



Solid Fuels and Heavy Hydrocarbon Liquids

Thermal Characterization and Analysis



Rafael Kandiyoti
Alan Herod
Keith Bartle

CONTENTS

Preface

viii

CHAPTER 1	Coal and Biomass: The Study of Solid Fuels and their Utilization	1
1.1	A Fuel for Producing Energy; a Carbon Source for Making Steel	2
1.2	The Widening Use of Coal, Oil and Gas	4
1.3	Processing Coals and Oils	6
1.4	Outline of the Book	8
CHAPTER 2	Fossil Fuels: Origins and Characterization Methods	13
2.1	Precursors and Formation of Fossil Hydrocarbons	13
2.2	Coal Petrography, Macerals and Rank	17
2.3	The Chemical Composition of Fossil Hydrocarbons	25
CHAPTER 3	Pyrolysis: Thermal Breakdown of Solid Fuels in a Gaseous Environment	36
3.1	Introduction to the Design of Pyrolysis Experiments	37
3.2	Product Distributions From Pyrolysis Experiments: General Trends	40
3.3	On the Design of Bench-Scale Pyrolysis Reactors: Wire-Mesh Reactors	43
3.4	The Design of Bench-Scale Fixed-Bed ("Hot-Rod") Pyrolysis Reactors	54
3.5	Bench Scale Fluidized-Bed & Entrained Flow Pyrolysis Reactors (Atmospheric Pressure)	57
3.6	Comparison of Results From Bench-Scale Pyrolysis Reactors	59
3.7	Case Studies – Pyrolysis of Coal Macerals	68
3.8	Case Studies: The Reactive Inertinites of Southern Hemisphere Coals	78
3.9	Case Studies: The Pyrolysis of Kerogens	80
3.10	Case Studies: The Pyrolysis of Biomass Materials	81

CHAPTER 4	High-Pressure Reactor Design & Applications: Pyrolysis, Hydropyrolysis and Gasification	91
4.1	Rates of Char Deactivation and Implications for Reaction Design	93
4.2	The Design of High-Pressure Wire-Mesh Reactors	95
4.3	The Design of High-Pressure Bench-Scale Fluidized-Bed Reactors	111
4.4	Comparing Gasification Data from Reactors with Different Configurations	117
4.5	Case Studies: Factors Governing Coal Reactivity in Pyrolysis & Gasification	127
4.6	Case Studies: Simulating Entrained-Flow Gasification in a Wire-Mesh Reactor	135
4.7	Case Studies: By-Product Formation and Trace Element Problems in a Pilot Gasifier Processing Coal and Biomass	142
4.8	Case Studies: Synergistic Effects in Biomass Processing & Problems in Refining Biomass Pyrolysis Tars	152
CHAPTER 5	Liquefaction: Thermal Breakdown in the Liquid Phase	161
5.1	Introduction: Coal Liquefaction	162
5.2	The British Coal Liquefaction Process	165
5.3	On the Design of Bench-Scale Liquefaction Experiments	166
5.4	Comparing Liquefaction in the Flowing-Solvent Reactor and a "Mini-Bomb"	173
5.5	Effect of Solvent Type on the Extent of Extraction	178
5.6	Flowing-Solvent Reactor: Successive Extract Fractions Released from Coal	180
5.7	A Two Stage Kinetic Model of Primary Coal Liquefaction	182
5.8	Brief Overview of Liquefaction	195
CHAPTER 6	Thermal Breakdown in Coals: Comparing Structural Changes in Pyrolysis and Liquefaction	199
6.1	Introduction	199
6.2	The Electron Spin Resonance (ESR) Spectrometry of Thermal Breakdown	201
6.3	Extractables as a Diagnostic Tool for Pre-Pyrolysis Phenomena	205
6.4	Hydrogen Donors in Coals: Liptinites and Others	211
6.5	Overview of Thermal Breakdown in Coals	214

CHAPTER 7	Analytical Techniques for Low Mass Materials: Method Development	217
7.1	Gas Chromatography	218
7.2	Supercritical Fluid Chromatography (SFC)	224
7.3	High Performance Liquid Chromatography	228
7.4	Combined Chromatographic Methods	232
7.5	Unified Chromatography	233
7.6	Mass Spectrometric Methods	234
7.7	Aliphatic Materials from Coal and Petroleum	246
7.8	Conclusion	253
CHAPTER 8	Analytical Techniques for High Mass Materials: Method Development	261
8.1	Introduction	261
8.2	SEC as Method to Examine Molecular Mass or Size Ranges of Complex Mixtures	262
8.3	Fractionation Methods to Isolate Molecules of Large Mass or Size	279
8.4	Application of SEC and Fractionation Methods to Samples	282
8.5	Aggregation of Small Polar Molecules to Appear as Large Molecules – in NMP?	295
8.6	Molecular Mass Methods – Mass Spectrometry of High Mass Materials >500 u.	300
8.7	ICP-MS for Metallic Trace Elements	312
8.8	Summary	314
8.9	Structural Features of Large Molecular Mass Material Identified by SEC and MALDI-MS	315
8.10	Summary of Structural Features of the Largest Molecules	324
CHAPTER 9	Concluding Remarks: Where to With Solid Fuels?	336
9.1	Characterizing Solid Fuels and Heavy Hydrocarbon Liquids	336
9.2	Solids Fuel Conversion to Gases and Liquids	341
9.3	Energy Demand – Energy Supplies: The Big Questions	344