concluded that the oxygen must originate from the calcium oxide itself.

It is believed that an alkaline earth metal oxide obtained by calcining the corresponding hydroxide or carbonate, contains, in addition to near stoichiometric quantities of O²⁻ anions, a small but non-trivial amount of O⁻ anions (a more detailed rationale will be given in the next Section). Briefly, at high-enough temperatures, O⁻ becomes unstable and diffuse from the bulk to the surface of the oxide. This eventually leads to the evolution of atomic oxygen which has been observed during calcination of magnesium hydroxide (Martens et al., 1976). Presently, we are unaware of corresponding observations for Ca(OH)₂. However, this oxygen moiety seems a very likely source of the CO evolved during pyrolysis of carbonaceous materials over CaO.

This diffusion process, would also eventually reverse the surface charge of the alkaline earth metal oxide, from a negative sign to a positive one. The oxide surface therefore would change from that of electron-donating (i.e., basic, as
determined by wet chemistry titration techniques (Take et al., 1971; Longwell et al., 1985a) at low temperatures, to that of electron-accepting (acidic) at high temperatures.

To assess the applicability of the above picture for calcium oxide employed in this research, one must identify a method which can 'titrate' the oxide surface in-situ at high temperatures. Obviously, this cannot be achieved by conventional (wet chemistry) titration techniques. The method we chose was to measure the effects of chemisorption (at temperatures over 400°C) of various gases or vapors (such as H₂, O₂, C₂H₄, toluene, etc.) on CaO surfaces on the electrical resistance of the calcine. The apparatus and procedure for the chemisorption studies over CaO are described in Section 4.2.4.

It was found that there was a strong and fast chemisorption reaction of hydrogen on the CaO surface. At 485°C, for example, the resistance of a fresh CaO sample prepared in-situ as described in the previous section, was 1.9 x 10⁹ ohms in the inert environment (1 atm helium). It was quickly reduced to 1.0 x 10⁹ ohms upon introduction of about 50 torr of hydrogen into the helium carrier gas. However when the H₂ was removed from the helium gas stream, the stone's resistance did not return to the original value. Instead, a steady state resistance of 1.4 x 10⁹ ohms was observed after about 5 minutes. This result suggested that part of the hydrogen chemisorption on CaO was irreversible, at least within the time scale of this experiment. The reversible part of the chemisorption can be cycled many times without significant changes in the steady
state measurements.

The equilibrium equation for the reversible part of the hydrogen chemisorption is hypothesized as

$$H_2(g) + 2 O^- (s) \rightarrow 2 OH^- (s) + 2 e^- (s) \quad \text{Eq.(5.9-1)}$$

The availability of more mobile charge carriers, namely the electrons liberated by Reaction (5.9-1) is a possible explanation for the observed decrease in the electrical resistance of the CaO on introducing $H_2$ (Ashmore, 1963). Increase in concentrations of mobile ionic species in a solid electrolyte, such as CaO with crystal defects, could be another explanation (Choudhary et al., 1980). However, the precise mechanism responsible for this effect is as yet uncertain.

The electrical resistance of the stone was also found to be a function of the hydrogen partial pressure in the system, as shown in Figure 5.9-1. It dropped sharply, as at $402^\circ C$, from $1.6 \times 10^{10}$ ohms in an inert (helium) environment, to $1.1 \times 10^{10}$ ohms when a small amount (about 0.3 torr) of hydrogen was introduced over CaO. It then declined at a slower rate, e.g., to $4.0 \times 10^9$ ohms in the presence of about 200 torr hydrogen. On the other hand, essentially no change in the CaO electrical resistance was observed when oxygen gas (which acts as an electron-accepting species) was introduced into the system under otherwise identical experimental conditions.

The results of resistance measurements, for CaO in equilibrium with various gaseous environments at $501^\circ C$ are summarized
Fig. 5.9-1 Effect of $H_2$ and $O_2$ Partial Pressures on the Electrical Resistance of CaO (Prepared from Calcining Iceland Spar).
in Table 5.9-1. Toluene and benzene contain aromatic \( \pi \)-electrons, and thus can act as electron-donating (basic) agents. The observed reduction in the CaO resistance upon exposure to either compound can therefore be explained by their becoming chemisorbed on the CaO surface and then supplying electrons to the calcine.

On the other hand, no significant resistance reduction was observed with heptane, cyclohexane, or ethylene implying an absence of chemisorption or inadequate basicity (electron donating power) for these compounds. The ethylene behavior is consistent with the fact that its \( \pi \)-electrons are more tightly bound than those of the aromatics and suggests that the mere presence of \( \pi \)-bonding will not guarantee high conversion activity over CaO.

5.9.2 The Existence of \( O^- \) Ion and Its Effect on The Surface Property of CaO

Based on the above observations, one can conclude that the surface of CaO, though well-known to be basic at low temperatures (Take et al., 1971), is indeed acidic in nature at higher temperatures (perhaps \( \geq 400^\circ C \)). This observation is, to the best of our knowledge, the first direct experimental evidence suggesting that the CaO surface actually behaves as a Lewis acid, i.e., an electron-acceptor (see Eq. 5.9-1) at these temperatures.

At this time, there is no experimental evidence that
Table 5.9-1 Electrical Resistance of Calcium Oxide\textsuperscript{(a)} as a Function of Gaseous Environment\textsuperscript{(b)}

<table>
<thead>
<tr>
<th>Gaseous Environment</th>
<th>Resistance ($\Omega \times 10^9$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>1.7</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.3</td>
</tr>
<tr>
<td>Heptane</td>
<td>1.7</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.7-1.8</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.5</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>1.7</td>
</tr>
</tbody>
</table>

\textsuperscript{(a)} Resistance measured at 501°C, the oxide was prepared by calcining an Iceland spar single crystal which was about 1.0 cm in thickness.

\textsuperscript{(b)} The liquid samples and C$_2$H$_4$ were so introduced that CaO was in equilibrium with about 2 torr of the various hydrocarbon gases in helium carrier gas at a total pressure of 1 atm.
directly supports the mechanism briefly described above to account for this interesting reversal of CaO surface behavior from basic to acidic at high temperature. However, the work of Martens et al., (1976) on the calcination of magnesium hydroxide sheds some light on the general picture of the formation of an alkaline each metal oxide from its corresponding hydroxide (and similarly from its carbonate). In their work, the formation of MgO by thermal decomposition of high purity Mg(OH)$_2$ was accompanied by evolution of molecular hydrogen (300-900°C) and atomic oxygen (600-900°C) in addition to the expected evolution of water. Each of these species was observed mass spectrometrically.

It is believed that 'residual water' remains within the crystal of an alkaline earth metal oxide derived by calcining the corresponding hydroxide even after decomposition of the hydroxide is apparently complete. The oxide has a cubic crystalline structure formed from recrystallization of the hexagonal structure of the parent hydroxide. The 'residual water' exists within the cubic oxide lattice, in the form of OH" groups. The evolution of molecular hydrogen can then be attributed to formation of H$_2$ within a cation vacancy in the oxide by reaction of two residual OH" anions (Derouane et al., 1974)

$$2 \text{OH}^- \rightleftharpoons 2 \text{O}^- + \text{H}_2$$

Eq.(5.9-2)

Or, to a lesser extent, it can originate from the thermal dissociation of individual residual OH" groups, followed by
recombination of hydrogen atoms which, due to their small sizes, can diffuse through the ionic lattice of the oxide relatively easily to form $H_2$:

$$\text{OH}^- \rightarrow 0^- + 1/2 \text{H}_2 \quad \text{Eq.(5.9-3)}$$

Either mechanism leads to the formation of $0^-$ ions which correspond to singly charged positive holes since a regular (defect-free) sublattice exactly balances the positive charges of the matrix of $Ca^{2+}$ sites by a corresponding number of $O^{2-}$ sites. The oxide crystals, thus obtained from decomposing the hydroxide, acquire a stoichiometric excess of $\xi$ oxygen atoms per magnesium atom. An overall charge balance is still maintained since the defect-containing crystal has the formula $Mg^{2+}O_\xi^{2-}$. $O_{2\delta}^-$. 

An alkaline earth oxide prepared from a corresponding carbonate is also believed to contain $0^-$ ions. This is presumably due to the evolution of a small amount of $CO$ in addition to the regular $CO_2$ evolution during calcination of the carbonate. To the best of our knowledge this behavior has not been confirmed although the following reaction of a residual $CO_3^{2-}$ site could give $CO$ evolution and a residual lattice inventory of $0^-$ ions:

$$CO_3^{2-} \rightarrow CO + 2 \text{O}^- \quad \text{Eq.(5.9-4)}$$

According to Martens et al (1976), in the case of magnesium oxide, the $0^-$ ions (or more likely the $O^- - O^-$ peroxy anion pair trapped adjacent to and electrically compensated by an $Mg^{2+}$
cation vacancy) become unstable above 800 K. The peroxy anion decays by releasing a positive hole, i.e., an \( O^- \) ion. Thus the \( O^- \) ion is no longer bound within a localized cation vacancy.

It was found that the unbound positive hole is very difficult to detect by electron paramagnetic reasonance (EPR) spectroscopy (Wertz and Henderson, 1977). This fact suggests that the concentration of \( O^- \) ions is very low or that these ions are extremely mobile within the \( O^{2-} \) sublattice. (This 'mobility' may be achieved by transport of electrons through the \( O^{2-} \) lattice.) Once the \( O^- \) ion reaches the oxide surface, it may recombine with another positive hole (\( O^- \) ion) and the resulting anion pair may undergo the following disproportionation reaction to release an oxygen atom

\[
2 \ O^- \rightarrow 0^{2-} + \text{anion vacancy} + 0^+ \quad \text{Eq.(5.9-5)}
\]

and leave both a regular \( O^{2-} \) anion and an anion vacancy at the oxide surface.

At low to moderate temperatures, the surfaces of alkaline earth metal oxides are probably negatively charged as indicated by the basicity measured at room temperature by non-aqueous titrations (Take et al., 1980; Longwell et al., 1985a). The subsurface (bulk) space-charge layer must carry compensating positive charges to maintain overall charge neutrality.

At high temperatures, as discussed earlier, \( O^- \) becomes mobile and diffuses from the bulk to the surface of the oxide, carrying with itself an effective positive charge through the
ionic lattice. After $O^{-}$ ions reach the surface and react according to Eq.(5.9-5), positive charges (associated with the anion vacancies) become permanently fixed on the stone surface. This process is believed to eventually reverse the surface charge of the alkaline earth metal oxide to a positive value. The oxide surface therefore changes from electron-donating (basic) at low temperatures to electron-accepting (acidic) at high temperatures.

The results of our chemisorption studies strongly indicate that this general picture of high temperature surface charge reversal for alkaline earth metal oxides prepared from their corresponding hydroxides or carbonates holds true for calcium oxide as well as magnesium oxide. One could then easily account for the origin of the oxygen evolved as CO during pyrolysis of pure hydrocarbon compounds over calcium oxide (Longwell et al., 1985a; Elliott, 1963)(also see Section 3.2.2).

The ability of CaO to selectively enhance the cracking of aromatic compounds may thus be due to promotion of an electron donor-acceptor chemisorption reaction by an electro-positive (acidic) CaO surface at high temperatures. Once chemisorbed on the CaO surface the aromatics undergo further reactions such as dissociation and polymerization to form coke, a small amount of light hydrocarbon gases and molecular hydrogen. The latter was found to be the major gaseous product in our studies of coal tar pyrolysis over CaO. Its formation may arise from the reverse of reaction (5.9-1) above
\[ 2 \text{OH}^- (s) + 2 e^- (s) \rightarrow 2 \text{O}^{2-} (s) + \text{H}_2 (g) \quad \text{Eq. (5.9-6)} \]

where hydrogen was from dehydrogenation of aromatics catalyzed by the CaO surface.
5.10 Modeling of Tar Cracking Over CaO

The external mass transfer limitations were shown to be insignificant in this study of coal tar-CaO interactions, since at constant contact time the overall tar conversion over CaO was insensitive to carrier gas flow rate (see Section 5.3.1).

The overall tar conversion was also found to be largely unaffected, when the size of CaO particle was varied over a limited range (from \(< 5\) micron, i.e., the powder typically used in this work, to about \(40\) micron). This suggested that, at least for the lighter tar molecules (\(\text{MW} \leq 500\) g/mole), the pore diffusion limitations are unimportant when powdered form CaO was employed (see Section 5.3.2). The global kinetics, for tar cracking over CaO powder, obtained in this work could therefore be considered to be an adequate approximation to the 'intrinsic' kinetics.

A useful, global kinetic model describing tar cracking behavior over CaO should account for the chemical complexity of the coal tar mixture as well as treat the transient behavior of calcium oxide activity due to coke formation on the oxide surface.

5.10.1 Important Parameters For Characterizing Tar Reactivity

There are many analytical procedures and techniques which are useful tools for characterizing either detailed or various
global properties of coal tar mixtures. These include, e.g.,
column chromatography, gas chromatography-mass spectroscopy
(GCMS), NMR, GPC, elemental analysis, and thermometric titra-
tion.

The method of GCMS would give very detailed compositional
information on the lower MW compounds in tar, but the amount
of effort required to achieve this makes it impractical to be
used in this work. Further, this amount of information would
likely be more than could be effectively utilized in a mathe-
matically treatable model. Column chromatography, which typi-
cally separates complex mixtures into fractions of known chemical
functionality, was also found inadequate to be used in this study
(see Section 5.8), mainly because of the problem of poor overall
material balance achievable.

It was observed, at least qualitatively, that tar fractions
of different molecular weight (MW) cracked over CaO at different
rate. This was so, presumably because (in the absence of pore
diffusion limitation) the molecular size (or more appropriately,
the number of aromatic ring clusters) of a tar molecule (which
associates qualitatively with the MW), is closely related to the
cracking reactivity of different aromatics system over CaO (Lai,
1986).

Furthermore, no MW sub fractions of tar were found to be
preferentially enriched in hetero-atoms and chemical chromophores
that exhibit high thermal reactivity over CaO (e.g., phenols).
This was demonstrated by first preparing tar fractions of more
narrow molecular weight (size) distribution (MWD), from a fresh sample of primary pyrolysis tar. Six such fractions (each >100 mg), where MWD curves are given in Figure 5.10-1, were prepared by using a preparative scale GPC column.

The elemental as well as acidic group (mostly phenolic) contents of each separated tar sample were then determined as a function of the average molecular weight of the tar fraction. The elemental oxygen analyses were performed by Huffman Laboratories, Inc. (Wheat Ridge, CO). The phenolic (acidic) oxygen functional group analyses were done in our laboratory via thermometric titration, a wet chemistry technique. A detailed description of the titration apparatus, and the operating procedures are given in Section 4.3.3.

The results of elemental oxygen analyses for the six separated coal tar samples are shown in Figure 5.10-2. The weight percentage of elemental oxygen was about 7.4 ± 1.8 % for all the tar fractions analyzed. No major dispersion in the distribution of elemental oxygen was observed, for the M.W. range of the primary pyrolysis coal tars of interest.

The results of enthalpimetric titration determinations of the phenolic oxygen content of each tar fraction, are given in Figure 5.10-3. It can be seen that about 50 - 60% of the elemental oxygen in each tar fraction was acidic in nature. However this value may be a lower estimate, since phenolics, being more polar and reactive, may be partially lost due to irreversible adsorption on the packing of the preparative scale GPC. The
Fig. 5.10-1 Performance of the Prep-GPC Used for Separating Coal Pyrolysis Tars.
Fig. 5.10-2  Oxygen Contents of Coal Tar Fractions

Fig. 5.10-3  Phenolic Oxygen Content of Coal Tar Fraction
titration results also indicated that phenolic oxygen contents were relatively evenly distributed throughout the MW range of the primary tar samples.

The molecular weight, which can be related to the average numbers of aromatics rings, was therefore chosen as the major structural parameter for characterizing the different cracking reactivity of different coal tar components over CaO. A simplifying approach of lumping the whole tar into four sub fractions (with MW ranges of < 340, 340-395, 395-575, and > 575 g/mole, respectively) was determined to be adequate for modeling purposes. The first two fractions corresponded to major peaks of tar sample separable by the GPC.

As discussed in Section 5.5, the global tar cracking kinetics and the CaO deactivation behavior were examined by studying how the CaO activity for overall tar cracking, changed as a function of cumulative feed/CaO weight ratio. In order for the four-lump model to be applicable, the data provided in Figure 5.5-1 were recast to give conversion information for each of the four tar lumps defined above.

Only the conversion data for cracking temperatures between 500 and 600°C were used for this purpose. The data obtained at 700°C, on the other hand, gave 100% conversion at 0.05 cumulative tar/CaO ratio, and therefore could not be used for kinetic study.

It was found that the response, per unit mass of tar, of the UV detector (at 405 nm) used for GPC, was approximately uniform over the MW range studied. The weight fraction and yield
of each tar lump could then be determined from the corresponding GPC areas (assuming 100% tar recovery from the GPC column) and knowledge of the total yield of tar that survived thermal treatment.

Conversion information on individual MW lumps thus determined is given, as a function of the cumulative tar/CaO ratio, in Figures 5.10-4 to 5.10-7 for tar cracking at 500, 525, 550 and 600°C respectively.

The general trend similar to that in Figure 5.5-1 was again observed, despite some scatter in the data. The activity of CaO for cracking each tar lump, typically decreased at a faster rate initially, then at a slower rate with increasing tar/CaO ratio (or equivalently, coke content of CaO). The only probable exception was at 500°C for tar lump-4 (MW > 575 g/mole), as shown in Figure 5.10-4, whose conversion appeared to be relatively insensitive to the coke content of CaO.

5.10.2 CaO Deactivation due to Coke Formation

The observed deactivation of the CaO tar cracking activity with increasing coke content was believed to be a direct consequence of indiscriminant adsorption and deposition of carbonaceous material onto the CaO surface (i.e., all CaO sites were equally available for coke deposition). The stone's sintering process, if it indeed occurred, would also reduce the overall activity of CaO by decreasing its effective surface area. Since
Cracking Temp. = 500°C
\( t_{\text{hetero}} = 0.12 \text{ s} \)

**Fig. 5.10-4** Effect of Cumulative Tar/CaO Ratio on Conversion of Different Tar Fractions.

* Conversion is defined as % conversion of corresponding fraction of tar that survived homogeneous thermal reactions.
** M.W. ranges (g/mole) of fractions of coal tar.
Fig. 5.10-5  Effect of Cumulative Tar/CaO Ratio on Conversion of Different Tar Fractions.

* Conversion is defined as % conversion of corresponding fraction of tar that survived homogeneous thermal reactions.
** M.W. ranges (g/mole) of fractions of coal tar.
Fig. 5.10-6  Effect of Cumulative Tar/CaO Ratio on Conversion of Different Tar Fractions.

* Conversion is defined as % conversion of corresponding fraction of tar that survived homogeneous thermal reactions.
** M.W. ranges (g/mole) of fractions of coal tar.
Fig. 5.10-7 Effect of Cumulative Tar/CaO Ratio on Conversion of Different Tar Fractions.

* Conversion is defined as % conversion of corresponding fraction of tar that survived homogeneous thermal reactions.
** M.W. ranges (g/mole) of fractions of coal tar.
most of the tar cracking reactions took place within half an hour, during which period CaO was essentially exposed to an inert helium environment (with typically less than $10^{-3}$ atm of CO$_2$ and H$_2$O present), the extent of this thermal sintering was therefore not expected to be significant.

The initial 'fast' deactivation was presumably due mainly to direct site suppression, i.e., the CaO lost activity because the active site was covered by the coke molecule (Dadyburjor, 1983).

The activity of CaO was never lost completely in the 'slow' deactivation regime, even after the amount of coke deposited was sufficient to provide several monolayers of coke on the CaO surface (assuming the surface area measured by N$_2$ BET adsorption technique was all available for coke formation and carbon atom (coke) surface areas of about 4 Å$^2$). This residual cracking activity might be due to the contribution from cracking over coke, over CaO-enhanced coke, and/or residual activity of CaO.

A small fraction of the CaO surface could be constantly available for tar cracking, even after extensive coking, presumably through segregation of surface deposits to form 3-dimensional islands of multilayer coke on the CaO, a process similar to that proposed by Somorjai and Zaera (1982) for surface reactions on platinum catalysts. The multilayer coke could also be formed by a growing filament mechanism (Baker and Harris, 1978) above surface activated sites. The slow decrease in cracking activity of stone during this latter stage could be mainly caused by the monotonically increasing filling of the pore by coke deposits (Dadyburjor, 1983).
5.10.3 Formulation of the Kinetic Model

A model was developed, based on the above discussions, to describe the kinetics of tar cracking reactions over a packed bed of CaO undergoing simultaneous deactivation due to coke deposition and surface area reduction. Since the concentration of coal tar was so dilute (typically less than $10^{-7}$ mole/cm$^3$) that there was no discernible temperature changes measured during a pyrolysis reaction, the packed bed was considered spatially and temporally isothermal.

The CaO packed bed could be treated as a plug flow reactor, since the axial dispersion would not be significant for an isothermal packed-bed with a ratio of bed depth (about 5 cm) to particle diameter (about 300 micron) much greater than 50 (Carberry, 1976).

By considering material balance, a set of continuity equations for each of the four tar lumps and the total coke formed on the CaO surface were derived as

$$
\frac{\partial f_i}{\partial z} = -\frac{\rho s A_d b}{F} r_i , \quad i=1,4 \quad \text{Eq.(5.10-1)}
$$

and

$$
\frac{\partial C}{\partial \theta} = \frac{\varepsilon \rho_1 A_d b}{FM_1} r_c \quad \text{Eq.(5.10-2)}
$$

where
$d_b$: bed depth (m);

$Z$: dimensionless axial distance from the top of packed bed, scaled by $d_b$;

$\rho_s$: bulk density of catalyst (kg/m$^3$ of reactor volume);

$A$: reactor cross-sectional area ($m^2$);

$F$: molar flow rate of feed (helium + tar), (mole/min);

$\varepsilon$: bed void fraction;

$\rho_1$: Vapor density of tar lump 1 at the cracking temperature (kg/m$^3$);

$M_1$: mean MW of tar lump 1 (kg/mole);

$\theta$: dimensionless time, scaled by $\varepsilon \rho_1 d_b A/FM_1$;

$f_i$: mole fraction of tar lump $i$ in the fluid;

$C$: CaO coke content (kg coke/kg of CaO);

$r_i$: rate of disappearance of tar lump $i$ [mole of lump $i$/(min * kgCaO)];

$r_C$: rate of coke formation on CaO, [kg coke/(min * kgCaO)].

The heterogeneous reactions of coal tar over CaO are presumably better described by Langmiur-Hinshelwood type kinetics than by a simple first order reaction. However, first order kinetics would be a good simplifying approximation if the reactant concentrations were very dilute (see also Section 5.6.1), as is the case in this study. The rate terms in Eq.(5.10-1) were proposed as
\[ \rho_{s_i} = \epsilon A_s N [\phi k_i f_i + (1-\phi) k_c f_i] \times \phi_A \quad \text{Eq. (5.10-3)} \]

where

- \( k_i \): specific rate coefficient for tar lump \( i \) cracking over cokeless CaO, \((\text{min} \times \text{m}^2/\text{g of CaO})^{-1}\);
- \( k_c \): rate coefficient for tar cracking over coke or coked CaO, \((\text{min} \times \text{m}^2/\text{g of stone})^{-1}\);
- \( N \): total concentration at the cracking temperature \((\text{moles/m}^3 \text{ of fluid})\);
- \( A_s \): specific surface area of cokeless CaO \((\text{m}^2/\text{g})\);
- \( \phi \): deactivation function;
- \( \phi_A \): area effectiveness factor.

The rate of coke formation, i.e., the term \( r_c \) in Eq. (5.10-2), was then proportional to the total cracking rate of lumps 1 through 4 (the conversion factor (by weight) for coke formed from cracked tar was experimentally determined to be about 0.8 - 0.85).

The first term in the bracket of Eq. (5.10-3) accounted for the initial rapid decay of the CaO activity, where \( k_i f_i(*N) \) represents the specific cracking rate (based on unit surface area of CaO) of tar lump \( i \) over the coke-free active sites, and the deactivation function (i.e., \( \phi \)) is a measure of the fraction (which varies from 1 to 0) of original active sites remaining active, i.e., not covered by coke deposits. The most common
approach in the literature is to empirically relate the number of sites covered by coke to the coke content of catalyst, since the direct information on the fraction of site covered by coke is yet unavailable.

It has been suggested that the relationship between the deactivation function ($\phi$) and the coke content of catalyst ($C$) could be adequately described by an exponential function (Froment and Bischoff, 1979; Lai, 1986):

$$\phi = \exp(-\alpha C) \quad \text{Eq. (5.10-4)}$$

where $\alpha$ is the deactivation coefficient (kg coke/kg of CaO)$^{-1}$.

Experimentally it was observed that the CaO deactivation behavior could be best described by introducing a different characteristic deactivation function for each corresponding tar lump. For the sake of simplicity for mathematical modeling, it was found that the use of one single deactivation function for all tar lumps was generally a good approximation, with the possible exception of tar lump 4 whose cracking rate appeared to be less affected by the CaO deactivation.

The value of $\alpha$ could be determined directly from the knowledge of change of catalyst activity and its coke content if the reaction could be described by simple (such as first order) kinetics and was studied in a differential reactor. In this thesis work, however, the experiments were carried out in an integral, fixed-bed reactor, and the cracking reaction kinetics
involve two coupled rate terms as given in Eq. (5.10-3), the deactivation coefficient therefore could not be determined \textit{a priori} and must be derived from data fitting (which will be described later).

The second term in Eq. (5.10-3) accounted for the residual activity of CaO after extensive coking had taken place, where \((1 - \phi)\) is the fraction of original sites that were covered by the coke deposits, and \(k_c f_i (\ast N)\) the specific cracking rate of tar lump \(i\) over the coke-covered sites.

As discussed in Section 5.10.2, the residual activity of CaO for tar cracking could be due to the contribution from cracking over coke, over CaO-coke sites, and/or over the residual coke-free CaO active sites. The exact mechanism responsible for the residual cracking activity is yet uncertain.

This is because that there was not enough information to provide evidence as to whether the selectivity for enhanced cracking of aromatics and phenolics, and the results of low relative yield of light hydrocarbon gases (both are characteristic of CaO chemistry) would change and had changed with increasing coke content of CaO. However, the same mathematical form of rate equation (Eq. 5.10-3) applies equally to any one of the mechanism described above.

\textbf{The Area Effectiveness Factor}

Also in Eq. (5.10-3), the variation with cracking temperature
(Figure 5.1-2) and with coke content of CaO (due to pore filling) of the effective surface area of CaO available for tar cracking, was accounted for by the term denoted area effectiveness factor, $\phi_A$. This quantity is a ratio of the surface area of CaO available at any time during tar cracking, to the initial CaO surface area prior to tar introduction.

In order to derive a relationship between this factor and the coke content of CaO, it was assumed that coke formation was uniform across the CaO surface. This was equivalent to assuming the tar cracking reactions were kinetically controlled and (with the exception of heavy tar fractions) were not rate limited by external or internal mass transfer. The conclusions from Section 5.3 indicated that this assumption was largely justified.

The width of the slit-shaped pores in CaO (prepared from Ca(OH)$_2$) used for cracking studies typically ranged from about 1.4 - 1.5 nm (the instrument limitation) to about 15 nm, as shown in Figure 5.1-3 (the BET measurement using N$_2$ as the adsorbate, was done by Porous Materials, Inc., Ithaca, NY). The most common slit widths were between 4 to 6 nm for CaO samples prepared for 700°C tar cracking runs. The pore-size distribution of CaO samples prepared for cracking runs below 700°C, though not experimentally determined, was expected to be similar to that shown in Figure 5.1-3, because complete calcination of Ca(OH)$_2$ (to prepare CaO) was always carried out at 500°C, and stone sintering was insignificant below 700°C.

The relationship between cumulative surface area and the
slit width of CaO pores could be determined from the pore size
distribution analysis. The dependence of the statistical thick-
ness of multilayers of adsorbed N₂ (a measure of the slit width),
on the relative pressure (P/P₀) (see Figure 5.1-3) was estimated
from the constant C used in the BET method (Beruto et al., 1980).
The specific surface area of CaO derived by this method (about
51 m²/g CaO) was in good agreement with that obtained by the BET
measurement (about 46 m²/g CaO).

It was found that a semi-log correlation (Eq. 5.10-5) could
satisfactorily describe the relationship between slit width of
pores (dₛ, in unit of nm) and the cumulative surface area (Sₐ,
m²/g CaO) of pores with slit width larger than dₛ:

\[ \ln(Sₐ) = -0.2114 \cdot dₛ + 4.2434 \]  
Eq.(5.10-5)

Obviously, the total number of CaO active sites (or equi-
valently, the 'active' surface area) would be better charac-
terized by adsorption studies using proper reagents such as benzene,
instead of nitrogen as the adsorbate. However, such measurements
required dedicated BET or TGA instruments with proper modifi-
cations (e.g., for benzene adsorption studies) and were not
performed in this work. Instead, the following discussions are
based on the assumption that all the CaO surface areas measured
by the nitrogen BET adsorption technique are also available for
tar cracking reactions.

The area effectiveness factor could therefore be calculated
from the coke content of CaO by using Eq.(5.10-5) and a knowledge of the critical dimensions of carbon atoms which presumably were the major constituents of coke deposits. For example, if each carbon atom in coke was assumed to have a linear dimension of about 0.2 nm and to occupy about 0.04 (nm)$^2$ of cross-sectional area (Weisz and Goodwin, 1966), then for CaO prepared at 700$^\circ$C cracking temperature, a 12 Wt% coke content corresponded to about six atomic layers of carbon on the CaO surface.

The area effectiveness factor for such a coked CaO would be about 0.8, since pores with widths less than 2.4 nm would be filled by the formation of coke. The effectiveness factor thus estimated is most probably an upper-limit value, since in practice accumulated coke deposits could cause pores to become so narrow that they were essentially 'choked' (i.e., they presented prohibitively high resistance to mass transfer) before they actually became completely filled.

The above proposed scheme for calculating area effectiveness factor was tested by actually measuring the available surface area of a coked CaO sample (with about 21 Wt% coke content) employed for a 700$^\circ$C tar cracking run. The agreement between the average value of the predicted effectiveness factor (about 0.5) and the experimentally determined value (about 0.43 - 0.53) for the coked CaO sample was quite good. This result suggested that the assumptions proposed in deriving the above relationship were probably adequate.

Also involved in deriving Eq.(5.10-3) was the assumption
that the specific (per unit surface area) cracking activity of CaO (and coked CaO) could be treated as constant at a given temperature. The changes in overall cracking activity of CaO, at different coke contents, could therefore be scaled according to the corresponding changes in the overall available surface area of the CaO.

Comparison of Experimental Data and Model Predictions

The coupled equations (5.10-1) and (5.10-2) were solved numerically, using the modified Euler's method. The computer program is given in Appendix F. The adjustable parameters in the kinetic model were: one rate constant \( k_1 \) for each tar lump (for cracking reactions over coke-free CaO), one rate constant \( k_c \) for all tar lumps (for tar cracking over coked CaO) (Eq. 5.10-3), and one deactivation coefficient, \( \alpha \), which determined the deactivation function \( \phi \) (Eq. 5.10-4).

The area effectiveness factor \( \phi_A \), on the other hand, was directly related to the coke content of CaO and the cracking temperature (see discussions in the last section), and was therefore not an adjustable parameter.

The adjustable parameters in Equations (5.10-3) and (5.10-4) were determined by best fitting the data on changes of conversion of tar lump \( i \) vs. cumulative tar/CaO ratio, obtained between 500 - 600°C cracking temperature (see Figures 5.10-4 to 5.10-7).

This was done by using the Powell computer routines that
perform non-linear least-squares regression and give the set of adjustable parameters used in the model that achieves best fit between model prediction and the data. The set of parameters thus derived were:

\[ k_1 = 7.57 \times 10^7 \exp \left(-\frac{26100}{RT}\right) \]
\[ k_2 = 3.82 \times 10^5 \exp \left(-\frac{15800}{RT}\right) \]
\[ k_3 = 1.27 \times 10^5 \exp \left(-\frac{13800}{RT}\right) \]
\[ k_4 = 3.60 \times 10^4 \exp \left(-\frac{12200}{RT}\right) \]
\[ k_c = 1.80 \times 10^6 \exp \left(-\frac{24200}{RT}\right) \]
\[ \alpha = 30.9 \]

where \( R = 1.987 \text{ cal/(g mole)(K)} \), and \( T \) is the absolute temperature.

The summaries of model prediction for tar cracking reactions under various conditions (i.e., between cracking temperature of 400 and 800°C, coal/Ca0 weight ratio of 0.2 to 2, and volatiles contact time of 0.06 to 0.24 sec) are given in Appendix G. The simplifying approach of using one single deactivation coefficient, \( \alpha \), for all four tar lumps generally resulted in over-predicting the yield of heavier tar lumps (especially at lower temperatures, see Figures 5.10-8 to 5.10-11), and sometimes under-predicting the yield of lighter tar lumps.

Fortunately, the heavier tar lumps typically represented only a small portion of the total tar, e.g., the yield of lump 4 tar was typically less than 10 Wt% and lump 3 less than 20 Wt%
Figure 5.10-8 Yield of Tar Lumps as a Function of Total Coke Content of CaO (Data and Model Predictions for Mode-4 Runs at 500°C Cracking Temperature).
Figure 5.10-9  Yield of Tar Lumps as a Function of Total Coke Content of CaO (Data and Model Predictions for Mode-4 Runs at 525°C Cracking Temperature).
Figure 5.10-10 Yield of Tar Lumps as a Function of Total Coke Content of CaO (Data and Model Predictions for Mode-4 Runs at 550°C Cracking Temperature).
Figure 5.10-11 Yield of Tar Lumps as a Function of Total Coke Content of CaO (Data and Model Predictions for Mode-4 Runs at 600°C Cracking Temperature).
of the total tar. The agreement between the model predicted overall tar yields (shown in lines in Figure 5.10-12) and the experimentally determined values (shown in various symbols), as a function of the average total coke content of CaO, was considered quite good (Figure 5.10-12).

The generality of this model was tested. The model (with parameters determined below 600°C and 15 Wt% coke content of CaO) was found to properly describe the tar cracking kinetics over CaO at 700 and 800°C and up to 20 Wt% of CaO coke content (see Figure 5.10-12). The apparent decrease in CaO activity at 800°C was mainly attributed to the reduction (by more than 50%) of its surface area, compared to that at 600°C.

The model was also used to predict the effect of volatiles contact time over CaO, on overall tar yield. The volatiles contact time was experimentally varied over a limited range (0.06 to 0.24 sec), by varying the absolute amounts of coal and CaO employed (0.5 to 2.0 g and 0.25 to 1.0 g, respectively) in the experiments, while keeping the coal/CaO ratio constant at 2 (W/W) and keeping the carrier gas flow rate constant.

The experimental results of overall tar yield (shown in symbols) as well as the model predictions (plotted as lines) are given in Figure 5.10-13, as a function of volatiles contact time over CaO. The prediction appears to be good for contact times less than 0.12 sec. The general trend of slight but apparent over prediction of overall tar yield for the runs at 0.24 sec volatiles contact time may suggest the existence of
Figure 5.10-12 Overall Tar Yields as a Function of Total Coke Content of CaO (Data and Model Predictions).

Average Total Coke Content (g/100g CaO)

Data

Model

Crack. Temp

500°C
525
550
600
700
800

Overall Tar Yield (g/100g Coal)
Fig. 5.10-13 Effect of Volatiles Contact Time on Overall Tar Yield (Data and Model Prediction).

* $t_{homo} = 2.0$ s; coal/CaO = 2.0 (w/w).
limitations for such a simplified model.

The model can also be used for predicting the profile of coke content of CaO as a function of bed depth. The results, plotted in Figures 5.10-14 to 5.10-16, show some interesting characteristics. At any given temperature and coal/CaO ratio, the CaO coke content declines with increasing bed depth, due to the corresponding decreasing concentration of tar available for coke formation. The rate of change of CaO coke content with the bed depth typically decreases slightly with increasing coal/CaO weight ratio, but increases significantly with increasing cracking temperature.

At higher temperature (e.g., 700°C, as shown in Figure 5.10-16), the model actually predicts complete tar conversion before the tar travels through the entire depth of the packed bed, for runs with coal/CaO weight ratios less than 0.4. This was qualitatively observed in the tar cracking experiments under similar conditions (i.e., at 700°C, with coal/CaO = 0.2).

In general, the decreasing trend of coke content profile with increasing bed depth was also visually observed. The color of the coked packed bed changed from dark black gradually to lighter black along the bed. Actual measurement of the weight of coke on CaO as a function of bed depth was not performed due to the instrument sensitivity limitations.

It is reminded that use of the proposed model must be done with care. For example, the assumption of describing the tar cracking reactions over CaO by first order kinetics will no longer
Fig. 5.10-14 Final Coke Content of CaO as a Function of Bed Depth (for 500°C Cracking Temperature).

* Weight ratio of Coal/CaO
Fig. 5.10-15 Final Coke Content of CaO as a Function of Bed Depth (for 600°C Cracking Temperature).

* Weight ratio of Coal/ CaO
Fig. 5.10-16 Final Coke Content of CaO as a Function of Bed Depth (for 700°C Cracking Temperature).

* Weight ratio of Coal/CaO
be valid at higher coal/CaO ratios, since competition of different coal tar constituents for the limited number of active sites on CaO surface will be a more realistic picture under these conditions.
6. **Conclusions and Recommendations**

6.1 **Conclusions**

The major conclusions of this study are summarized as follows:

(1) The extra-particle secondary reactions of the prompt primary tar generated from pyrolysis of a thin packed bed of Pittsburgh Seam No. 8 Bituminous coal (300 - 350 micron in sizes), were minimized in the tar generation reactor in this study. This is presumably due to a) the use of a low heating rate (3°C/min) that generates tars at relatively low temperatures (mostly between 430 - 490°C) where secondary reactions are insignificant, b) diluting the caking coal with an inert — SiC, and c) rapid dilution and removal of the volatiles from the coal by a superimposed helium flow that minimizes the volatiles contact time with the coal.

(2) Vapor phase secondary cracking of the tar between 600 and 800°C appears to occur mainly to the aliphatic fraction of coal tar as suggested by the NMR results. The absolute amounts of aromatic hydrogen remain relatively constant independent of the different degrees of tar conversion, indicating that the aromatic rings of coal tar are largely intact in the secondary reactions. The preferred aliphatic bond breakage occurs at positions beta or further away from the aromatic ring.

(3) The reactivity of the tar for homogeneous secondary cracking decreases with increasing tar formation temperature
over the cracking temperature range studied (500 - 800°C).
This is probably because the low temperature tar has higher
eratio of aliphatic to aromatic hydrogen, as suggested by the
\( ^1\text{H}-\text{NMR} \) results both of this work and of Serio's experiments

(4) The major products from the vapor phase cracking of
coal tar between 600 and 700°C are CH\(_4\), C\(_2\)H\(_4\), C\(_3\)H\(_6\), carbon oxides
and some H\(_2\). Between 700°C and 800°C (the highest temperature
studied), dehydrogenation and formation of coke on reactor walls
also occur.

(5) The presence of CaO (prepared from calcining micron-
size Ca(OH)\(_2\) or CaCO\(_3\) powder) significantly enhances the cracking
rate of prompt coal tar (by one to two orders of magnitude at
a coal/CaO weight ratio of 2), when compared to that for the
vapor phase tar pyrolysis in the absence of CaO.

(6) The major products for tar cracking over CaO are
coke and hydrogen. The relative yields of light hydrocarbon
gases (based on the amount of tar loss) are significantly lower
in the presence of CaO than in its absence.

(7) At the same conversion level, surviving tars have
significantly higher aliphatic to aromatic hydrogen ratios
and H/C atomic ratios when cracked over CaO, suggesting the
existence of special CaO-aromatics chemistry that enhances the
pyrolysis of the aromatic-rich fraction (with lower H/C ratio)
of tar.

(8) Vapor phase thermal cracking reduces the average
molecular weight (MW) of secondary tars mainly through breakage of the aliphatic linkages rather than the aromatic ring systems. Tar pyrolysis over CaO reduces the average MW by selectively enhancing the removal of higher MW molecules.

(9) The acidic content (mainly phenolics) of coal tar becomes susceptible to vapor phase thermal treatment above 700°C. This is indicated by a reduction in relative and absolute amounts of tar phenolic content as well as a corresponding increase in the yields of carbon oxides, especially the carbon monoxide. The content and absolute yield of phenolics in coal tar are further reduced in the presence of CaO between 400 and 800°C cracking temperature range. The CaO presumably enhances the removal of phenolics through the formation of calcium half-salts, at least at low temperatures (below 500°C).

(10) The specific metabolically induced bacterial cell mutagenicity of coal tar increases drastically due to homogeneous thermal cracking at 700 and 800°C, but is moderated in the presence of CaO, especially at 700°C.

(11) The MgO prepared from calcining MgCO₃ powder at 400°C (instead of the 500°C typically used for calcining Ca(OH)₂) is also active in catalyzing coal tar cracking. The specific tar cracking reactivity of MgO (based on the unit N₂ BET surface area of the freshly calcined stone) at 700°C is about half that of CaO. A possible explanation for this difference is discussed under conclusion (15).

(12) Tar pyrolysis over CaO in the presence of externally
introduced reactive gas(es) (such as steam or a mixture of CO₂, CO, CH₄, and H₂), results in decreased overall tar conversion as well as a significant reduction in CaO surface area (when compared to that for CaO runs in pure helium). Steam gasification of coke (which is catalyzed by CaO) is indicated by significant increases in H₂ yield and by reductions in the relative amount of coke (based on the weight of coal tar cracked) formed on CaO.

(13) CaO prepared from calcined CaCO₃ has larger average pore dimensions (> 10 nm) than that from Ca(OH)₂ (about 4 to 6 nm). Therefore, the higher molecular weight tar constituents (which should have higher affinity for the CaO surface if transport limitations are insignificant) should experience less resistance to intra-particle mass diffusion and, as was observed in this study, be cracked more efficiently over CaO prepared from CaCO₃ than that for CaO from Ca(OH)₂.

(14) The tar cracking activity of coked CaO can only be partially regenerated by O₂ burnoff of the coke deposits. However, essentially complete regeneration of activity can be achieved by appending the O₂ burnoff by hydration of the coke-free, deactivated CaO sample, and then recalcining it in-situ. The presence of sulfate in CaO enhances the stone sintering process.

(15) The CaO surface is well-known to be basic at room temperatures. However, the results of high temperature (400 - 500°C) chemisorption experiments lend strong support to the
picture that the surface of solid CaO functions as a Lewis acid (electron acceptor) at high temperatures (perhaps $\geq 400^\circ C$). The ability of CaO to selectively enhance the cracking of aromatics is presumably due to thermally promoted electron donor chemisorption reactions of these compounds with acidic sites on the CaO surface. The reversal of CaO surface properties is presumably achieved by diffusion of $O^-$ ions (which correspond to net positively charged defects in the CaO crystal) from the CaO bulk phase to the surface at high temperatures. This picture is in agreement with the fact that specific tar cracking activity of MgO is lower than that of CaO (see conclusion (11)), since the $O^-$ concentration in MgO would be lower due to the fact that its peroxide formation is less favored in the oxide crystal than that for CaO.

(16) The activity of CaO for tar cracking typically decreases at a faster rate initially, then at a slower rate with increasing coke content of CaO. This is presumably due to direct CaO active site suppression initially and, in the latter stage, pore filling of the stone by coke deposits from tar cracking. The residual cracking activity of coked stone persists even after the amount of coke deposited is sufficient to provide several monolayers of coke on the CaO surface. This might be due to contributions from CaO-enhanced cracking over coke, and/or residual activity of the CaO itself. However, the exact mechanism responsible for the residual activity is uncertain. Information on the effect of CaO coke content on
selectivity for cracking aromatics, phenolics vs. aliphatics, would shed further light on this question.

(17) A model is developed that uses molecular weight as a global parameter to characterize the different thermal reactivity of different tar fractions over CaO. The model describes the loss of CaO activity by considering both the site-poisoning mechanism and the process of pore filling (choking) due to coke deposition on the CaO surface. It is shown to properly describe the heterogeneous cracking of coal tar over a wide range of conditions, i.e., 0.05 - 0.5 (g/g) cumulative tar/CaO ratios, 0.06 - 0.24 sec volatiles contact times, and 400 - 800°C cracking temperatures.
6.2 Recommendations

Experimental

(1) Study the effect of coke content of CaO on the change in its selectivity for enhanced cracking of aromatics and phenolics (as compared to that of aliphatics), and for significantly lower relative yields of light hydrocarbon gases (than those for vapor phase cracking in the absence of CaO). This study would provide information for determining a mechanism responsible for residual stone activity described in conclusion (16).

(2) Identify conditions that would allow for extended period operation of tar cracking over CaO with less deactivation due to coke formation, or stone sintering. Gasification and removal of coke deposits in the presence of a reactive gaseous environment such as steam (conclusion (12)) could be enhanced by CaO which is a good gasification catalyst. Study the potential of maintaining the CaO cracking activity under conditions such as at elevated pressures of steam and/or CO₂, would be of great practical interest. This would require some modification of the reactor system for safety considerations.

(3) Study the effect of aging of coal, e.g., by different degree of pretreatment with air. This would better simulate the properties of coal tar produced in the commercial processes.

(4) Study further the activity of other alkaline earth metal oxide (i.e., MgO, SrO, BaO, dolomite or sulfated stones)
for the heterogeneous pyrolysis of coal tar. The information would be of practical use (e.g., commercially available dolomite contains MgCO₃ as well as CaCO₃, which can be calcined to produce corresponding oxides), and also of special interest from the mechanistic point of view.

(5) Use the technique of resistivity measurement to continue the study of chemisorption reactions of model compounds at moderate temperatures (in the absence of their pyrolysis), and the effect of reactive gases on these chemisorptions. Further improvement of the setup (e.g., the electrical contact, the power supply, etc.) for resistivity measurement is necessary.

(6) Use the thermo-gravimetric analyzer, approximating a differential reactor, to further study the kinetics of CaO—aromatics interactions. This would generally allow simultaneous determination of the changes in the stone's activity as well as the increases in the amount of coke formed. Experiments with model compounds would significantly simplify the analytical and data analyses.

(7) Employ surface characterization techniques (e.g., LEED, XPS) and a single crystal of CaO to examine, under better defined conditions, the interactions of aromatics with the CaO surface, and perhaps the morphology and distribution of coke deposited on the CaO from cracking reactions. These would allow more fundamental understanding of the CaO-aromatics chemistry as well as the deactivation mechanism for the stone.
(8) Perform further capillary column GC analyses of the light oils for experiments under different conditions. Although the light oil yields are found to be little affected by the presence of CaO in the base case study (in inert helium environment), the results may be different in the presence of reactive gas (e.g., H₂, steam) environment.

(9) Separate and characterize the tar mixture by additional chromatographic techniques. The use of HPLC, for example, combined with proper column packing material and elution procedure, would separate coal tar into fractions of similar ring numbers or functional groups with improved resolution and material balance. This may provide additional information on, and allow selection of, a more fundamental set of lumps for modeling tar cracking. It would also help to identify the fraction(s) that is (are) responsible for the mutagenic activity changes of the secondary coal tar at temperatures above 700°C.

**Modeling**

(10) Improve the lumping model for heterogeneous cracking of tar with more detailed analytical information. Determine the generality of the model by testing it on other types of coal tar to see if lumps are relatively insensitive to other properties of coal tar.
(11) Eventually extend the lumping model to account for the actual processes of reactant mass transfer, adsorption, surface reaction, and desorption, as well as a better description for the stone deactivation (e.g., considering the change of surface areas measured by benzene adsorption instead of by \(N_2\) adsorption BET analysis).
7. References


Collin, P.J., R.J. Tyler, and M.A. Wilson, "^{1}H-NMR Study of Tars from Flash Pyrolysis of Three Australian Coals," Fuel, 59, 497 (1980).


Cremer, E. and W. Nitsch, "Influence of the Pressure of CO\textsubscript{2} on the Rate of Decomposition of CaCO\textsubscript{3}," Electrochem., 66, 697 (1962).


8. Appendices

Appendix A

Calculation of Volatiles Residence Time

The volatiles residence time (R.T.) is calculated, based on the plug flow assumption, as follows:

\[ R.T. \ [\text{sec}] = \frac{\text{Reactor Length (or Bed Thickness)} \ [\text{cm}]}{\text{Linear Velocity of Gas} \ [\text{cm/sec}]} \]

\[ = \frac{a \ [\text{cm}^2]}{5000 \ [\text{scc/min}] \times \text{MFC}} \times \frac{T_0}{T_{R_1}} \times \frac{P_{R_1}}{P_0} \times L \times \epsilon \]

where

- 5000 = range of mass flow controller [scc/min],
- MFC = reading on indicator of mass flow controller [percent],
- \( T_0 \) = reference temperature for MFC (\( = 273 \) K),
- \( T_{R_1} \) = temperature of reactor-1 (\( i = 1, 2 \)) [K],
- \( P_0 \) = reference pressure for MFC (\( = 14.7 \) psi),
- \( P_{R_1} \) = pressure in reactor-1 (\( i = 1, 2 \)) [psi],
- \( a \) = cross-sectional area of reactor tube
  \[ = \pi \left(\text{I.D.}\right)^2/4 = 1.98 \ [\text{cm}^2] \]
- \( L \) = isothermal reactor length or packed-bed thickness [cm]
- \( \epsilon \) = voidage of the packed-bed

Constants used:

<table>
<thead>
<tr>
<th>Bulk specific volume</th>
<th>Voidage</th>
</tr>
</thead>
<tbody>
<tr>
<td>[cc/gm]</td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>1.5579</td>
</tr>
<tr>
<td>SiC</td>
<td>0.5988</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.8786</td>
</tr>
<tr>
<td>C.C.Q. (12.6 wt percent of Ca(OH)(_2))</td>
<td>0.9454</td>
</tr>
</tbody>
</table>
(1) For first bed (mode-1, -3, and -4)

\[
\text{Bed Thickness} = \frac{(1 \text{ gm coal})(1.5579 \frac{CC}{gm}) + (12 \text{ gm SiC})(0.5988 \frac{CC}{gm})}{1.98 \text{ cm}^2}
\]

\[= 4.42 \text{ [cm]}\]

\[L = \text{average traveling distance of volatiles generated in the first bed} = \text{Bed Thickness/2} = 2.21 \text{ [cm]},\]

\[\epsilon = (1 \text{ gm coal } \times \epsilon_{\text{coal}} + 12 \text{ gm SiC } \times \epsilon_{\text{SiC}})/13 \text{ gm} = 0.48,\]

\[T_{R_1} = (300 + 550)/2 = 425 \text{ [°C]} = 698 \text{ [K]},\]

\[P_{R_1} = \text{(measured value) [psi]},\]

(2) For Reactor-2 (Used in mode-3)

\[L = 12 + (4 + 4)/2 \text{ [inch]} = 40.64 \text{ [cm]},\]

\[\epsilon = 1.0,\]

\[T_{R_2} = \text{volatile cracking temperature [K]},\]

\[P_{R_2} = \text{(measured value) [psi]},\]

(3) For Reactor-2 (Used in mode-4)

\[(L)_{\text{hetero}} = \text{Bed Thickness (measured value) [cm]}\]

\[(\epsilon)_{\text{hetero}} = 0.52 \text{ (for the case of 12.6 wt percent C.C.Q.)}\]

\[(R.T.)_{\text{hetero}} = \frac{\text{Bed Thickness [cm]}}{\text{Linear Velocity of Gas [cm/sec]}}\]

\[= (\frac{1.98[cm^2] \times 60 \text{ [sec/min]}}{5000 \text{ [scc/min] } \times \text{ MFC}})(\frac{273}{14.7})(\frac{P_{R_2}}{T_{R_2}})\]

\[\times (L)_{\text{hetero}} \times (0.52) \text{ [sec]}\]

\[(L)_{\text{homo}} = 40.64 - (L)_{\text{hetero}} \text{ [cm]}\]

\[(\epsilon)_{\text{homo}} = 1.0\]
This is the most complete text of the thesis available. The following page(s) were not included in the copy of the thesis deposited in the Institute Archives by the author:

pg. 366
\[
(R.T.)_{homo} = \left( \frac{1.98 \text{ cm}^2}{5000 \text{ scc/min}} \right) \times 60 \left[ \frac{\text{ sec/min}}{\text{ min}} \right] \times \frac{T}{T_{R2}} \left( \frac{273}{14.7} \right) ^{\frac{P_{R2}}{T_{R2}}} \times (L)_{homo} \times (1.0) [\text{ sec}]
\]
Appendix B

Calculation of Evolution Rate of Gaseous Products

The evolution rate of each gaseous product is calculated from the corresponding area of the peak for each gas on the chromatogram, according to the following formula:

$$\text{(Evolution Rate)}_{ij} = \frac{A_{ij}}{A_{0j}} \frac{\text{RF}_{0i}}{\text{RF}_{ij}} \frac{\text{EXA}_j}{\text{ESF}_j} \times \text{CFR} \times [C_{0i}] \times \rho_i \times X \ [\text{mg/min}]$$

where

- $A$ = area of the chromatogram [arbitrary units]
- $\text{RF}$ = response factor [area/cc at 20°C]
- $\text{EXA}$ = external area factor; area for 0.1 cc injection of standard (CH4 or H2S) determined during calibration runs
- $\text{ESF}$ = external standard factor; area for 0.1 cc injection of standard (CH4 or H2S) determined during normal runs; compensates for changes in sensitivity of detectors
- $\text{CFR}$ = flow rate of carrier gas [scc/min]
- $[C_{0i}]$ = concentration of tracer gas [mole fraction]
- $\rho_i$ = density [mg/cc at 20°C]
- $X$ = conversion factor = 1.073 [cc at 20°C/cc at 0°C]

Subscripts:

- $0$ = tracer (argon)
- $i$ = gas species ($i = 1, 2, ..., 15$)
- $j$ = detector ($1 = \text{FID}; 2 = \text{FPD}; 3 = \text{HWD}$)
Appendix C

Redistribution of Extra Tars Recovered From Walls of Reactor and Valve

If the rate of tar deposition on the walls of reactor and valve is directly proportional to the true evolution rate of coal tars, i.e.,

\[ \frac{dA}{dt} = K \frac{dX}{dt} \]

where

- \( A \) = cumulative amount of adsorbed tars on walls,
- \( X \) = cumulative amount of tars truly evolved,
- \( K \) = proportionality constant,

then

\[ A_f - A_i = K(X_f - X_i) \]

where subscripts \( i \) = initial and \( f \) = final

and \( A_i = X_i = 0 \).

The total amount of tars actually collected by tar filters is \( Y_f \):

\[ Y_f = X_f - A_f = \left( \frac{1}{K} - 1 \right) A_f \]

The proportionality constant \( K \) can therefore be determined from known values of \( Y_f \) and \( A_f \):

\[ K = \frac{A_f}{Y_f + A_f} \]

and the corresponding \( X_t \) (corrected cumulative amount of tars evolved by time \( t \)) can be calculated as

\[ X_t = \frac{Y_t}{1 - K} \]
Example:

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Tars Trapped by Tar Filters (wt. percent of coal)</th>
<th>Corrected Cumulative Tar Yields (wt. percent of coal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>0.73</td>
<td>1.09</td>
</tr>
<tr>
<td>370</td>
<td>1.83</td>
<td>2.76</td>
</tr>
<tr>
<td>400</td>
<td>3.80</td>
<td>5.67</td>
</tr>
<tr>
<td>430</td>
<td>7.91</td>
<td>11.80</td>
</tr>
<tr>
<td>460</td>
<td>11.36</td>
<td>16.95</td>
</tr>
<tr>
<td>490</td>
<td>13.08</td>
<td>19.51</td>
</tr>
<tr>
<td>600</td>
<td>14.50</td>
<td>21.63</td>
</tr>
<tr>
<td>700</td>
<td>14.80</td>
<td>22.08</td>
</tr>
</tbody>
</table>

a. Extra tars (from walls of reactor and valve) = 7.28 wt. percent of coal.

b. \( K = 0.330 \).
Appendix D: Calibration and Operating Procedures of the Thermometric Titration System

The acidic hydroxyl content of a coal tar sample was typically determined by the non-aqueous thermometric titration technique as follows. First, a teflon coated magnetic stirrer was placed into the titration vessel containing a known amount (30-50 mg) of solvent-free tar sample. After the apparatus was assembled, dry and CO$_2$-free nitrogen was allowed to purge the system for about 3 minutes to remove any adsorbed moisture from the glass vessel surface. One ml of pyridine was then introduced to the titration vessel with the magnetic stirrer on the dissolve the tar sample completely before adding 5 ml of acetone via the automatic pipettor.

Power to the bridge and galvanometer was then turned on. A period of typically 5-10 minutes was allowed to elapse to permit the galvanometric reading to stabilize. The bridge was then zeroed if necessary. Before inserting the titrant admission capillary tubing into the solution the syringe pump was run until a drop of titrant appeared on the needle tip. The pump was stopped and the needle tip washed with isopropanol and acetone. The capillary tubing was then put in place in the vessel as shown in Figure 4.3-1, and the titrator and chart recorders switched on.

The end point of the titration was reached when a marked rise in solution temperature occurred which was indicated by
a sharp rise in the recorded curve of galvanometer voltage output vs. time. (A typical result is plotted in Figure D-1). This was due to the exothermic reaction, shown as equation (4.3-1), which gave rise to a small but sharp heatup of the solution. This reaction occurred near end point when there existed a very small amount of excess alcoholic alkali acting as catalyst for dimerization of the acetone.

The titration time, $T_{Ep}$, was determined as that of the tangential end point, shown in Figure D-1 at the dotted line (Vaughan and Swithinbank, 1970). The phenolic group concentration of the tars was then related to the difference between this $T_{Ep}$ and the blank 'reference' value. To obtain the blank value, the titration time for a solution of only 5 ml acetone and 1 ml pyridine was determined.

The titrant (a nominal 1 N solution of KOH in dry isopropanol) was first calibrated by titrating it against a standard solution of 1N HCl in water, using bromthymol blue (Lamotte Chemical, Code 2410) as the pH value indicator. The performance of the enthalpimetric titration apparatus was then ascertained by titrating known amounts of model compounds such as benzoic acid and m-cresol with the standardized non-aqueous titrant. The results, after correction for the indicator blank, are given in Table D-1. The major contribution to the observed errors was believed to be the uncertainty associated with the gravimetric determination of the small amounts of compound used.
Fig. D-1  A typical titration curve for a coal tar sample.

* The stoichiometric end-point is chosen to be the point where the tangent to the steep temperature rise leaves the titration curve at the lower temperature end.
Table D-1  Results of Titration of Standard Compounds

<table>
<thead>
<tr>
<th>Standard Compound</th>
<th>Amount Used (mg)</th>
<th>Amount Experimentally Determined (mg)</th>
<th>Percent Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic Acid</td>
<td>5.6</td>
<td>5.4</td>
<td>-3.6</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>10.9</td>
<td>9.9</td>
<td>-9.2</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>12.0</td>
<td>13.0</td>
<td>+8.3</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>11.4</td>
<td>11.2</td>
<td>-1.8</td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td>12.3</td>
<td>11.8</td>
<td>-4.1</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>10.1</td>
<td>10.5</td>
<td>+4.0</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>10.3</td>
<td>10.9</td>
<td>+5.8</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>9.8</td>
<td>9.5</td>
<td>-3.1</td>
</tr>
</tbody>
</table>

```c
COMPILER NOSTACK
C *** DATA LOGGER ***
C
C CODED BY KEN SAWADA ON 11/06/81
C REVISED BY C.S.CHANG ON 1/04/83
C
DIMENSION SAMPLE(5,2),NAMSPL(5,5),TEMP(20),TAR(20,4),OIL(20,2),
1       TARCUM(20),OILCUM(20),OBYT(20),COND(10,2),COAL(2),
2       GAS(30,16,3),TGAS(30,3),TGYLD(30,3),DT(15),ESF(3),
3       AREA(30,3),RF(30,3),DENSTY(30),EXAREA(3),TEMPRI(16),
4       ASTORE(30,16,3),H(16),Y(16),GASSUM(10,16),TGASUM(10),
5       CMLGAS(30,16)
C
INTEGER RUNNO(5),MODE(5),NAMGAS(30,10),EXTGAS(3,10),HR(16),MIN(16),
1       DATE(5),FILENO(3),METHOD(3),DETCR(3),NPEAK(3),PEAKNO(30,3),
2       LOOP(16),FLAG(30),MISS(30,16,3)
C
C (FILE OPEN)
C
C --- MAIN FILE
CALL FOPEN(1,'HISTORY')
CALL FOPEN(2,'GASNAME')
   OPEN 3,'TABLE',ATT='OP'
   OPEN 4,'SUMMARY',ATT='OP'
C --- CUMULATIVE YIELD OF TAR & LIGHT OIL
CALL FOPEN(7,'TARPLOT')
CALL FOPEN(8,'OILPLOT')
C --- GAS EVOLUTION RATE VS. TEMP. OF R1
CALL FOPEN(21,'GROUP1')
CALL FOPEN(22,'GROUP2')
CALL FOPEN(23,'GROUP3')
CALL FOPEN(24,'GROUP4')
CALL FOPEN(31,'H2')
CALL FOPEN(32,'O2')
CALL FOPEN(33,'AR')
CALL FOPEN(34,'N2')
CALL FOPEN(35,'CO2')
CALL FOPEN(36,'UNK')
CALL FOPEN(37,'CH4')
CALL FOPEN(38,'C2H4')
CALL FOPEN(39,'CO')
CALL FOPEN(40,'C2H6')
CALL FOPEN(41,'H2S')
CALL FOPEN(42,'H2O')
CALL FOPEN(43,'C3H6')
CALL FOPEN(44,'C3H8')
CALL FOPEN(45,'C4')
C
C (DATA INPUT)
C
C --- RUN INFORMATION
READ(1,1) RUNNO,MODE
1 FORMAT(111,4A1)
```
TYPE "OK1"
C --- RUN CONDITION
C COND(1,J)=(MAX.) TEMPERATURE OF REACTOR (J).
C COND(2,J)=HEATING RATE OF REACTOR (J).
C COND(3,J)=SOAKING TIME OF REACTOR (J).
C COND(4,1)=(1/P) MAXIMUM FLOW RATE (SCC/MIN)
C COND(4,2)=(1/P) ACTUAL FLOW RATE IN THE RUN (%)
C COND(4,J)=(O/P) RESIDENCE TIME OF REACTOR (J).
C COND(5,J)=PRESSURE OF REACTOR (J).
C COND(6,J)=PARTICLE SIZE (LOWER LIMIT) OF REACTOR (J).
C COND(7,J)=PARTICLE SIZE (UPPER LIMIT) OF REACTOR (J).
READ FREE(1) NSCOND
C NCOND=NUMBER OF CONDITIONS
READ FREE(1) ((COOL (1,J),J=1,2),I=1,NCOND)
TYPE "OK2"
C --- SAMPLE SIZE
READ FREE(1) NSAMPLE
C NSAMPLE=NUMBER OF SAMPLE SPECIES
DO 5 I=1,NSAMPLE
READ(1,2) (NAMESP(I,J),J=1,5)
2 FORMAT(5A2)
READ FREE(1) (SAMPLE(I,J),J=1,2)
5 CONTINUE
TYPE "OK3"
COAL(1)=SAMPLE(1,1)
COAL(2)=SAMPLE(1,2)
C --- CALCULATION OF RESIDENCE TIME
RMFC=COND(4,2)/100.0
RT1=3.479E-4*(14.7+COND(5,1))/RMFC
COND(4,1)=RT1
COND(4,2)=0.0
IF(MODE(1) .EQ. 1) GO TO 1113
IF(MODE(1) .EQ. 4) GO TO 1111
RT2=8.490*(14.7+COND(5,2))/((273.15+COND(1,2))*RMFC)
GO TO 1112
1111 BDEPTH=0.8902*SAMPLE(3,2)
RT2=0.2089*(40.64-0.55*BDEPTH)*(14.7+COND(5,2))
1 ((273.15+COND(1,2))*RMFC)
1112 COND(4,2)=RT2
1113 CONTINUE
C --- TAR- AND OIL-TEMPERATURE HISTORY
READ FREE(1) NTPNT
C NTPNT=NUMBER OF TEMPERATURE (R1) POINTS
DO 10 I=1,NTPNT
10 READ FREE(1) TEMP(I),TAR(I,1),OIL(I,1)
READ FREE(1) TARR1,TARR2,TAR3WV
READ FREE(1) PCHAR,SCCHAR
TYPE "OK4"
C
C (CALCULATION OF TAR AND LIGHT OIL YIELDS)
C BASE=COAL(1)
IF(MODE(1) .EQ. 2) BASE=COAL(2)
STAR1=0.0
SOIL=0.0
DO 20 I=1,NTPNT
STAR1=STAR1+TAR(1,1)
SOIL=SOIL+OIL(1,1)
20 CONTINUE
STAR2=TARR1+TARR2+TAR3WV
STAR=STAR1+STAR2
DO 30 I=1,NTPNT
TAR(1,2)=TAR(1,1)/STAR1
TAR(1,3)=TAR(1,1)+STAR2*TAR(1,2)
TAR(1,2)=TAR(1,2)*100.0
TAR(1,4)=TAR(1,3)/BASE*100.0
OIL(1,2)=OIL(1,1)/BASE*100.0
OBYT(1)=OIL(1,1)/TAR(1,3)
30 CONTINUE
TARCUM(1)=TAR(1,4)
OILCUM(1)=OIL(1,2)
DO 40 I=2,NTPNT
TARCUM(I)=TARCUM(I-1)+TAR(1,4)
OILCUM(I)=OILCUM(I-1)+OIL(1,2)
40 CONTINUE

C

(OUTPUT OF TAR AND LIGHT OIL YIELDS)

C

WRITE(3,500) RUNNO,MODE
WRITE(4,500) RUNNO,MODE
500 FORMAT(1H ,6X,"***** SUMMARY OF THE EXPERIMENT *****" )
   1 1H ,5X,' RUN NO=','111,4A1,'(MODE=','111,4A1,'')'/
   WRITE(3,600) ((COND(I,J),J=1,2),I=1,NCOND)
600 FORMAT(1H ,5X,"--- CONDITIONS ---"/28X,'REACTOR1',2X,'REACTOR2'/
   1 1H ,5X,'TEMPERATURE ',2F10.2/
   2 1H ,5X,'HEATING RATE ',2F10.2/
   3 1H ,5X,'SOAKING TIME ',2F10.2/
   4 1H ,5X,'RESIDENCE TIME ',2F10.3/
   5 1H ,5X,'PRESSURE ',2F10.2/
   6 1H ,5X,'PARTICLE SIZE (MIN)',2F10.0/
   7 1H ,5X,'PARTICLE SIZE (MAX)',2F10.0/
   WRITE(3,605)
605 FORMAT(1H ,5X,"--- SAMPLE SIZE ---"/)
   WRITE(3,610)
610 FORMAT(19X,'REACTOR1',7X,'REACTOR2')
   WRITE(3,620) ((NAMSPL(1,J),J=1,5),(SAMPLE(I,J),J=1,2)),I=1,NSAMPL
620 FORMAT(1H ,5X,5A2,2G15.7)
   WRITE(4,630)
630 FORMAT(1H ,5X,"--- CONDITIONS ---"/41X,"--- SAMPLE SIZE ---"/)
   1 28X,'REACTOR1',2X,'REACTOR2',32X,'REACTOR1',7X,'REACTOR2')
   WRITE(4,640) ((COND(1,J),J=1,2),(NAMSPL(1,J),J=1,5),(SAMPLE(1,J),
   1 J=1,2)),I=1,3)
640 FORMAT(1H ,5X,'TEMPERATURE ',2F10.2,20X,5A2,2G15.7/
   1 1H ,5X,'HEATING RATE ',2F10.2,20X,5A2,2G15.7/
   2 1H ,5X,'SOAKING TIME ',2F10.2,20X,5A2,2G15.7/
   WRITE(4,650) ((COND(1,J),J=1,2),I=4,NCOND)
650 FORMAT(1H ,5X,'RESIDENCE TIME ',2F10.3/
   1 1H ,5X,'PRESSURE ',2F10.2/
C
C *** GAS ANALYSIS DATA ***
C
C (GAS NAMES)
C
C     TYPE 'OK19'
READ FREE(2) NGAS
     TYPE 'OK20'
     DO 100 I=1,NGAS
     DO 101 J=1,16
     DO 101 K=1,3
     GAS(I,J,K)=0.0
    101 CONTINUE
     FK(1)=0.0
     READ(2,3) (NAMGAS(I,J),J=1,10),(RF(I,J),J=1,3),DENSTY(I)
TYPE 'OK21'
3 FORMAT (10A1,4G10.5)
10 CONTINUE
EXAREA(1)=9510
EXAREA(2)=0.
EXAREA(3)=289

(GAS DATA)

TYPE 'OK22'
READ FREE(1) ESF
TYPE 'OK18'
DO 105 I=1,3
105 READ (1,34) (EXTGAS(I,J), J=1,10)
34 FORMAT (10A1)
WRITE (3,900) RUNNO, MODE, ESF
900 FORMAT (1H1, 5X, 'GAS ANALYSIS', 3X, 'RUN NO=', 'I1,4A1,2X
1     ', 'MODE=', 'I1,4A1,' )'/
2     1H, '3X, 'FID', '8X, 'FPD', '8X, 'HWD'/
3     1H, '5X, 'EXTERNAL STANDARD FACTOR =', '3(F6.2,5X))
WRITE (3,901) (EXTGAS(I,J), J=1,10), I=1,3)
901 FORMAT (1H1, 5X, 'EXTERNAL GAS', 9X, 'I2X,10A1,1X,10A1,1X,10A1/) READ FREE(1) NCONFG, CFLOW, CARGON
WRITE (3,902) NCONFG, CFLOW, CARGON
902 FORMAT (1H1, 5X, 'CONFIGURATION NO. =', 'I5/
1     1H, '5X, 'Carrier FLOW =', 'F7.2/
2     1H, '5X, 'ARGON CONCENTRATION=', 'F7.4)
TYPE 'OK5'

LOOP DATA

READ FREE(1) NLOOP
DO 110 I=1,NLOOP
READ FREE(1) LOOP(I), HR(I), MIN(I), TEMPR1(I), (DATE(J), J=1,5)
TYPE 'LOOP=', LOOP(I)
WRITE (3,910) LOOP(I), HR(I), MIN(I), TEMPR1(I), (DATE(J), J=1,5)
910 FORMAT (//1H1, 5X, '---LOOP NO.=', 'I1,2,3X,' 'TIME=', 'I2,' 'I2,' 'I2,' 'I2,' 'TEMP(R1)=', 'F7.2/
1     1H, '5X,' 'DATE OF ANALYSIS =', 'I2,' 'I2,' 'I2,' 'I2,' 'I2,' 'I2,' '/
2     12,' 'I2,' 'I2//)
READ FREE(1) NFILE
DO 20 J=1,NFILE
READ FREE(1) DETCTR(J), METHOD(J), FILENO(J)
READ FREE(1) NPEAK(J)
NPEAKJ=NPEAK(J)
DO 130 K=1,NPEAKJ
READ FREE(1) PEAKNO(K,J), AREA(K,J)
IF (PEAKNO(K,J) .EQ. 3) ATRACE=AREA(K,J)
130 CONTINUE
120 CONTINUE
DO 140 J=1,NFILE
WRITE (3,920) FILENO(J), METHOD(J), DETCTR(J)
920 FORMAT (//1H1, 5X, '<<< FILE NO.=', 'I3,' 'METHOD NO.=', 'I3,' 'DETECTOR NO.=', 'I2,
1     10X, 'PEAK NO.', 'I4,' 'NAM=', 'I10X, 'AREA', 'I10X, 'EVL. RATE')
NPEAKJ=NPEAK(J)
DO 150 K=1,NPEAKJ
NNN=PEAKNO(K,J)

C --- CALCULATION OF EVOLUTION RATE
C
AA=AREA(K,J)/ATRACE
JJJ=DETCTR(J)
BB=RF(3,3)/RF(NNN,JJJ)
IF(RF(NNN,JJJ) .EQ. 0.0) BB=0.0
CC=ESF(3)*EXAREA(JJJ)/(ESF(JJJ)*EXAREA(3))
XCONV=1.073
ER=AA*BB*CC*CARGON*CFLOW*DENSTY(NNN)*XCONV

C TYPE ER,AA,BB,CC,AREA(K,J),ATRACE (FOR DEBUGGING)
GAS(NNN,I,JJJ)=ER
ASTORE(NNN,I,JJJ)=AREA(K,J)
IF(ER .GT. 0.0) MISS(NNN,I,JJJ)=1
FLAG(NNN)=1
WRITE(3,930) NNN,(NAMGAS(NNN,L),L=1,10),AREA(K,J),ER
930 FORMAT(1H,11X,15,5X,10A1,2G15.7)
C TYPE AA,BB,CC,DENSTY(NNN),CARGON,CFLOW (FOR DEBUGGING)

150 CONTINUE
140 CONTINUE
110 CONTINUE
C
C --- CHECK OF MISSING DATA
C
WRITE(3,10000)

10000 FORMAT(1H1 /' *** MISSING DATA POINTS ***'/)
DO 400 NNN=1,NGAS
DO 410 J=1,3
MISLOW=0
MISUP=0
DO 420 I=1,NLOOP
IF(MISS(NNN,I,J) .EQ. 0) GO TO 420
MISLOW=1
GO TO 430
420 CONTINUE
430 CONTINUE
DO 440 I=1,NLOOP
IF(MISS(NNN,NLOOP+1-I,J) .EQ. 0) GO TO 440
MISUP=NLOOP+1-I
GO TO 450
440 CONTINUE
450 CONTINUE
IF(MISLOW.EQ.0 .OR. MISUP.EQ.0) GO TO 470
IF(MISLOW .GT. MISUP) GO TO 470
DO 460 I=MISLOW,MISUP
IF(MISS(NNN,I,J) .EQ. 0) MISS(NNN,I,J)=-1
460 CONTINUE
470 CONTINUE
WRITE(3,20000) (NAMGAS(NNN,L),L=1,10),J,(MISS(NNN,I,J),I=1,NLOOP)
20000 FORMAT(1H ,10A1,'(',12,')',5X,16I5)
410 CONTINUE
400 CONTINUE
--- TOTAL AMOUNT OF GAS PRODUCT AND GAS YIELD
(NUMERICAL INTEGRATION BY TRAPEZOIDAL RULE)

NLOOP1=NLOOP1-1
DO 200 I=1,NLOOP1
INTRVL=HR(I+1)*60+MIN(I+1)-HR(I)*60-MIN(I)
DT(I)=FLOAT(INTRVL)
200 CONTINUE
DO 210 NNN=1,NGAS
IF(FLAG(NNN),EQ.,0) GO TO 210
DO 220 J=1,3

(PREPARATION FOR MISSING DATA --- THEY ARE SKIPPED)

DO 230 I=1,NLOOP1
230 H(I)=0.0
KOUNT=1
Y(I)=GAS(NNN,1,J)
DO 240 I=1,NLOOP1
H(KOUNT)=H(KOUNT)+DT(I)
Y(KOUNT+1)=GAS(NNN,I+1,J)
IF(MISS(NNN,I+1,J),GE.,0) KOUNT=KOUNT+1
240 CONTINUE
IF(J,NE.,1) GO TO 246
DO 245 I=1,NLOOP1
245 CMLGAS(NNN,I)=0.0
246 CONTINUE
S=0.0
10=1
DO 250 I=1,KOUNT
S=S+0.5*H(I)*(Y(I)+Y(I+1))
IF(J,NE.,1) GO TO 250
255 10=10+1
CMLGAS(NNN,10)=S/(BASE*10.0)
IF(MISS(NNN,10+1,J),LT.,0) GO TO 255
250 CONTINUE
TGAS(NNN,J)=S
TGYLD(NNN,J)=S/(BASE*10.)
TGAS=MG/GM OF COAL/MIN; TGYLD=WT%/GM OF COAL/MIN

--- PRINT OUT BY GAS SPECIES

WRITE(3,940)
940 FORMAT(1H1,**** EVOLUTION RATE OF GAS PRODUCT *****)
XMAX=1.3E32
DO 300 NNN=1,NGAS
IF(FLAG(NNN),EQ.,0) GO TO 300
C GROUP1=(H2O,CH4,CO2)
C GROUP2=(C2H4,C2H6)
C GROUP3=(C3H6,C3H8)
C GROUP4=(H2,H2S,CO)
IF(NNN .NE. 1) GO TO 22
NW=24
NWGAS=31
JJJ=3
KKK=10
SYMB=202.
22 IF(NNN .NE. 2) GO TO 33
NW=99
NWGAS=32
JJJ=3
KKK=0
SYMB=202.
33 IF(NNN .NE. 3) GO TO 44
NW=99
NWGAS=33
JJJ=3
KKK=0
SYMB=202.
44 IF(NNN .NE. 4) GO TO 55
NW=99
NWGAS=34
JJJ=3
KKK=0
SYMB=202.
55 IF(NNN .NE. 5) GO TO 6
NW=21
NWGAS=35
JJJ=3
KKK=8
SYMB=202.
6 IF(NNN .NE. 6) GO TO 7
NW=99
NWGAS=36
JJJ=3
KKK=0
SYMB=202.
7 IF(NNN .NE. 7) GO TO 8
NW=21
NWGAS=37
JJJ=1
KKK=1
SYMB=203.
8 IF(NNN .NE. 8) GO TO 9
NW=22
NWGAS=38
JJJ=1
KKK=2
SYMB=202.
9 IF(NNN .NE. 9) GO TO 1000
NW=24
NWGAS=39
JJJ=3
KKK=9
SYMB=203.
1000 IF(NNN .NE. 10) GO TO 11
    NW=22
    NWGAS=40
    JJJ=1
    KKK=3
    SYMB=203.
11 IF(NNN .NE. 11) GO TO 12
    NW=24
    NWGAS=41
    JJJ=2
    KKK=0
    SYMB=204.
12 IF(NNN .NE. 12) GO TO 13
    NW=21
    NWGAS=42
    JJJ=3
    KKK=7
    SYMB=204.
13 IF(NNN .NE. 13) GO TO 14
    NW=23
    NWGAS=43
    JJJ=1
    KKK=4
    SYMB=202.
14 IF(NNN .NE. 14) GO TO 15
    NW=23
    NWGAS=44
    JJJ=1
    KKK=5
    SYMB=203.
15 IF(NNN .NE. 15) GO TO 16
    NW=99
    NWGAS=45
    JJJ=1
    KKK=6
    SYMB=203.
16 CONTINUE
WRITE(3,945) (NAMGAS(NNN,J), J=1,10)
945 FORMAT(/1H ,5X,'(T10A1,')'/1H ,10X,'TIME',5X,'TEMP(R1)',5X,'AREA',
1     11X,'FID',12X,'FPD',12X,'HWD',9X,'NORMALIZED',5X,'CUMULATIVE')
C    TYPE NNN,NW
    IF(NW .GT. 90) GO TO 111
    WRITE(NW,955) XMAX,SYMB
111 CONTINUE
WRITE(NWGAS,955)XMAX,SYMB
DO 310 I=1,NLOOP
    GNORM=GAS(NNN,I, JJJ)/(BASE*10.)
    IF(KKK .EQ. 0) GO TO 112
    GASSUM(KKK,I)=GNORM
310 CONTINUE
WRITE(3,950) LOOP(I),HR(I),MIN(I),TEMPR1(I),ASTORE(NNN,I, JJJ),
1     (GAS(NNN,I,J), J=1,3),GNORM,CMLGAS(NNN,I)
950 FORMAT(1H ,5X,12,2X,12,':',12,3X,F8.2,2X,6G15.7)
C    TYPE NW,1,TEMPR1(I)
IF(1 .EQ. 1) GO TO 320
IF(TEMPR1(I) .LT. TEMPR1(I-1)) GO TO 310
IF(MISS(NNN,1,JJJ) .LT. 0) GO TO 310

C TYPE I

320 CONTINUE
WRITE(NWGAS,955) TEMPR1(I),G.norm
IF(NW.GT.90) GO TO 310
WRITE(NW,955) TEMPR1(I),G.norm
955 FORMAT(1H,5X,G15.7,1H,G15.7)
310 CONTINUE
WRITE(3,960) (TGAS(NNN,J),J=1,3),TGYLD(NNN,J),TGYLD(NNN,J),J=1,3),1,
TGYLD(NNN,J)
960 FORMAT(/1H,35X,TOTAL,2X,4G15.7/1H,35X,YIELD,2X,4G15.7)
IF(KKK.EQ.0) GO TO 300
TGASUM(KKK)=TGYLD(NNN,J)
300 CONTINUE
WRITE(4,970)
970 FORMAT(/1H,5X,--- GAS ---//
1 1H,10X,TIME,5X,TEMP(R1),5X,CH4,5X,C2H4,5X,C2H6,
2 5X,C3H6,5X,C3H8,5X,C4,5X,H2O,5X,CO2,5X,CO,
3 5X,H2)
DO 350 I=1,NLOOP
WRITE(4,980) LOOP(I),HR(I),MIN(I),TEMPR1(I),GASSUM(J,J),J=1,10
350 CONTINUE
WRITE(4,990) TGASUM(J),J=1,10
990 FORMAT(/1H,19X,GASYLD,4X,10F9.5)
WRITE(4,995) NCONFIG
995 FORMAT(1H,34X,FID,9X,FPD,9X,HWD,
1 11X,CONFIGURATION NO. =',15)
WRITE(4,996) ESF,CFLOW
996 FORMAT(1H,5X,EXTERNAL STANDARD FACTOR =',3(F7.2,5X),1,
5X,CARRIER FLOW =',F7.2)',SCC/MIN')
ARSPCT=CARGON*100.0
WRITE(4,997) (EXTGAS(I,J),J=1,10),I=1,3),ARSPCT
997 FORMAT(1H,5X,EXTERNAL GAS,
1 2X,10A1,2X,10A1,2X,10A1,4X,
2 'ARGON CONCENTRATION =',F7.4,')
CALL RESET
STOP
END

:UDD:CSCHANG
Appendix F. Computer Program ("KINE") Used for Kinetic Modeling of Heterogeneous Cracking Reactions of Tar over CaO.

COMPILER DOUBLE PRECISION
COMPILER NOSTACK

C
C KINETIC MODEL FOR TAR CRACKING REACTIONS OVER CaO
C CODED BY CLIFF C.S. CHANG ON 9/17/85

C DIMENSION YIE(4),FRA(4),FRAC(4,8,80),COKE(8,80),CKO(4),
  1 AE(4),ALFA(4),DEN(4),AA(4),COE(4,8,80),TOT(4),AVG(4),
  2 FYIE(4),CK2(4)
C REAL MMW(4),NMOL
C
C OPEN FILE
C CALL FOPEN(31,'DATA')
C
C READ IN CRACKING TEMP (C), HELIUM FLOW (SCCM), & REACTOR PRESSURE (PSIG)
C READ FREE(31) TCRAC,FLOW,PSIG
TCRAC=TCRAC+273.
PSI=PSIG+14.7
FF=FLOW/22400.
TYPE " "
TYPE " *** RESULTS OF MODEL PREDICTION ***"
TYPE " "
TYPE " * FOR TAR CRACKING REACTIONS OVER CaO *"
TYPE " "
TYPE " CRACK TEMP(C) = "TCRAC-273"," CONTACT TIME = 0.12 SEC."
C TYPE " REACTOR PRESSURE (PSI) = "PSI
C TYPE " MOLAR FLOW RATE = "FF,"MOLE/MIN"
C
C VOID FRACTION OF PACKED BED
C EPS=0.52
C
C READ IN AMOUNTS OF COAL & CAO (G) USED.
C READ FREE(31) WCOL,WCAO
C TYPE " COAL/CaO (gm/gm) = "WCOL,"/",WCAO
C TYPE " REACTOR PRESSURE (PSI) = "PSI
C TYPE " MOLAR FLOW RATE = "FF,"MOLE/MIN"
C CC TYPE "INPUT WT OF COAL & CAO :"
C CC ACCEPT WCOL,WCAO
C TYPE "WT OF COAL = "WCOL," WT OF CAO = "WCAO
C TYPE "OK2"
C TYPE " "
C TYPE " CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL)
C READ IN YIELDS OF TAR FRACTIONS 1 TO 4 IN THE FEED. (G/G OF COAL)
READ *FREE(31) (YIE(I), I=1,4)
DO 650 I=1,4
  TYPE " INITIAL YIELD OF",I," = ",YIE(I)
  CONTINUE
  TYPE "OK3"

READ IN NTIME & NDEPTH

TYPE "INPUT NDEPTH & NTIME : "
ACCEPT NDEPTH,NTIME
READ *FREE(31) NDEPTH,NTIME
  TYPE "OK4"

MW IS IN TERMS OF KG/MOLE.
TOTAL RXN TIME IS TAKEN AS 50 MIN.

MMW(1)=.29
MMW(2)=.37
MMW(3)=.45
MMW(4)=1.
  TYPE "OK5"

CALCULATE INITIAL MOLE FRACTIONS OF TAR FRACTIONS.

DO 10 I=1,4
  FRA(I)=(YIE(I)*WCOL)/(MMW(I)*FF*50.*1000.)
  TYPE "INITIAL FRACTION",I," = ",FRA(I)
  CONTINUE
  DO 15 K=1,NTIME
  DO 16 I=1,4
  15 CONTINUE
  16 FRAC(I,1,K)=FRA(I)

COKE(J,1)=0.
  TYPE "OK6"

PRE-EXP FACTORS & ACTIVATION ENERGIES

TYPE "INPUT PRE-EXP FACTORS 1 TO 4 :
ACCEPT CKO(1),CKO(2),CKO(3),CKO(4)
  TYPE "INPUT ACT. ENERGY 1 TO 4 :
ACCEPT AE(1),AE(2),AE(3),AE(4)
READ *FREE(31) (CKO(I), I=1,4)
READ *FREE(31) (AE(I), I=1,4)
RR=1.987

BULK DENSITY OF CATALYST (KG CAO/M3 OF RXTOR VOLUME)

DENC=50.2
PSL=PSIG+14.7

RXTOR CROSS-SECTIONAL AREA IN M2.

AREA=2.85E-04
TOTAL GAS CONCENTRATION (MOLES/M3) IN THE RXTOR.

\[ \text{NMOLE} = \frac{(273 \times \text{PSI})}{(\text{TCRAC} \times 14.7 \times 0.0224)} \]

TYPE "NMOLE =",NMOLE

DEACTIVATION CONSTANT

READ FREE(31) (ALFA(1), I=1,4)
TYPE "INPUT ALFA 1 TO 4 :"
ACCEPT ALFA(1),ALFA(2),ALFA(3),ALFA(4)
TYPE "ALFA(1) = ",ALFA(1)," ALFA(2) = ",ALFA(2)

DENSITY OF TAR IN VAPOR PHASE IN THE RXTOR. (KG/M3)

DO 30 I=1,4
DEN(I)=(PSI*MWW(I)*1.0E+06)/(14.7*82.05*TCRAC)
TYPE " DENSITY OF" ,I," = ",DEN(I)," (AT REACTION CONDITIONS)"
30 CONTINUE
TYPE "OK7"

BED DEPTH IN M.

BEDDEP=0.035*WCA0/0.5

CALCULATE A1 AND B VALUES.

TYPE " "
TYPE " CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN) : 
TYPE " -- FOR COKEFREE Ce0 --"
DO 35 I=1,4
CK2(I)=EXP(CKO(I)-AE(I))/(RR*TCRAC)*60.*EPS
TYPE " CK2(" ,I," ) = ",CK2(I)
35 CONTINUE
CC=DEN(1)*AREA*BEDDEP*NMOLE/FF
DO 20 I=1,4
AA(I)=(CC*CK2(I))/DEN(1)
20 AA(I)=CC*CK2(I))/DEN(1)
TYPE "OK8"

CALCULATE K'S FOR RESIDUAL + COKE CRACKING ACTIVITY

READ FREE(31) CK0,CAE
CKK=EXP(CK0-CAE/(RR*TCRAC))*60.*EPS
TYPE " -- FOR COKEE Ce0 --"
TYPE " CKK = ",CKK
ACOK=CKK*CC/DEN(1)

FRACTION OF TAR CRACKED TO FORM COKE,CF,IS SET AS 0.8

CF=0.8
BB=(CF*CC*EPS)/(DEN*MMW(1))

MODIFIED EULER'S METHOD
CNDEP=NDEPTH
CNTIME=NTIME
DELT=1./CNDEP
TMAX=(FF*MMW(1)*50.)/(EPS*DEN(1)*AREA*BEDDEP)

C
TYPE "MAX TIME =",TMAX
DELT=TMAX/CNTIME
NNDEP=NDEPTH-1
AVA=1.
DO 100 K=1,NTIME-1
   DO 205 J=1,NDEPTH
C
CALC % OF AVAILABLE AREA OF CAO, AVA
C
MONDAY COKE FORMED ON 50 m2/g CAO CORRESPONDS TO 2.5 WT% COKE CONTENT ON CAO, LINEAR DIMENSION OF CARBON ATOM IS ASSUMED TO BE 2 ANSTROM
C
XX=COKE(J,K)*4/(0.025*AVA)
CC
TYPE "XX =",XX
IF(XX.LE.14) GO TO 125
YY=EXP(-0.02114*XX+1.2477)
OAREA=EXP(-0.02114*14.+1.2477)
AVA=YY/OAREA
GO TO 126

125 AVA=1.
126 CONTINUE
IF(TCRAC.LT.974) GO TO 135
AVA=AVA*(50.-0.3*(TCRAC-973))/50.
135 CONTINUE
C
TYPE "PREDICTED FINAL AREA EFFECTIVENESS FACTOR =",AVA
DO 200 I=1,4
   PHE=EXP((-1)*ALFA(I)*COKE(J,K))
   COE(I,J,K)=PHE*AA(I)+(1-PHE)*ACOK
IF(J.EQ.NDEPTH) GO TO 200
C
C CALCULATE FRACTION OF TAR LUMP I IN THE FLUID
C
FRAC(I,J+1,K)=FRAC(I,J,K)-DELT*COE(I,J,K)*FRAC(I,J,K)*AVA
IF(FRAC(I,J+1,K).LT.0.) FRAC(I,J+1,K)=0.

200 CONTINUE
205 CONTINUE
CC
TYPE "OK9"
DO 250 J=1,NDEPTH
   SSUM=0.
   DO 225 I=1,4
      IF(J.EQ.NDEPTH) GO TO 226
      SSUM=SSUM+DEN(1)*COE(I,J,K)*MMW(I)*0.5*(FRAC(I,J,K)+FRAC(I,J+1,K))*AVA/CC
      GO TO 225
225 SSUM=SSUM+DEN(1)*COE(I,J,K)*MMW(I)*FRAC(I,J,K)*AVA/CC

226 CONTINUE
C
C CALCULATE COKE CONTENT OF CAO AS FUNCTIONS OF TIME AND DISTANCE
C
COKE(J,K+1)=COKE(J,K)+BB*DELT*SSUM
CONTINUE
DO 255 I=1,4
TYPE "FRAC",1," AT EXIT AT TIME",K," = ",FRAC(I,NDEPTH,K)
CONTINUE
DO 501 I=1,NNDEP
TYPE " FINAL COKE CONTENT AT POSITION",I," = ",COKE(I,NTIME)
CONTINUE
TYPE "OK10"
DO 400 I=1,4
TOK(I)=0.
DO 500 K=1,NTIME
TOK(I)=TOK(I)+FRAC(I,NDEPTH,K)
CONTINUE
AVG(I)=TOK(I)/CNTIME

CALCULATE OVERALL YIELD OF SECONDARY TAR LUMP I CRACKED OVER CAO
FYIE(I)=AVG(I)*MMW(I)*50000.*FF/WCOL
CONTINUE
goto 600
CONTINUE
goto 605

CALCULATE AVERAGE COKE CONTENT OF CAO AFTER CRACKING RUN IS COMPLETE
AVCO=TOKO/CNDEP
CONTINUE
TYPE " "
TYPE " "
TYPE " PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL) :
CONTINUE
TYPE " FRACTION ",I," YIELD = ",FYIE(I)
CONTINUE
TYPE " "
TYPE " PREDICTED TOTAL TAR YIELD (g/g COAL) ":,OYIE
TYPE " PREDICTED AVERAGE COKE CONTENT OF CAO (g/g CaO) ":,AVCO
CALL RESET
STOP
END

:UDD:CSCHANG
Appendix G. Sample Input File ("DATA") to the Kinetic Model Program
- "KINE" (Given in Appendix F):

** DATA File for 500 C Cracking Run **

500,1010,3.9
(CRACKING TEMP IN DEGREE C, HE FLOW RATE IN SCCM, PRESSURE IN PSIG)

0.1,0.5
(WT OF COAL IN GM, WT OF CaO IN GM)

0.0654,0.0665,0.0587,0.0384
(YIELDS OF TAR LUMPS IN FEED, DETERMINED FROM MODE-3 RUNS, GM/GM COAL)

8,80
(NO. OF STEPS ALONG DISTANCE AND TIME)
(LIMITED BY AVAILABLE COMPUTER MEMORY SIZE FOR MATRIX OPERATION)

17.96,12.67,11.57,10.31
(PRE-EXP FACTORS FOR KINETIC CONSTANTS FOR COKEFREE CaO)

26050.,15790.,13780.,12200.
(ACTIVATION ENERGIES FOR KINETIC CONSTANTS FOR COKEFREE CaO)

30.9,30.9,30.9,30.9
(CaO DEACTIVATION COEFFICIENT)

14.22,24200
(PRE-EXP FACTOR AND ACT. ENERGY FOR K'S FOR COKED CaO)

** DATA File for 525 C Cracking Run **

525.,985.,4
.1,.5
0.0643,0.0653,0.0575,0.0387
8,80
17.96,12.67,11.57,10.31
26050.,15790.,13780.,12200.
30.9,30.9,30.9,30.9
14.22,24200
** DATA File for 550 C Cracking Run **

550.,950.,4
.1,.5
0.0634,0.0643,0.0567,0.0392
8,80
17.96,12.67,11.57,10.31
26050.,15790.,13780.,12200.
30.9,30.9,30.9,30.9
14.22,24200

** DATA File for 600 C Cracking Run **

600.,895.,4
.1,.5
0.0613,0.0621,0.0548,0.0399
8,80
17.96,12.67,11.57,10.31
26050.,15790.,13780.,12200.
30.9,30.9,30.9,30.9
14.22,24200

** DATA File for 700 C Cracking Run **

700.,805.,4
.1,.5
0.0631,0.051,0.0399,0.0350
8,80
17.96,12.67,11.57,10.31
26050.,15790.,13780.,12200.
30.9,30.9,30.9,30.9
14.22,24200

** DATA File for 800 C Cracking Run **

800.,725.,4
.1,.5
0.0734,0.0285,0.0215,0.0286
8, 80
17.96, 12.67, 11.57, 10.31
26050, 15790, 13780, 12200.
30.9, 30.9, 30.9, 30.9
14.22, 24200

: UDD: CSCHANG
Appendix H. Results of "KINE" Model Prediction for Tar Cracking
Reactions Over CaO

*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP (C) = 500.0000000000000
CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = .1000000000000000 / .5000000000000000
REACTOR PRESSURE (PSI) = 18.60000000000000
MOLAR FLOW RATE = 4.508928571428571D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.54000000000000D-02
INITIAL YIELD OF 2 = 6.64999999999999D-02
INITIAL YIELD OF 3 = 5.87000000000000D-02
INITIAL YIELD OF 4 = 3.84000000000000D-02

DENSITY OF 1 = 5.78542846527658 (AT REACTION CONDITIONS)
DENSITY OF 2 = 7.38140873155977 (AT REACTION CONDITIONS)
DENSITY OF 3 = 8.97738899784296 (AT REACTION CONDITIONS)
DENSITY OF 4 = 19.9497533285399 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2( 1) = 84.7954283902856
CK2( 2) = 340.407090585674
CK2( 3) = 419.380123011245
CK2( 4) = 332.771601318450

-- FOR COKED CaO --
CCK = 6.71744005586939

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 2.767348522815021D-02
FINAL COKE CONTENT AT POSITION 2 = 2.52093542103107D-02
FINAL COKE CONTENT AT POSITION 3 = 2.282744836969955D-02
FINAL COKE CONTENT AT POSITION 4 = 2.054720600542827D-02
FINAL COKE CONTENT AT POSITION 5 = 1.838702771795992D-02
FINAL COKE CONTENT AT POSITION 6 = 1.636310718892158D-02
FINAL COKE CONTENT AT POSITION 7 = 1.448840009386789D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.000000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 5.02957160496846D-02
FRACTION 2 YIELD = 2.355653008242048D-02
FRACTION 3 YIELD = 1.614221768344364D-02
FRACTION 4 YIELD = 1.393474030380281D-02

PREDICTED TOTAL TAR YIELD (g/g COAL) : .103929204119352
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) : 2.094892292068522D-02

UDD: CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP (C) = 500.0000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = .2000000000000000 / .5000000000000000
REACTOR PRESSURE (PSI) = 18.6000000000000
MOLAR FLOW RATE = 4.508928571428571D-09 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.540000000000000D-02
INITIAL YIELD OF 2 = 6.649999999999999D-02
INITIAL YIELD OF 3 = 5.870000000000000D-02
INITIAL YIELD OF 4 = 3.840000000000000D-02
DENSITY OF 1 = 5.78542846527658 (AT REACTION CONDITIONS)
DENSITY OF 2 = 7.38140873155977 (AT REACTION CONDITIONS)
DENSITY OF 3 = 8.97738899784296 (AT REACTION CONDITIONS)
DENSITY OF 4 = 19.9497533285399 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2( 1) = 84.7954283902856
CK2( 2) = 340.407090585674
CK2( 3) = 419.380123011245
CK2( 4) = 332.771601318450
-- FOR COKED CaO --
CK = 6.71744005586939

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 4.318216728004020D-02
FINAL COKE CONTENT AT POSITION 2 = 4.070954876509520D-02
FINAL COKE CONTENT AT POSITION 3 = 3.82308356826563D-02
FINAL COKE CONTENT AT POSITION 4 = 3.575614556671034D-02
FINAL COKE CONTENT AT POSITION 5 = 3.329735686149256D-02
FINAL COKE CONTENT AT POSITION 6 = 3.086799287550403D-02
FINAL COKE CONTENT AT POSITION 7 = 2.848297644517881D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.000000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 5.278241168621484D-02
FRACTION 2 YIELD = 2.997978701206182D-02
FRACTION 3 YIELD = 2.195080467290078D-02
FRACTION 4 YIELD = 1.756189211258121D-02

PREDICTED TOTAL TAR YIELD (g/g COAL) : .122174895483759
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) : 3.592599710436485D-02

: UDD: CSCHANG

: UDD: CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP (C) = 500.000000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = .3000000000000000 / .5000000000000000
REACTOR PRESSURE (PSI) = 18.60000000000000
MOLAR FLOW RATE = 4.508928571428571D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.54000000000000000D-02
INITIAL YIELD OF 2 = 6.64999999999999999D-02
INITIAL YIELD OF 3 = 5.87000000000000000D-02
INITIAL YIELD OF 4 = 3.84000000000000000D-02
DENSITY OF 1 = 5.78542846527658 (AT REACTION CONDITIONS)
DENSITY OF 2 = 7.38140873155977 (AT REACTION CONDITIONS)
DENSITY OF 3 = 8.97738899784296 (AT REACTION CONDITIONS)
DENSITY OF 4 = 19.9497533285399 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN) :
-- FOR COKEFREE CaO --
CK2(1) = 84.7954283902856
CK2(2) = 340.407090585674
CK2(3) = 419.380123011245
CK2(4) = 332.771601318450
-- FOR COKED CaO --
CCK = 6.71744005586939

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 5.404148234354468D-02
FINAL COKE CONTENT AT POSITION 2 = 5.175983765013404D-02
FINAL COKE CONTENT AT POSITION 3 = 4.944980647380171D-02
FINAL COKE CONTENT AT POSITION 4 = 4.711479073656421D-02
FINAL COKE CONTENT AT POSITION 5 = 4.475936903791270D-02
FINAL COKE CONTENT AT POSITION 6 = 4.238939122507821D-02
FINAL COKE CONTENT AT POSITION 7 = 4.001206229828223D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.000000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 5.442017645052697D-02
FRACTION 2 YIELD = 3.454933057760533D-02
FRACTION 3 YIELD = 2.641552496795371D-02
FRACTION 4 YIELD = 2.023041746581315D-02

PREDICTED TOTAL TAR YIELD (g/g COAL) : .135615449461899
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) : 4.717939271224558D-02

: UDD: CSCHANG
: UDD: CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP(C) = 500.0000000000000
CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = 0.6000000000000000 / 0.5000000000000000
REACTOR PRESSURE (PSI) = 18.60000000000000
MOLAR FLOW RATE = 4.508928571428571D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.54000000000000D-02
INITIAL YIELD OF 2 = 6.64999999999999D-02
INITIAL YIELD OF 3 = 5.87000000000000D-02
INITIAL YIELD OF 4 = 3.84000000000000D-02
DENSITY OF 1 = 5.7854284527658  (AT REACTION CONDITIONS)
DENSITY OF 2 = 7.581408731559777 (AT REACTION CONDITIONS)
DENSITY OF 3 = 8.97738899784296  (AT REACTION CONDITIONS)
DENSITY OF 4 = 19.949753285399  (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2(1) = 84.7954283902856
CK2(2) = 340.407090585674
CK2(3) = 419.380123011245
CK2(4) = 332.771601318450
-- FOR COKED CaO --
CCK = 6.71744005586939

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 7.523157536846217D-02
FINAL COKE CONTENT AT POSITION 2 = 7.342481095727209D-02
FINAL COKE CONTENT AT POSITION 3 = 7.159207752440187D-02
FINAL COKE CONTENT AT POSITION 4 = 6.973207205005363D-02
FINAL COKE CONTENT AT POSITION 5 = 6.78438950199170D-02
FINAL COKE CONTENT AT POSITION 6 = 6.592674112205810D-02
FINAL COKE CONTENT AT POSITION 7 = 6.398044855233269D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.00000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 5.710478531323772D-02
FRACTION 2 YIELD = 4.297465151071634D-02
FRACTION 3 YIELD = 3.474046290691587D-02
FRACTION 4 YIELD = 2.503038880267801D-02

PREDICTED TOTAL TAR YIELD (g/g COAL): .159850288533548
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO): 6.972916033552527D-02

:UDD:CSCHANG

:UDD:CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP(C) = 500.000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = 1.00000000000000 / 0.500000000000000
REACTOR PRESSURE (PSI) = 18.6000000000000
MOLAR FLOW RATE = 4.508928571428571D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.54000000000000D-02
INITIAL YIELD OF 2 = 6.64999999999999D-02
INITIAL YIELD OF 3 = 5.87000000000000D-02
INITIAL YIELD OF 4 = 3.84000000000000D-02

DENSITY OF 1 = 5.7854284527658 (AT REACTION CONDITIONS)
DENSITY OF 2 = 7.38140873155977 (AT REACTION CONDITIONS)
DENSITY OF 3 = 8.9773899784296 (AT REACTION CONDITIONS)
DENSITY OF 4 = 19.9497533285399 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):

-- FOR COKEFREE CaO --
CK2( 1) = 84.7954283902856
CK2( 2) = 340.407090585674
CK2( 3) = 419.380123011245
CK2( 4) = 332.771601318450

-- FOR COKED CaO --
CCK = 6.71744005586939

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 9.290398979776902D-02
FINAL COKE CONTENT AT POSITION 2 = 9.14386956437147D-02
FINAL COKE CONTENT AT POSITION 3 = 8.996034385949653D-02
FINAL COKE CONTENT AT POSITION 4 = 8.846695059260379D-02
FINAL COKE CONTENT AT POSITION 5 = 8.695705590665509D-02
FINAL COKE CONTENT AT POSITION 6 = 8.542945976173477D-02
FINAL COKE CONTENT AT POSITION 7 = 8.388307204542751D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = .997660649869781

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 5.875436699499681D-02
FRACTION 2 YIELD = 4.857843025651700D-02
FRACTION 3 YIELD = 4.042444254605035D-02
FRACTION 4 YIELD = 2.821495591366997D-02

PREDICTED TOTAL TAR YIELD (g/g COAL) = .175972195711234
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) = 8.846378375558142D-02

:UDD:CSCHANG

:UDD:CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP(C) = 525.0000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = 1000000000000000.0 / 5000000000000000
REACTOR PRESSURE (PSI) = 18,7000000000000
MOLAR FLOW RATE = 4.397321428571428D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.429999999999999D-02
INITIAL YIELD OF 2 = 6.530000000000000D-02
INITIAL YIELD OF 3 = 5.750000000000000D-02
INITIAL YIELD OF 4 = 3.870000000000000D-02

DENSITY OF 1 = 5.63431071013686 (AT REACTION CONDITIONS)
DENSITY OF 2 = 7.18860331982979 (AT REACTION CONDITIONS)
DENSITY OF 3 = 8.74289592952272 (AT REACTION CONDITIONS)
DENSITY OF 4 = 19.4286576211616 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):

-- FOR COKEFREE CaO --
CK2(1) = 144.253977688893
CK2(2) = 469.752521943116
CK2(3) = 555.486413785664
CK2(4) = 426.791680148257

-- FOR COKED CaO --
CK = 11.0045310895172

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 3.347924462852503D-02
FINAL COKE CONTENT AT POSITION 2 = 3.005515302625782D-02
FINAL COKE CONTENT AT POSITION 3 = 2.671999177133428D-02
FINAL COKE CONTENT AT POSITION 4 = 2.351748971231241D-02
FINAL COKE CONTENT AT POSITION 5 = 2.049225963563242D-02
FINAL COKE CONTENT AT POSITION 6 = 1.76857126053551D-02
FINAL COKE CONTENT AT POSITION 7 = 1.513166557991940D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.00000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 4.199548793342802D-02
FRACTION 2 YIELD = 1.618120390339741D-02
FRACTION 3 YIELD = 1.086722788251459D-02
FRACTION 4 YIELD = 1.095654493706719D-02

PREDICTED TOTAL TAR YIELD (g/g COAL): 8.000046465640720D-02
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO): 2.415334901469455D-02

:UDD:CSCHANG

:UDD:CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP(C) = 525.00000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = .2000000000000000 / .5000000000000000
REACTOR PRESSURE (PSI) = 18.700000000000
MOLAR FLOW RATE = 4.3973214285714287D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.429999999999999D-02
INITIAL YIELD OF 2 = 6.530000000000000D-02
INITIAL YIELD OF 3 = 5.750000000000000D-02
INITIAL YIELD OF 4 = 3.870000000000000D-02
DENSITY OF 1 = 5.63431071013686 (AT REACTION CONDITIONS)
DENSITY OF 2 = 7.18860331982979 (AT REACTION CONDITIONS)
DENSITY OF 3 = 8.74289592952272 (AT REACTION CONDITIONS)
DENSITY OF 4 = 19.4286576211616 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2( 1) = 144.253977688893
CK2( 2) = 469.752521943116
CK2( 3) = 555.486413785664
CK2( 4) = 426.791680148257
-- FOR COKED CaO --
CCK = 11.0045310895172

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 5.084749219334453D-02
FINAL COKE CONTENT AT POSITION 2 = 4.764094669605524D-02
FINAL COKE CONTENT AT POSITION 3 = 4.439672305832213D-02
FINAL COKE CONTENT AT POSITION 4 = 4.112877649029180D-02
FINAL COKE CONTENT AT POSITION 5 = 3.785579745220890D-02
FINAL COKE CONTENT AT POSITION 6 = 3.460140288636891D-02
FINAL COKE CONTENT AT POSITION 7 = 3.139397057384934D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.0000000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 4.596637656445389D-02
FRACTION 2 YIELD = 2.342600535750722D-02
FRACTION 3 YIELD = 1.720150555027243D-02
FRACTION 4 YIELD = 1.520733198277267D-02

PREDICTED TOTAL TAR YIELD (g/g COAL) = 0.101801219455006
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) = 4.13392235066401D-02

:UDD: CSCHANG
:UDD: CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP (C) = 525.000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = .300000000000000 / .500000000000000
REACTOR PRESSURE (PSI) = 18.7000000000000
MOLAR FLOW RATE = 4.397321428571428D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.42999999999999D-02
INITIAL YIELD OF 2 = 6.53000000000000D-02
INITIAL YIELD OF 3 = 5.75000000000000D-02
INITIAL YIELD OF 4 = 3.87000000000000D-02
DENSITY OF 1 = 5.63431071013686 (AT REACTION CONDITIONS)
DENSITY OF 2 = 7.18860331982979 (AT REACTION CONDITIONS)
DENSITY OF 3 = 8.74289592952272 (AT REACTION CONDITIONS)
DENSITY OF 4 = 19.426576211616 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2( 1) = 144.253977688893
CK2( 2) = 469.752521943116
CK2( 3) = 555.486413785664
CK2( 4) = 426.791680148257
-- FOR COKED CaO --
CK = 11.0045310895172

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 6.274764604133427D-02
FINAL COKE CONTENT AT POSITION 2 = 5.987499560089091D-02
FINAL COKE CONTENT AT POSITION 3 = 5.694827791921838D-02
FINAL COKE CONTENT AT POSITION 4 = 5.39693711281740D-02
FINAL COKE CONTENT AT POSITION 5 = 5.094236474585293D-02
FINAL COKE CONTENT AT POSITION 6 = 4.787419466749465D-02
FINAL COKE CONTENT AT POSITION 7 = 4.477467319485269D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.00000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 4.855208155855243D-02
FRACTION 2 YIELD = 2.894061438576779D-02
FRACTION 3 YIELD = 2.225604216622770D-02
FRACTION 4 YIELD = 1.837044201495874D-02

PREDICTED TOTAL TAR YIELD (g/g COAL) = 0.118119180125507
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) = 5.403104301021794D-02

:UDD: CSCHANG

:UDD: CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP(C) = 525.000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = 0.600000000000000 / 0.500000000000000
REACTOR PRESSURE (PSI) = 18.7000000000000
MOLAR FLOW RATE = 4.397321428571428D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.42999999999999D-02
INITIAL YIELD OF 2 = 6.53000000000000D-02
INITIAL YIELD OF 3 = 5.75000000000000D-02
INITIAL YIELD OF 4 = 3.87000000000000D-02
DENSITY OF 1 = 5.63431071013686 (AT REACTION CONDITIONS)
DENSITY OF 2 = 7.18860331982979 (AT REACTION CONDITIONS)
DENSITY OF 3 = 8.74289592952272 (AT REACTION CONDITIONS)
DENSITY OF 4 = 19.4286576211616 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2(1) = 144.253977688893
CK2(2) = 469.752521943116
CK2(3) = 555.486413785664
CK2(4) = 426.791680148257
-- FOR COKED CaO --
CCK = 11.0045310895172

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 8.583075274772615D-02
FINAL COKE CONTENT AT POSITION 2 = 8.360147164115146D-02
FINAL COKE CONTENT AT POSITION 3 = 8.134016419354467D-02
FINAL COKE CONTENT AT POSITION 4 = 7.904272768258520D-02
FINAL COKE CONTENT AT POSITION 5 = 7.670594539935685D-02
FINAL COKE CONTENT AT POSITION 6 = 7.432721857592209D-02
FINAL COKE CONTENT AT POSITION 7 = 7.190447309817380D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.00000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 5.267374142470547D-02
FRACTION 2 YIELD = 3.885204951698129D-02
FRACTION 3 YIELD = 3.166620285361842D-02
FRACTION 4 YIELD = 2.395919355977383D-02

PREDICTED TOTAL TAR YIELD (g/g COAL) = 0.147151187393044
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) = 7.903839712910123D-02

:UDD:CSCHANG

:UDD:CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP(C) = 550.0000000000000
CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = 0.1000000000000000 / 0.5000000000000000
REACTOR PRESSURE (PSI) = 18.7000000000000
MOLAR FLOW RATE = 4.241071428571428D-02MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.340000000000000D-02
INITIAL YIELD OF 2 = 6.429999999999999D-02
INITIAL YIELD OF 3 = 5.670000000000000D-02
INITIAL YIELD OF 4 = 3.920000000000000D-02
DENSITY OF 1 = 5.46315910897839 (AT REACTION CONDITIONS)
DENSITY OF 2 = 6.97023748386899 (AT REACTION CONDITIONS)
DENSITY OF 3 = 8.47731585875958 (AT REACTION CONDITIONS)
DENSITY OF 4 = 1.8384796861324 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2(1) = 27.609607516141
CK2(2) = 635.685113701522
CK2(3) = 723.307797448442
CK2(4) = 539.162946709673
-- FOR COKED CaO --
CK = 17.4950717186029

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 3.994013659572109D-02
FINAL COKE CONTENT AT POSITION 2 = 3.530223970357014D-02
FINAL COKE CONTENT AT POSITION 3 = 3.072993512708691D-02
FINAL COKE CONTENT AT POSITION 4 = 2.630956437706714D-02
FINAL COKE CONTENT AT POSITION 5 = 2.21394899397933D-02
FINAL COKE CONTENT AT POSITION 6 = 1.831780001875041D-02
FINAL COKE CONTENT AT POSITION 7 = 1.492605487449723D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.000000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 3.190076835917734D-02
FRACTION 2 YIELD = 9.652345092898008D-03
FRACTION 3 YIELD = 6.577677020782797D-03
FRACTION 4 YIELD = 8.103930242807397D-03

PREDICTED TOTAL TAR YIELD (g/g COAL): 5.643472071566554D-02
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO): 2.728709625426157D-02
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP(C) = 550.0000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = 0.2000000000000000 / 0.5000000000000000
REACTOR PRESSURE (PSI) = 18.7000000000000
MOLAR FLOW RATE = 4.241071428571428D-02MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.34000000000000000D-02
INITIAL YIELD OF 2 = 6.429999999999999D-02
INITIAL YIELD OF 3 = 5.67000000000000000D-02
INITIAL YIELD OF 4 = 3.92000000000000000D-02
DENSITY OF 1 = 5.46315910897839 (AT REACTION CONDITIONS)
DENSITY OF 2 = 6.97023748368699 (AT REACTION CONDITIONS)
DENSITY OF 3 = 8.4773158587958 (AT REACTION CONDITIONS)
DENSITY OF 4 = 18.83844796861324 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2( 1) = 237.609607516141
CK2( 2) = 635.685113701522
CK2( 3) = 723.307797448442
CK2( 4) = 539.162946709673
-- FOR COKED CaO --
CCK = 17.4950717186029

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 5.921534724290733D-02
FINAL COKE CONTENT AT POSITION 2 = 5.51235315649139D-02
FINAL COKE CONTENT AT POSITION 3 = 5.09425834652880D-02
FINAL COKE CONTENT AT POSITION 4 = 4.66848035531696D-02
FINAL COKE CONTENT AT POSITION 5 = 4.237533114388605D-02
FINAL COKE CONTENT AT POSITION 6 = 3.805028368403284D-02
FINAL COKE CONTENT AT POSITION 7 = 3.375984977272670D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.000000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 3.7668832090130452D-02
FRACTION 2 YIELD = 1.748843849671674D-02
FRACTION 3 YIELD = 1.302735140621045D-02
FRACTION 4 YIELD = 1.285889237014151D-02

PREDICTED TOTAL TAR YIELD (g/g COAL): 8.106300317437323D-02
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO): 4.692472852894134D-02

:UDD:CSCHANG

:UDD:CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP(C) = 550.000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = .300000000000000 / .500000000000000
REACTOR PRESSURE (PSI) = 18.700000000000
MOLAR FLOW RATE = 4.241071428571428D-02MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.340000000000000D-02
INITIAL YIELD OF 2 = 6.429999999999999D-02
INITIAL YIELD OF 3 = 5.670000000000000D-02
INITIAL YIELD OF 4 = 3.920000000000000D-02
DENSITY OF 1 = 5.46315910897839 (AT REACTION CONDITIONS)
DENSITY OF 2 = 6.970237483686899 (AT REACTION CONDITIONS)
DENSITY OF 3 = 8.4773158375958 (AT REACTION CONDITIONS)
DENSITY OF 4 = 18.8384796861324 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2( 1) = 237.609607516141
CK2( 2) = 635.685113701522
CK2( 3) = 723.307797448442
CK2( 4) = 539.162946709673
-- FOR COKED CaO --
CCK = 17.4950717186029

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 7.224626872550151D-02
FINAL COKE CONTENT AT POSITION 2 = 6.865269512931869D-02
FINAL COKE CONTENT AT POSITION 3 = 6.497274646620825D-02
FINAL COKE CONTENT AT POSITION 4 = 6.120158304493920D-02
FINAL COKE CONTENT AT POSITION 5 = 5.738548999065496D-02
FINAL COKE CONTENT AT POSITION 6 = 5.338771973547466D-02
FINAL COKE CONTENT AT POSITION 7 = 4.935902825689358D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.000000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 4.150212982627595D-02
FRACTION 2 YIELD = 2.369153081916639D-02
FRACTION 3 YIELD = 1.855267908963094D-02
FRACTION 4 YIELD = 1.651275439726546D-02

PREDICTED TOTAL TAR YIELD (g/g COAL) = .100259094132339
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) = 6.124843325994725D-02

:UDD: CSCHANG

:UDD: CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP (C) = 550.000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = .600000000000000 / .500000000000000
REACTOR PRESSURE (PSI) = 18.7000000000000
MOLAR FLOW RATE = 4.241071428571428D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.340000000000000D-02
INITIAL YIELD OF 2 = 6.429999999999999D-02
INITIAL YIELD OF 3 = 5.670000000000000D-02
INITIAL YIELD OF 4 = 3.920000000000000D-02
DENSITY OF 1 = 5.46315910897839 (AT REACTION CONDITIONS)
DENSITY OF 2 = 6.97023748386899 (AT REACTION CONDITIONS)
DENSITY OF 3 = 8.4773158587958 (AT REACTION CONDITIONS)
DENSITY OF 4 = 18.8384796861324 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
--- FOR COKEFREE CaO ---
CK2 (1) = 237.609607516141
CK2 (2) = 635.685113701522
CK2 (3) = 723.307737484442
CK2 (4) = 539.162946709673
--- FOR COKED CaO ---
CCK = 17.4950717186029

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 9.768283142711587D-02
FINAL COKE CONTENT AT POSITION 2 = 9.488797928967955D-02
FINAL COKE CONTENT AT POSITION 3 = 9.206079063681392D-02
FINAL COKE CONTENT AT POSITION 4 = 8.918997717419748D-02
FINAL COKE CONTENT AT POSITION 5 = 8.626792749403142D-02
FINAL COKE CONTENT AT POSITION 6 = 8.328844734070264D-02
FINAL COKE CONTENT AT POSITION 7 = 8.024561875709242D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = .993711144468202

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 4.749394081711256D-02
FRACTION 2 YIELD = 3.496400474744759D-02
FRACTION 3 YIELD = 2.895768904792304D-02
FRACTION 4 YIELD = 2.290618400333707D-02

PREDICTED TOTAL TAR YIELD (g/g COAL) = .134321818615820
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) = 8.919002996137480D-02
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP (C) = 550,000000000000 CONTACT TIME = 0.12 SEC.
COAL/ CaO (gm/gm) = 1.00000000000000 0.50000000000000
REACTOR PRESSURE (PSI) = 18.700000000000
MOLAR FLOW RATE = 4.241071428571428D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.340000000000000000D-02
INITIAL YIELD OF 2 = 6.429999999999990000D-02
INITIAL YIELD OF 3 = 5.670000000000000000D-02
INITIAL YIELD OF 4 = 3.920000000000000000D-02
DENSITY OF 1 = 5.46315910897839 (AT REACTION CONDITIONS)
DENSITY OF 2 = 6.97023748336899 (AT REACTION CONDITIONS)
DENSITY OF 3 = 8.4773158975958 (AT REACTION CONDITIONS)
DENSITY OF 4 = 18.8384796861324 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2( 1) = 237.609607516141
CK2( 2) = 635.685113701522
CK2( 3) = 723.307797448442
CK2( 4) = 539.162946709673
-- FOR COKED CaO --
CCK = 17.4950717186029

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 0.18801215039643
FINAL COKE CONTENT AT POSITION 2 = 0.116418170244871
FINAL COKE CONTENT AT POSITION 3 = 0.114044260281345
FINAL COKE CONTENT AT POSITION 4 = 0.111662483960960
FINAL COKE CONTENT AT POSITION 5 = 0.109263254928729
FINAL COKE CONTENT AT POSITION 6 = 0.106840076514205
FINAL COKE CONTENT AT POSITION 7 = 0.104387849194871

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 0.887285998982984

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 5.1095440246298885D-02
FRACTION 2 YIELD = 4.239985667466165D-02
FRACTION 3 YIELD = 3.598917093112279D-02
FRACTION 4 YIELD = 2.701633076029800D-02

PREDICTED TOTAL TAR YIELD (g/g COAL) = 0.156500798612381
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) = 0.111685644102563

:UDD:CSCSHANG
:UDD:CSCSHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP (C) = 600.000000000000 CONTACT TIME = 0.12 SEC.
COAL/COA (gm/gm) = 0.100000000000000 / 0.500000000000000
REACTOR PRESSURE (PSI) = 18.7000000000000
MOLAR FLOW RATE = 3.995535714285714D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.13000000000000D-02
INITIAL YIELD OF 2 = 6.21000000000000D-02
INITIAL YIELD OF 3 = 5.48000000000000D-02
INITIAL YIELD OF 4 = 3.99000000000000D-02

DENSITY OF 1 = 5.15026339826944 (AT REACTION CONDITIONS)
DENSITY OF 2 = 6.37102571503342 (AT REACTION CONDITIONS)
DENSITY OF 3 = 7.99178803179740 (AT REACTION CONDITIONS)
DENSITY OF 4 = 17.7595289595498 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2(1) = 591.693092575010
CK2(2) = 1105.13470265938
CK2(3) = 1171.98835362472
CK2(4) = 826.58526533532

-- FOR COKED CaO --
CCK = 40.8327732657408

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 5.352600145590668D-02
FINAL COKE CONTENT AT POSITION 2 = 4.553433281995171D-02
FINAL COKE CONTENT AT POSITION 3 = 3.736472904266758D-02
FINAL COKE CONTENT AT POSITION 4 = 2.92636773691524D-02
FINAL COKE CONTENT AT POSITION 5 = 2.165434486149299D-02
FINAL COKE CONTENT AT POSITION 6 = 1.506368108672060D-02
FINAL COKE CONTENT AT POSITION 7 = 9.907692056488675D-03

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.000000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 1.029776070366739D-02
FRACTION 2 YIELD = 1.813381881241443D-03
FRACTION 3 YIELD = 1.246347313518910D-03
FRACTION 4 YIELD = 3.113126834960514D-03

PREDICTED TOTAL TAR YIELD (g/g COAL) = 1.647061673338825D-02
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) = 3.156050961989040D-02
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP(C) = 600.0000000000000
CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = .2000000000000000 / .5000000000000000
REACTOR PRESSURE (PSI) = 18.7000000000000
MOLAR FLOW RATE = 3.995535714285714D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.130000000000000D-02
INITIAL YIELD OF 2 = 6.210000000000000D-02
INITIAL YIELD OF 3 = 5.480000000000000D-02
INITIAL YIELD OF 4 = 3.990000000000000D-02
DENSITY OF 1 = 5.1502639826944 (AT REACTION CONDITIONS)
DENSITY OF 2 = 6.57102571503342 (AT REACTION CONDITIONS)
DENSITY OF 3 = 7.99178803179740 (AT REACTION CONDITIONS)
DENSITY OF 4 = 17.7595289595498 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2( 1) = 591.693092575010
CK2( 2) = 1105.13470263938
CK2( 3) = 1171.98835362472
CK2( 4) = 826.585265335352
-- FOR COKED CaO --
CK = 40.8327732657408

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 7.683451331644939D-02
FINAL COKE CONTENT AT POSITION 2 = 7.028873350190357D-02
FINAL COKE CONTENT AT POSITION 3 = 6.347285243022090D-02
FINAL COKE CONTENT AT POSITION 4 = 5.634456285037498D-02
FINAL COKE CONTENT AT POSITION 5 = 4.890079202098901D-02
FINAL COKE CONTENT AT POSITION 6 = 4.120157218876745D-02
FINAL COKE CONTENT AT POSITION 7 = 3.341018298415141D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.00000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 1.811484447380212D-02
FRACTION 2 YIELD = 7.479821259283976D-03
FRACTION 3 YIELD = 5.901099204170422D-03
FRACTION 4 YIELD = 7.747581141621787D-03

PREDICTED TOTAL TAR YIELD (g/g COAL): 3.924334607887830D-02
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO): 5.654094299116425D-02

:UDD:CSCHANG
:UDD:CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP(C) = 600.000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = 0.300000000000000 / 0.500000000000000
REACTOR PRESSURE (PSI) = 18.7000000000000
MOLAR FLOW RATE = 3.995535714285714D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.130000000000000D-02
INITIAL YIELD OF 2 = 6.210000000000000D-02
INITIAL YIELD OF 3 = 5.480000000000000D-02
INITIAL YIELD OF 4 = 3.990000000000000D-02
DENSITY OF 1 = 5.15026339826944 (AT REACTION CONDITIONS)
DENSITY OF 2 = 6.57102571503342 (AT REACTION CONDITIONS)
DENSITY OF 3 = 7.99178803179740 (AT REACTION CONDITIONS)
DENSITY OF 4 = 17.7595289595498 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2( 1) = 591.693092575010
CK2( 2) = 1105.13470263938
CK2( 3) = 1171.98835362472
CK2( 4) = 826.58526535352
-- FOR COKED CaO --
CCK = 40.8327732657408

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 9.267192630398313D-02
FINAL COKE CONTENT AT POSITION 2 = 8.694122103490870D-02
FINAL COKE CONTENT AT POSITION 3 = 8.105179953536902D-02
FINAL COKE CONTENT AT POSITION 4 = 7.494282242334688D-02
FINAL COKE CONTENT AT POSITION 5 = 6.856511859130272D-02
FINAL COKE CONTENT AT POSITION 6 = 6.187947490056365D-02
FINAL COKE CONTENT AT POSITION 7 = 5.486398576434405D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.000000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 2.4354572507877716D-02
FRACTION 2 YIELD = 1.399404682962959D-02
FRACTION 3 YIELD = 1.154789977500021D-02
FRACTION 4 YIELD = 1.207079931991063D-02

PREDICTED TOTAL TAR YIELD (g/g COAL) = 6.196731843241760D-02
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) = 7.488959442176948D-02

:UDD:CSCHANG

:UDD:CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP(C) = 600.000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = .4000000000000000 / .500000000000000
REACTOR PRESSURE (PSI) = 18.700000000000
MOLAR FLOW RATE = 3.995535714285714D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.130000000000000D-02
INITIAL YIELD OF 2 = 6.210000000000000D-02
INITIAL YIELD OF 3 = 5.480000000000000D-02
INITIAL YIELD OF 4 = 3.990000000000000D-02
DENSITY OF 1 = 5.15026339826944 (AT REACTION CONDITIONS)
DENSITY OF 2 = 6.57102571503342 (AT REACTION CONDITIONS)
DENSITY OF 3 = 7.99178803179740 (AT REACTION CONDITIONS)
DENSITY OF 4 = 17.7595289595498 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2( 1) = 591.693092575010
CK2( 2) = 1105.13470263938
CK2( 3) = 1171.98835362472
CK2( 4) = 826.585265335352
-- FOR KOEDED CaO --
CCK = 40.8327732657408

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = .105175399741979
FINAL COKE CONTENT AT POSITION 2 = 9.992042596250693D-02
FINAL COKE CONTENT AT POSITION 3 = 9.458707881908129D-02
FINAL COKE CONTENT AT POSITION 4 = 8.911313726677278D-02
FINAL COKE CONTENT AT POSITION 5 = 8.345574310329910D-02
FINAL COKE CONTENT AT POSITION 6 = 7.757572332247789D-02
FINAL COKE CONTENT AT POSITION 7 = 7.143259915944294D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = .989064890298894

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 2.887027999007089D-02
FRACTION 2 YIELD = 1.944030601473177D-02
FRACTION 3 YIELD = 1.636595662911602D-02
FRACTION 4 YIELD = 1.540316684797893D-02

PREDICTED TOTAL TAR YIELD (g/g COAL) = 8.007970948189759D-02
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) = 8.907638030470524D-02

:UDD: CSCHANG

:UDD: CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP(C) = 600.0000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = 1.000000000000000 / 0.500000000000000
REACTOR PRESSURE (PSI) = 18.7000000000000
MOLAR FLOW RATE = 3.99553714285714D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.130000000000000D-02
INITIAL YIELD OF 2 = 6.210000000000000D-02
INITIAL YIELD OF 3 = 5.480000000000000D-02
INITIAL YIELD OF 4 = 3.990000000000000D-02
DENSITY OF 1 = 5.15026339826944 (AT REACTION CONDITIONS)
DENSITY OF 2 = 6.57102571503342 (AT REACTION CONDITIONS)
DENSITY OF 3 = 7.9917805719740 (AT REACTION CONDITIONS)
DENSITY OF 4 = 17.7595289959948 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN) :
-- FOR COKEFREE CaO --
CK2( 1) = 591.693092575010
CK2( 2) = 1105.13470263938
CK2( 3) = 1171.98853562472
CK2( 4) = 826.585265335352
-- FOR COKED CaO --
CCK = 40.8327732657408

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO) :
FINAL COKE CONTENT AT POSITION 1 = .151237873003228
FINAL COKE CONTENT AT POSITION 2 = .146669203950327
FINAL COKE CONTENT AT POSITION 3 = .142254487879200
FINAL COKE CONTENT AT POSITION 4 = .137893174347300
FINAL COKE CONTENT AT POSITION 5 = .133540553499911
FINAL COKE CONTENT AT POSITION 6 = .129168591692429
FINAL COKE CONTENT AT POSITION 7 = .124756403919316

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = .715694773141119

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL) :
FRACTION 1 YIELD = 4.135579102096528D-02
FRACTION 2 YIELD = 3.636276563429529D-02
FRACTION 3 YIELD = 3.159532807081104D-02
FRACTION 4 YIELD = 2.507859949037614D-02

PREDICTED TOTAL TAR YIELD (g/g COAL) : .134392484216448
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) : .138041464809220
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP (C) = 700.000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = 0.100000000000000 / 0.500000000000000
REACTOR PRESSURE (PSI) = 18.7000000000000
MOLAR FLOW RATE = 3.593750000000000D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.309999999999999D-02
INITIAL YIELD OF 2 = 5.100000000000000D-02
INITIAL YIELD OF 3 = 3.990000000000000D-02
INITIAL YIELD OF 4 = 3.500000000000000D-02
DENSITY OF 1 = 4.62094547450074 (AT REACTION CONDITIONS)
DENSITY OF 2 = 5.89568905367336 (AT REACTION CONDITIONS)
DENSITY OF 3 = 7.17043263284597 (AT REACTION CONDITIONS)
DENSITY OF 4 = 15.9342947396577 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2(1) = 2769.44796414800
CK2(2) = 2816.5030645167
CK2(3) = 2651.54301334710
CK2(4) = 1702.97317717012
-- FOR COKED CaO --
CK = 171.278535882025

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 7.958806957886209D-02
FINAL COKE CONTENT AT POSITION 2 = 5.398462139573260D-02
FINAL COKE CONTENT AT POSITION 3 = 2.449978404283940D-02
FINAL COKE CONTENT AT POSITION 4 = 3.295782429734687D-03
FINAL COKE CONTENT AT POSITION 5 = 1.691596516487142D-04
FINAL COKE CONTENT AT POSITION 6 = 1.026295562568500D-05
FINAL COKE CONTENT AT POSITION 7 = 6.019728780232800D-07

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.0000000000000

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 0.000000000000000
FRACTION 2 YIELD = 0.000000000000000
FRACTION 3 YIELD = 0.000000000000000
FRACTION 4 YIELD = 5.532604824136402D-08

PREDICTED TOTAL TAR YIELD (g/g COAL) = 5.532604824136402D-08
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) = 2.824101858666982D-02
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP(C) = 700.00000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = .20000000000000000 / .50000000000000000
REACTOR PRESSURE (PSI) = 18.70000000000000
MOLAR FLOW RATE = 3.59375000000000D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.309999999999999D-02
INITIAL YIELD OF 2 = 5.100000000000000D-02
INITIAL YIELD OF 3 = 3.990000000000000D-02
INITIAL YIELD OF 4 = 3.500000000000000D-02
DENSITY OF 1 = 4.62094547450074 (AT REACTION CONDITIONS)
DENSITY OF 2 = 5.89568905367336 (AT REACTION CONDITIONS)
DENSITY OF 3 = 7.17043265284597 (AT REACTION CONDITIONS)
DENSITY OF 4 = 15.9342947396577 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2(1) = 2769.44796414800
CK2(2) = 2816.50306485167
CK2(3) = 2651.54301334710
CK2(4) = 1702.97317717012
-- FOR COKED CaO --
CCK = 171.278535882025

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = .115315675747435
FINAL COKE CONTENT AT POSITION 2 = 9.46617598382190D-02
FINAL COKE CONTENT AT POSITION 3 = 7.19155632144602D-02
FINAL COKE CONTENT AT POSITION 4 = 4.50991884707521D-02
FINAL COKE CONTENT AT POSITION 5 = 1.61597055047871D-02
FINAL COKE CONTENT AT POSITION 6 = 1.091022704165431D-03
FINAL COKE CONTENT AT POSITION 7 = 7.663626546329386D-05

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = .991809718899900

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION    1 YIELD = .0000000000000000
FRACTION    2 YIELD = .0000000000000000
FRACTION    3 YIELD = .0000000000000000
FRACTION    4 YIELD = 3.586012940072523D-06

PREDICTED TOTAL TAR YIELD (g/g COAL) : 3.586012940072523D-06
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) : 5.433627598689306D-02

:UDD:CSCHANG

:UDD:CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP (C) = 700.000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = .3000000000000000 / .5000000000000000
REACTOR PRESSURE (PSI) = 18.700000000000
MOLAR FLOW RATE = 3.593750000000000D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.309999999999999D-02
INITIAL YIELD OF 2 = 5.100000000000000D-02
INITIAL YIELD OF 3 = 3.990000000000000D-02
INITIAL YIELD OF 4 = 3.500000000000000D-02
DENSITY OF 1 = 4.6209454750074 (AT REACTION CONDITIONS)
DENSITY OF 2 = 5.89568905367336 (AT REACTION CONDITIONS)
DENSITY OF 3 = 7.17043263284597 (AT REACTION CONDITIONS)
DENSITY OF 4 = 15.9342947396577 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
--- FOR COKEFREE CaO ---
CK2(  1) = 2769.44796414800
CK2(  2) = 2816.50306485167
CK2(  3) = 2651.54301334710
CK2(  4) = 1702.97317717012
--- FOR COKED CaO ---
CK = 171.278535882025

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = .141756106415307
FINAL COKE CONTENT AT POSITION 2 = .122208392353660
FINAL COKE CONTENT AT POSITION 3 = .1023315728422
FINAL COKE CONTENT AT POSITION 4 = .8072426274422137D-02
FINAL COKE CONTENT AT POSITION 5 = .555472316724148D-02
FINAL COKE CONTENT AT POSITION 6 = .2610634896636309D-02
FINAL COKE CONTENT AT POSITION 7 = .3901414884971701D-03

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = .932867097134259

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION  1 YIELD = .0000000000000000
FRACTION  2 YIELD = .0000000000000000
FRACTION  3 YIELD = .0000000000000000
FRACTION  4 YIELD = 1.127669723982345D-04

PREDICTED TOTAL TAR YIELD (g/g COAL) = 1.127669723982345D-04
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) = .015306545808401D-02

:UDD:CSCHANG

:UDD:CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP (C) = 700.000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = 500000000000000/500000000000000
REACTOR PRESSURE (PSI) = 18.700000000000
MOLAR FLOW RATE = 3.593750000000000D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.309999999999999D-02
INITIAL YIELD OF 2 = 5.100000000000000D-02
INITIAL YIELD OF 3 = 3.990000000000000D-02
INITIAL YIELD OF 4 = 3.500000000000000D-02
DENSITY OF 1 = 4.620945475450074 (AT REACTION CONDITIONS)
DENSITY OF 2 = 5.89568905367336 (AT REACTION CONDITIONS)
DENSITY OF 3 = 7.17043263284597 (AT REACTION CONDITIONS)
DENSITY OF 4 = 15.9342947396577 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2(1) = 2769.44796414800
CK2(2) = 2816.50306485167
CK2(3) = 2651.54301334710
CK2(4) = 1702.97317717012
-- FOR COKE CaO --
CCK = 171.278535882025

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = 202910980782437
FINAL COKE CONTENT AT POSITION 2 = 182201343744292
FINAL COKE CONTENT AT POSITION 3 = 163164999904209
FINAL COKE CONTENT AT POSITION 4 = 144882145772200
FINAL COKE CONTENT AT POSITION 5 = 126674320675190
FINAL COKE CONTENT AT POSITION 6 = 107791844557881
FINAL COKE CONTENT AT POSITION 7 = 8.718191325831356D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 0.703901667572375

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 8.061120678183814D-03
FRACTION 2 YIELD = 6.438925933651094D-03
FRACTION 3 YIELD = 5.255525739858324D-03
FRACTION 4 YIELD = 6.135570665755814D-03

PREDICTED TOTAL TAR YIELD (g/g COAL) = 2.588914301744905D-02
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) = 0.146248564018661

:UDD: CSCHANG

:UDD: CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP (C) = 700.000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = 1.00000000000000 / .500000000000000
REACTOR PRESSURE (PSI) = 18.700000000000
MOLAR FLOW RATE = 3.593750000000000D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 6.309999999999999D-02
INITIAL YIELD OF 2 = 5.100000000000000D-02
INITIAL YIELD OF 3 = 3.990000000000000D-02
INITIAL YIELD OF 4 = 3.500000000000000D-02

DENSITY OF 1 = 4.62094547450074 (AT REACTION CONDITIONS)
DENSITY OF 2 = 5.89568909367336 (AT REACTION CONDITIONS)
DENSITY OF 3 = 7.1704263284597 (AT REACTION CONDITIONS)
DENSITY OF 4 = 15.9342947396577 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2(1) = 2769.44796414800
CK2(2) = 2816.50306485167
CK2(3) = 2651.54301334710
CK2(4) = 1702.97317717012

-- FOR COKED CaO --
CCK = 171.278535882025

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = .258711920589887
FINAL COKE CONTENT AT POSITION 2 = .236556885718971
FINAL COKE CONTENT AT POSITION 3 = .217228206882449
FINAL COKE CONTENT AT POSITION 4 = .199612431519227
FINAL COKE CONTENT AT POSITION 5 = .182956278730842
FINAL COKE CONTENT AT POSITION 6 = .166584035530050
FINAL COKE CONTENT AT POSITION 7 = .148652261613234

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = .500360946758359

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 2.344325677829988D-02
FRACTION 2 YIELD = 1.888961181988548D-02
FRACTION 3 YIELD = 1.494342089071054D-02
FRACTION 4 YIELD = 1.420433701855937D-02

PREDICTED TOTAL TAR YIELD (g/g COAL): 7.148062650745526D-02
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO): .202108223111658

:UDD: CSCHANG
:UDD: CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP.(C) = 800.0000000000000 CONTACT TIME = 0.12 SEC.
COAL/ CaO (gm/gm) = .2000000000000000 / .5000000000000000
REACTOR PRESSURE (PSI) = 18.7000000000000
MOLAR FLOW RATE = 3.236607142857143D-02MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 7.339999999999999D-02
INITIAL YIELD OF 2 = 2.850000000000000D-02
INITIAL YIELD OF 3 = 2.150000000000000D-02
INITIAL YIELD OF 4 = 2.860000000000000D-02
DENSITY OF 1 = 4.1902885991539 (AT REACTION CONDITIONS)
DENSITY OF 2 = 5.34623061437481 (AT REACTION CONDITIONS)
DENSITY OF 3 = 6.5021723683423 (AT REACTION CONDITIONS)
DENSITY OF 4 = 14.4492719307427 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2( 1) = 9721.89912859567
CK2( 2) = 6029.40665452653
CK2( 3) = 5152.09171582118
CK2( 4) = 3066.30496871019
-- FOR COKED CaO --
CCK = 549.959883497830

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = .102321230753522
FINAL COKE CONTENT AT POSITION 2 = 8.100474002363626D-02
FINAL COKE CONTENT AT POSITION 3 = 5.970477208281189D-02
FINAL COKE CONTENT AT POSITION 4 = 3.658123578007446D-02
FINAL COKE CONTENT AT POSITION 5 = 1.39607963761990D-02
FINAL COKE CONTENT AT POSITION 6 = 2.227546998090987D-03
FINAL COKE CONTENT AT POSITION 7 = 6.617298515352849D-04

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = .273162139328082

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = .0000000000000000
FRACTION 2 YIELD = .0000000000000000
FRACTION 3 YIELD = .0000000000000000
FRACTION 4 YIELD = 2.549612151518545D-04

PREDICTED TOTAL TAR YIELD (g/g COAL): 2.549612151518545D-04
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO): 4.712207073830353D-02

:UDD:CSCHANG

:UDD:CSCHANG
*** RESULTS OF MODEL PREDICTION ***

* FOR TAR CRACKING REACTIONS OVER CaO *

CRACK TEMP (C) = 800.000000000000 CONTACT TIME = 0.12 SEC.
COAL/CaO (gm/gm) = 1.000000000000000 / .500000000000000
REACTOR PRESSURE (PSI) = 18.700000000000000
MOLAR FLOW RATE = 3.236607142857143D-02 MOLE/MIN

CHARACTERIZATION OF FEED (FROM YIELDS OF MODE-3 RUNS) (g/g COAL):
INITIAL YIELD OF 1 = 7.339999999999999D-02
INITIAL YIELD OF 2 = 2.850000000000000D-02
INITIAL YIELD OF 3 = 2.150000000000000D-02
INITIAL YIELD OF 4 = 2.860000000000000D-02
DENSITY OF 1 = 4.19028859915399 (AT REACTION CONDITIONS)
DENSITY OF 2 = 5.34623061437481 (AT REACTION CONDITIONS)
DENSITY OF 3 = 6.50217236883423 (AT REACTION CONDITIONS)
DENSITY OF 4 = 14.4492719307427 (AT REACTION CONDITIONS)

CALCULATED VALUE OF REACTION RATE COEFFICIENT (1/MIN):
-- FOR COKEFREE CaO --
CK2( 1) = 9721.89912859567
CK2( 2) = 6029.40665452653
CK2( 3) = 5152.091715982118
CK2( 4) = 3066.30496871019

-- FOR COKED CaO --
CCK = 549.959883497830

PREDICTED FINAL COKE PROFILE IN PACKED BED (g/g CaO):
FINAL COKE CONTENT AT POSITION 1 = .17188577887583
FINAL COKE CONTENT AT POSITION 2 = .154945384269090
FINAL COKE CONTENT AT POSITION 3 = .142300411159226
FINAL COKE CONTENT AT POSITION 4 = .132919425786175
FINAL COKE CONTENT AT POSITION 5 = .123201360122920
FINAL COKE CONTENT AT POSITION 6 = .107705885801110
FINAL COKE CONTENT AT POSITION 7 = .8719969661996182D-02

PREDICTED FINAL AREA EFFECTIVENESS FACTOR = 1.020543136231915D-16

PREDICTED OVERALL YIELD OF EACH TAR LUMP (g/g COAL):
FRACTION 1 YIELD = 2.445791779351975D-02
FRACTION 2 YIELD = 1.100608593041356D-02
FRACTION 3 YIELD = 8.673601710712341D-03
FRACTION 4 YIELD = 1.327777888746062D-02

PREDICTED TOTAL TAR YIELD (g/g COAL) = 5.741538432210628D-02
PREDICTED AVERAGE COKE CONTENT OF CaO (g/g CaO) = 132088027114527

: UDD: CSCHANG

: UDD: CSCHANG
## Summary of the Experiment

**Run NO-32 (MODE-1-5-00)**

### Conditions

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<th>Parameter</th>
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### Sample Size

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<th>Reactor 2</th>
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### Char

- **Primary**: 60.510%, **Secondary**: 0.00%

### Oil

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### Gas

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<th>C2H4</th>
<th>C3H4</th>
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**Gas Yield**: 2.57838, 2.22282, 0.61080, 0.22456, 0.1886, 0.0000

**External Standard Factor**: 406.28, 0.00
**External Gas**: CH4, H2S, CH4
**Carrier Flow**: 21070.00 SCC/MIN
**Configuration no.**: 1
**Argon Concentration**: 2.13%
### SUMMARY OF THE EXPERIMENT

#### CONDITIONS

<table>
<thead>
<tr>
<th></th>
<th>Reactor 1</th>
<th>Reactor 2</th>
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<tr>
<td>Temperature</td>
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<td>Heating Rate</td>
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<td>Soaking Time</td>
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#### SAMPLE SIZE

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#### TAR

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TRAY TOTAL: 0.1558999 (15.68999)
EXTRA TOTAL: 0.6730002E-01 (6.730001)
FROM R1: 0.000000
FROM R2: 0.000000
FROM BFW: 0.6730002E-01

#### OIL

<table>
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#### CHAR

|                 |            |            |
|-----------------|------------|
| PRIMARY         | 0.79%      |
| SECONDARY       | 0.00%      |

#### GAS

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GAS YLD: .280417 .38229 .49811 .32829 .21691 .00000

---

EXTERNAL STANDARD FACTOR: 520.00
EXTERNAL SAE: CH4: 15.22
CONFIGURATION NO.: 1
CARRIER FLOW: 9410.00 SCC/MIN
ARGON CONCENTRATION: 2.1300%
### Summary of the Experiment

**Run No:** 34  (Mud: 3-450)

#### Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reactor 1</th>
<th>Reactor 2</th>
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<tbody>
<tr>
<td>Temperature</td>
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#### Sample Size

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<th>Component</th>
<th>Reactor 1</th>
<th>Reactor 2</th>
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#### Tar

<table>
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<tr>
<th>Temperature</th>
<th>Raw Data</th>
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<th>OMILTY %</th>
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**Trap Total:** .112999  **(11.2999%)**  **Additional Total:** .1095000  **(10.9500%)**

#### Char

- **Primary:** 61.0500%  **Secondary:** 0.0000%

#### Gas

<table>
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**GASOLYD:** 3.00146  **CH4:** 0.2198  **H2:** 0.57326  **C3H8:** 0.53623  **20445:** 0.00000

**External Standard Factor:** 100.00  **External Gas:** 0.00  **Configuration No.:** 1

**Carrier Flow:** 675.00 SCF/Min  **Argon Concentration:** 2.0100%
### SUMMARY OF THE EXPERIMENT

**RUN NO-20 (MODE-3-700)**

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--- OIL ---

--- CHAR ---

### GAS ---

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**GAS**

**CONFIGURATION NO.**: 1
**CARRIER FLOW**: 670.00 SCC/MIN
**ARGON CONCENTRATION**: 0.1300 %
### SUMMARY

**EXPERIMENT SUMMARY**

**RUN NO-12 (MODE-3-700)**

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--- GAS ---

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*1-Apr-91 10:21:14 PAGE 1*
### SUMMARY OF THE EXPERIMENT

**RUN NO-28** (MODE-3-900)

--- CONDITIONS ---

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|       | 1.012207 | 2.14221 | .54493 | .54493 | .0190 | .0000 |

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### SUMMARY

#### EXPERIMENT

**RUN NO. 24**

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--- OIL ---

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**DASTLD:** 2.76793, 0.00337, 0.15009, 0.15679, 0.0000

**EXTRACTION FACTOR:** 497.48

**CHROMOSCOPE:** FID

**EXTERNAL GAS:** CH4

**EXTERNAL STANDARD FACTOR:** 0.97

**HOLD:** 7.53

**CONCENTRATION:** 2.1300 %
### SUMMARY OF THE EXPERIMENT

**RUN #: 33 (MODE-4-500)**

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TRAP TOTAL: .1400999
EXTRA TOTAL: .1400999

--- CHAR ---

| Primary | 51.00% | Secondary | 11.130 |

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GAS YLD 2.52734 .29547 .68346 .95707 .42465 .00000

EXTERNAL STANDARD FACTOR 1.044.29 .00 7.75 1100.00 SCC/MIN
EXTERNAL CARBON 90% 92% 12% 18%
### SUMMARY OF THE EXPERIMENT

#### CONDITIONS

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#### CHAR

- Primary: 60.540%
- Secondary: 7.270%

#### GAS

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**GASYLD:** 3.59943  1.22271  0.7287  0.74173  0.0000  0.0000

**FID**  **FPD**  **HWD**  **CONFIGURATION NO.:** 1
### SUMMARY OF THE EXPERIMENT

**Run No-26 (Mode=1-900)**

#### Conditions

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#### Sample Size

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#### IAX

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| Trap Total | 3.3390000E-01 | 3.339999 |
| Extra Total | 2.4650000E-01 | 2.465000 |

#### Oil

<table>
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<tr>
<th>Temp</th>
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<th>CMLTY %</th>
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#### Char

Primary: 8.123% Secondary: 6.790%

#### Gas

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Gas Yield: 1.32551, 1.91194, 0.57474, 0.55935, 0.05827, 0.00000

**External Standard Factor**: 1.10370

**FPD**: 0.0, 7.12

**MWD Configuration No.**: 1

**Carrier Flow**: 725.00 SL/Min

**External Gas**: CH4, H2S, CH4

**Argon Concentration**: 2.1300%
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### SAMPLE SIZE ###

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**TRAP TOTAL:** 3.64000E-01
**EXTRA TOTAL:** .421000E-01
**FROM R1:** 4.210000

### OIL ###

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### CHAR ###

| PRIMARY | .4285% | SECONDARY | .740% |

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**EXTERNAL STANDARD FACTOR:** 4103.70 .00 7.42 CARRIER FLOW = 725.00 SCC/MIN

**EXTERNAL GAS:** CH4 H2E CH4 ARGIN CONCENTRATION = 2.1000%