

Supercritical Extraction Of Coal

by

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## TABLE OF CONTENTS

|                            |    |
|----------------------------|----|
| ACKNOWLEDGEMENTS . . . . . | ii |
|----------------------------|----|

### Chapter

page

|      |                                                         |    |
|------|---------------------------------------------------------|----|
| I.   | INTRODUCTION AND OBJECTIVES . . . . .                   | 1  |
| II.  | THEORY OF SUPERCRITICAL EXTRACTION (SCE) . . . . .      | 5  |
|      | Supercritical Solvents . . . . .                        | 5  |
|      | Critical States: Stability and Equilibrium . . . . .    | 14 |
|      | Phase Equilibria Involved in SCE of                     |    |
|      | Hydrocarbons . . . . .                                  | 18 |
|      | Modelling Phase Equilibrium of SCE . . . . .            | 28 |
|      | Approaches to Modelling of SCE . . . . .                | 29 |
|      | Expanded Liquid Approach . . . . .                      | 29 |
|      | Compressed Gas Approach . . . . .                       | 32 |
|      | Approaches Which Do Not Require Critical                |    |
|      | Data . . . . .                                          | 33 |
|      | Review of Equations of State as Applied to              |    |
|      | SCE . . . . .                                           | 36 |
|      | Hildebrand Solubility Parameter . . . . .               | 43 |
| III. | NATURE OF COAL . . . . .                                | 46 |
|      | Coal Properties and Their Significance in SCE           |    |
|      | of Coal . . . . .                                       | 47 |
|      | The Porous Nature of Coal . . . . .                     | 48 |
|      | Porous Structure of Coal . . . . .                      | 49 |
|      | Measurement of Pore Structure . . . . .                 | 50 |
|      | Thermal Behaviour of Coal . . . . .                     | 52 |
| IV.  | SOME PROCESSES WHICH USE SUPERCRITICAL FLUIDS . . . . . | 58 |
|      | Description of Kerr McGee Critical Solvent              |    |
|      | Deashing (CSD) Process . . . . .                        | 59 |
|      | Description of Supercritical Gas Extraction             |    |
|      | Process . . . . .                                       | 62 |
|      | Mechanism of SCE . . . . .                              | 66 |
|      | Extracts from SCE of Coal . . . . .                     | 72 |
|      | Problem Areas and Needed Improvements in SCE of         |    |
|      | Coal Processes . . . . .                                | 77 |
| V.   | EXPERIMENTAL WORK . . . . .                             | 79 |
|      | Objectives . . . . .                                    | 79 |

|                                                                                                            |     |
|------------------------------------------------------------------------------------------------------------|-----|
| Experimental Systems . . . . .                                                                             | 82  |
| Description of High Temperature Semi-Batch<br>SCE system . . . . .                                         | 83  |
| Description of the Low Temperature Semi-<br>Batch SCE System . . . . .                                     | 89  |
| Description of Analytical Facilities and<br>Procedure . . . . .                                            | 93  |
| Feed Preparation . . . . .                                                                                 | 93  |
| Post-treatment Analysis . . . . .                                                                          | 95  |
| Experimental Design . . . . .                                                                              | 97  |
| Data Compilation and Management . . . . .                                                                  | 100 |
| VI. RESULTS OF EXPERIMENTAL WORK . . . . .                                                                 | 105 |
| SCE with the High Temperature System . . . . .                                                             | 107 |
| Results of the Experimental Work . . . . .                                                                 | 112 |
| Analysis and Discussion of Results of High<br>Temperature System . . . . .                                 | 116 |
| Accuracy of Material Balance Results . . . . .                                                             | 116 |
| Analysis of Effects of Design Parameters<br>on Supercritical Extraction . . . . .                          | 126 |
| Comparison of SCE Results for Different<br>Solvent Strengths . . . . .                                     | 140 |
| Residua Analysis . . . . .                                                                                 | 141 |
| Summary of Analyses on SCE at High<br>Temperatures . . . . .                                               | 144 |
| SCE with the Low Temperature System . . . . .                                                              | 147 |
| VII. PROCESS DESIGN AND ECONOMIC CONSIDERATIONS OF SCE<br>OF COAL . . . . .                                | 152 |
| Method of Economic Analysis . . . . .                                                                      | 153 |
| Implementation of ESCOE method . . . . .                                                                   | 156 |
| Comparison of Supercritical Gas Extraction<br>(SGE) Process with Other Liquefaction<br>Processes . . . . . | 157 |
| Process Comparisons . . . . .                                                                              | 160 |
| Process Complexity . . . . .                                                                               | 160 |
| Efficiency . . . . .                                                                                       | 161 |
| Development Status . . . . .                                                                               | 163 |
| Liquefaction Products . . . . .                                                                            | 164 |
| Comparative Economics of Coal Liquefaction<br>Processes . . . . .                                          | 165 |
| Optimization Considerations for SGE . . . . .                                                              | 174 |
| Process Design Implications of Experimental<br>Findings . . . . .                                          | 177 |
| VIII. CONCLUSIONS . . . . .                                                                                | 180 |

|                                                                                                                             |     |
|-----------------------------------------------------------------------------------------------------------------------------|-----|
| Mechanism of Supercritical Extraction of Coal<br>at Temperatures Close to Coal Pyrolysis<br>Reaction Temperatures . . . . . | 181 |
| Supercritical Extraction of Coal near Ambient<br>Temperatures with Carbon Dioxide . . .                                     | 183 |
| Process Design Alternatives . . . . .                                                                                       | 184 |
| IX. RECOMMENDATIONS FOR FURTHER RESEARCH . . . . .                                                                          | 186 |
| BIBLIOGRAPHY . . . . .                                                                                                      | 188 |

## Appendix

|                                                                                          | <u>page</u> |
|------------------------------------------------------------------------------------------|-------------|
| A. OPERATING PROCEDURES FOR EXPERIMENTAL SYSTEMS .                                       | 199         |
| Procedure for Operating the High Temperature<br>System . . . . .                         | 199         |
| Procedure for Operating the Low Temperature<br>System . . . . .                          | 201         |
| B. SAMPLE CALCULATIONS FOR HIGH TEMPERATURE SYSTEMS                                      | 203         |
| High Temperature System Run Data Log . . . . .                                           | 203         |
| Sample Calculation: Percent Extraction . . . . .                                         | 204         |
| Extract Fractionation Data Log . . . . .                                                 | 205         |
| Sample Calculations: Extract Fractionation and<br>Extract Amounts for each Run . . . . . | 208         |
| Residue Data Log . . . . .                                                               | 210         |
| Sample Calculations: Residua . . . . .                                                   | 211         |
| Sample Calculations: Gas . . . . .                                                       | 212         |
| C. SAMPLE CALCULATIONS FOR LOW TEMPERATURE SYSTEMS                                       | 213         |
| Low Temperature System Run Data Log . . . . .                                            | 213         |
| Sample Calculations: Low Temperature System .                                            | 214         |
| D. SAMPLE CALCULATION: HILDEBRAND SOLUBILITY<br>PARAMETER . . . . .                      | 215         |
| E. STATISTICAL ANALYSIS . . . . .                                                        | 216         |
| Selection of Experimental Design . . . . .                                               | 216         |
| Calculation of Main Effects: Averaging<br>Individual Measures of Effects . . . . .       | 218         |
| Calculation of Interaction Effects . . . . .                                             | 219         |
| Quicker methods of Calculating Effects: Yates<br>Algorithm . . . . .                     | 220         |
| Sample Calculation: Standard Deviation . . . . .                                         | 222         |

|      |                                                                 |     |
|------|-----------------------------------------------------------------|-----|
|      | Diagnostic Checks . . . . .                                     | 223 |
| F.   | ASSUMPTIONS FOR COST ESTIMATION . . . . .                       | 226 |
|      | Cost Assumptions . . . . .                                      | 226 |
| G.   | PRODUCT STREAMS OF SELECTED LIQUEFACTION<br>PROCESSES . . . . . | 228 |
| H.   | SAMPLE CALCULATIONS: ECONOMIC ANALYSIS . . . . .                | 229 |
| VITA | . . . . .                                                       | 232 |

## LIST OF TABLES

| <u>Table</u>                                                                                                  | <u>page</u> |
|---------------------------------------------------------------------------------------------------------------|-------------|
| 1. Transport Properties for a Typical Liquid,<br>Supercritical Fluid, and Gas . . . . .                       | 8           |
| 2. Surface Areas of Two American Coals by Different<br>Methods . . . . .                                      | 53          |
| 3. Effect of SRC Process Variables on Recovery of Coal<br>Liquids with CSD Unit . . . . .                     | 63          |
| 4. Product Mix of A Self-Sufficient SGE Design . . . . .                                                      | 70          |
| 5. Typical Elemental Analysis of SCE Feed and Products<br>For a Low Rank British Coal . . . . .               | 74          |
| 6. Analysis of the Feed Coal (Wyodak 1) . . . . .                                                             | 94          |
| 7. Extraction of Coal with Carbon Dioxide . . . . .                                                           | 101         |
| 8. Extraction of Heat-Pretreated Coal with Carbon<br>Dioxide . . . . .                                        | 102         |
| 9. Extraction of Coal with Carbon Dioxide After<br>Pretreatment with Solvents . . . . .                       | 103         |
| 10. SCE Extraction with High Temperature System . . . . .                                                     | 104         |
| 11. Critical Properties of Solvents Used in<br>Supercritical Extractions . . . . .                            | 106         |
| 12. Hildebrand Solubility Parameters at the Extraction<br>Conditions of the High Temperature System . . . . . | 110         |
| 13. Summary of Experimental Conditions and Percent<br>Extraction . . . . .                                    | 114         |
| 14. Amount of Extract Collected During Each Sampling<br>Period . . . . .                                      | 115         |
| 15. Comparison of Analyses from Soxhlet Extraction and<br>Filtration Procedures . . . . .                     | 117         |
| 16. Extract Fraction Distribution for each Sampling<br>Period . . . . .                                       | 118         |

|     |                                                                                                                                 |     |
|-----|---------------------------------------------------------------------------------------------------------------------------------|-----|
| 17. | Overall Material Balance . . . . .                                                                                              | 119 |
| 18. | Extraction Residua Analysis . . . . .                                                                                           | 120 |
| 19. | Effect Analysis for Percent Extraction of Dried Coal<br>with Toluene . . . . .                                                  | 128 |
| 20. | Nomenclature Used in the Effect Analysis of<br>Fractional Extraction Completion and Extract<br>Component Distribution . . . . . | 133 |
| 21. | Effect Analysis of Fractional Extraction Completion                                                                             | 135 |
| 22. | Effect Analysis of Extract Component Distribution                                                                               | 138 |
| 23. | Time Distributions of Average Extract Components and<br>Fractional Extraction Completion for Two<br>Solubility Ranges . . . . . | 142 |
| 24. | Summary of Extractions with Low Temperature System                                                                              | 151 |
| 25. | Value Factors for Selected Synfuel Conversion<br>Products . . . . .                                                             | 158 |
| 26. | Comparative Complexity of Different Liquefaction<br>Processes . . . . .                                                         | 162 |
| 27. | Variation of Energy Prices of Selected Hydrocarbons<br>and Fuels with Hydrogen/Carbon Ratio . . . . .                           | 168 |
| 28. | Comparative Cost of Selected Coal Liquefaction<br>Processes . . . . .                                                           | 170 |
| 29. | Economics of Coal Liquefaction Processes . . . . .                                                                              | 171 |
| 30. | Sensitivity of SGE I Economics to Percent Extraction<br>and Extract Value Factor . . . . .                                      | 173 |
| 31. | Economics of Satellite SGE Plants . . . . .                                                                                     | 176 |
| 32. | Extract Components at Different Periods of Each Run                                                                             | 209 |
| 33. | Calculations for Carrying Out and Checking Yates<br>Algorithm . . . . .                                                         | 221 |
| 34. | Fifteen Ordered Effects and Probability Points . .                                                                              | 224 |

## LIST OF FIGURES

| <u>Figure</u>                                                                                                                    | <u>page</u> |
|----------------------------------------------------------------------------------------------------------------------------------|-------------|
| 1. Density of Carbon Dioxide . . . . .                                                                                           | 6           |
| 2. Solubility of p-iodochlorobenzene in Ethylene at<br>15°C . . . . .                                                            | 7           |
| 3. Ternary Diagrams for Representation of SCE in the<br>Presence of an Entrainer . . . . .                                       | 10          |
| 4. Solubility of Naphthalene in Compressed Ethylene . .                                                                          | 12          |
| 5. Classes of Fluid Phase Equilibria (Van Konynenberg<br>and Scott) . . . . .                                                    | 21          |
| 6. The Phase Diagrams if the Critical Temperatures of<br>Pure Components are Well Separated (Street) . . .                       | 23          |
| 7. Pressure-Composition Diagram for an Isotherm where<br>Solid-Fluid Equilibria Exists (Street) . . . . .                        | 24          |
| 8. Temperature-Composition Projection of Ethylene-<br>Naphthalene Above the Critical Locus (Kurnik) . .                          | 26          |
| 9. Phase Behaviour of Hydrocarbon-Water Systems . . . .                                                                          | 27          |
| 10. Solubility of Carbon Dioxide in Air at 143°K<br>(Prausnitz) . . . . .                                                        | 38          |
| 11. Conversion of Coal Reacted at 400°C in Tetralin . .                                                                          | 56          |
| 12. Conversion of Coal Reacted at 400°C in Naphthalene .                                                                         | 57          |
| 13. Kerr McGee Critical Solvent Deashing Process . . . .                                                                         | 61          |
| 14. Conceptual Design of SGE by Catalytic Inc. . . . .                                                                           | 67          |
| 15. Conceptual Design of SCE Complex by Catalytic Inc. .                                                                         | 68          |
| 16. Conceptual Design of SCE Complex by NCB . . . . .                                                                            | 69          |
| 17. Average Molecular Weights of Extract Fractions From<br>SCE of Low Rank British Coals for a Constant Time<br>Period . . . . . | 75          |

|     |                                                                                                   |     |
|-----|---------------------------------------------------------------------------------------------------|-----|
| 18. | Average Structure of Extract Fractions from a SCE of<br>a Low Rank British Coal . . . . .         | 76  |
| 19. | High Temperature Supercritical Extraction System . .                                              | 86  |
| 20. | Low Temperature Extraction System . . . . .                                                       | 90  |
| 21. | Feed Preparation . . . . .                                                                        | 96  |
| 22. | Product Analysis Procedure . . . . .                                                              | 98  |
| 23. | Alternate Extract Fractionation Procedure . . . . .                                               | 99  |
| 24. | Experimental Conditions in Terms of Reduced<br>Temperatures and Pressures of the Solvent . . .    | 111 |
| 25. | Micrographs of Dried Raw Coal and Residua from<br>Extractions with Supercritical Solvents . . . . | 145 |
| 26. | A Synfuel Complex Where SGE Char is Fed to an<br>Indirect Liquefaction Process . . . . .          | 159 |
| 27. | A Satellite SGE Plant . . . . .                                                                   | 175 |
| 28. | A Design for SCE of Coal with the Aid of Entrainers                                               | 178 |
| 29. | Normal Plot of Effects on Asphaltols Distribution                                                 | 225 |

## Chapter I

### INTRODUCTION AND OBJECTIVES

Sharply increasing oil prices and dwindling resources have resulted in intense research efforts to develop more energy efficient processes for using hydrocarbon resources other than oil and natural gas. Coal, being the most abundant hydrocarbon source, is receiving considerable attention as an alternative resource to crude oil and natural gas. Coal conversion processes can be classified under two general categories, namely coal liquefaction and coal gasification. Supercritical extraction of coal is viewed as a coal liquefaction route.

Coal liquefaction processes can be further classified as indirect or direct. In indirect processes, coal is first gasified to form synthesis gas which is then catalytically converted to liquid products. Direct liquefaction processes convert coal directly to liquid products, light gases, and residua which consist of unreacted coal and mineral matter. The direct processes typically use high temperatures and pressures (typically 400°C and 13.8 MPa respectively). In most direct liquefaction processes coal is slurried with a liquid and pumped through a reactor following a fired pre-heater. The slurrying medium partially hydrogenates and stabilizes the thermally-ruptured free radicals.

The product slate of indirect liquefaction processes includes a wide variety of products. Fischer-Tropsch and M-Gasoline processes are two examples of indirect liquefaction processes. Large commercial liquefaction plants, namely SASOL I and SASOL II in South Africa, utilize Fischer-Tropsch (F-T) technology. M-Gasoline, developed by Mobil, is more specific in product slate and produces mainly gasoline. A commercial size plant is being built in New Zealand to convert natural gas using the M-Gasoline process. Another venture close to commercialization is Tennessee Eastman's Coal Gasification/Acetic Anhydride plant.

The commercialization schedules of direct liquefaction processes lag in comparison to indirect liquefaction processes. The processes which are furthest along in the development program are, the Exxon Donor Solvent (EDS) process, Solvent Refined Coal (SRC) I and II, the H-coal process, and the Supercritical Gas Extraction (SGE) process. The SGE process is being developed in England by the National Coal Board (NCB).

Although the high solvency power of compressed gases was experimentally demonstrated as early as 1879 [1], this high solvency property of compressed gases has only been recently exploited.

Supercritical extraction processes use fluids at near critical temperatures and at pressures higher than the critical to selectively extract and/or fractionate non-volatile solid and/or liquid solutes. In the presence of such supercritical fluids the volatility of the solutes is enhanced several orders of magnitude. SCE is effective at temperatures much lower than fractionation by distillation. At present, most commercial ventures and efforts are focused on supercritical extraction of high priced, heat-labile natural products using non-toxic, cheap gases which have near ambient critical temperatures. The most widely used supercritical solvents are carbon dioxide and ethylene. Two present applications of supercritical extraction in coal liquefaction are;

1. Supercritical extraction of coal, which is being developed by NCB.
2. Kerr-McGee Critical Solvent Deashing(CSD), which separates ash and unreacted coal from heavy coal liquids formed in direct liquefaction processes.

The main objective of this dissertation was to explore some of the phenomenological aspects of Super Critical Extraction (SCE) of coal. Exploratory experiments on extraction of coal with commercially promising solvents, e.g. water as well as with solvents which model different classes

of chemicals, were performed. The possible use of entrainers to modify the solvency power of supercritical solvents was also studied. Theoretical work mainly concentrated on understanding the complex sequence of changes of the coal and the solvent. Process design and optimization considerations are discussed and some alternatives to present commercializations efforts are suggested.

This dissertation consists of 9 Chapters. Chapter I introduces the topics and the objectives. The theory of SCE is discussed in Chapter II, including description of supercritical solvents and the thermodynamics of SCE. The physical and chemical properties of coal which are important in understanding the SCE are discussed in Chapter III. Some of the present applications of supercritical fluids are reviewed in Chapter IV. Experimental work is described in Chapter V and the results are discussed in Chapter VI. Process design alternatives and economics are discussed in Chapter VII. Overall conclusions are presented in Chapter VIII followed by the recommendations for further research in Chapter IX.

## Chapter II

### THEORY OF SUPERCRITICAL EXTRACTION (SCE)

#### 2.1 SUPERCRITICAL SOLVENTS

Supercritical fluids are fluids near their critical temperatures, at pressures higher than the critical. As shown in Figure 1 [2], at those conditions solvent densities are generally similar to that of a typical liquid. In the presence of such supercritical fluids volatility of solutes are usually enhanced several orders of magnitude primarily because of the thermodynamic nonideality of the mixture (Figure 2 [3]). Comparison of transport properties of gases, liquids, and supercritical fluids (SCF) are shown in Table 1. Extraction with supercritical fluids is called supercritical extraction(SCE).

Supercritical extraction and liquid extraction are similar in the need of solvent regeneration but differ in methods of solvent regeneration. In liquid extraction solvent is regenerated at a subsequent stage with distillation. The solvent regeneration methods in SCE are many. The simplest method of solvent regeneration is reduction of pressure. Due to pressure reduction, the solvency power of the gas disappears and the extracted material precipitates. The di-

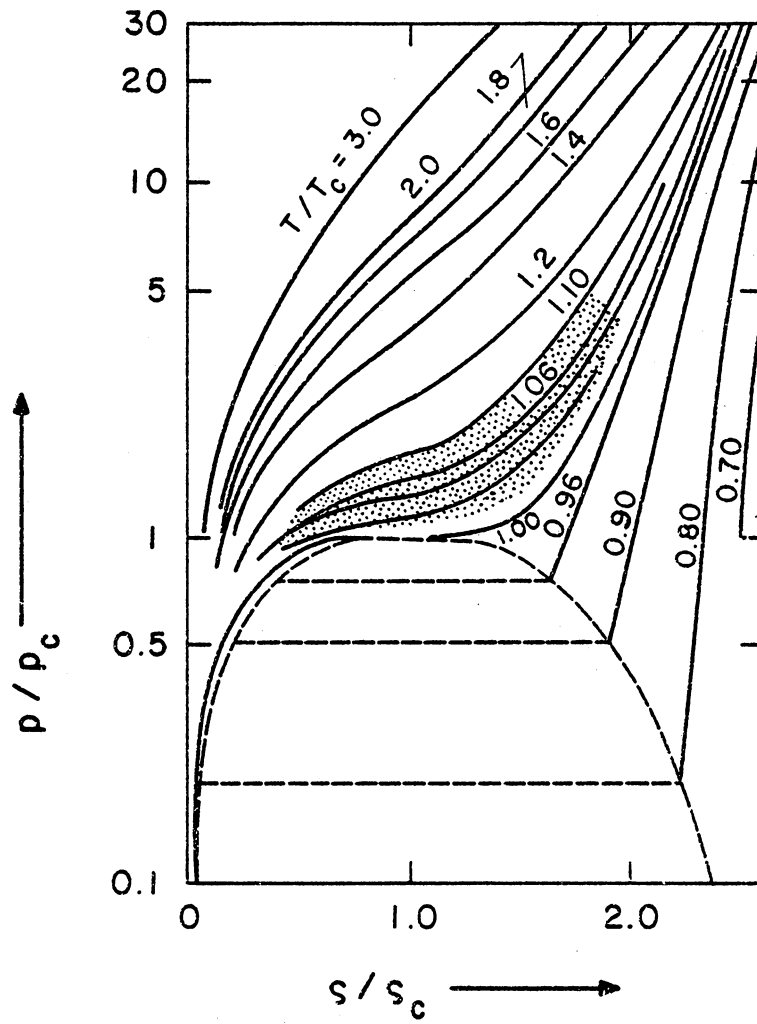


Figure 1: Density of Carbon Dioxide

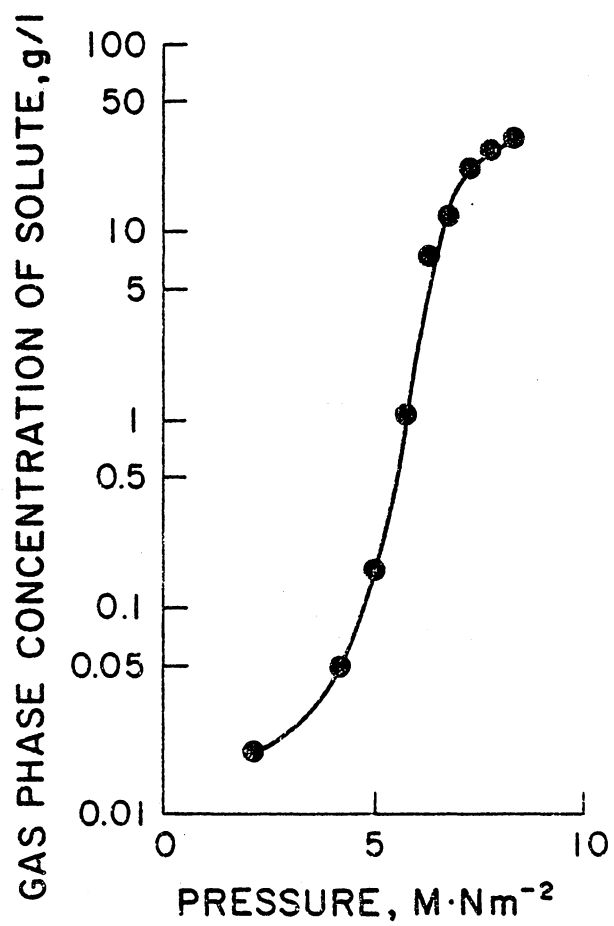


Figure 2: Solubility of p-iodochlorobenzene in Ethylene at 15°C

TABLE 1

Transport Properties for a Typical Liquid,  
Supercritical Fluid and Gas

| Property                                        | Phase            |                  |                  |
|-------------------------------------------------|------------------|------------------|------------------|
|                                                 | SCF              | Gas              | Liquid           |
| Density<br>(kg/m <sup>3</sup> )                 | 500              | 10               | 1000             |
| Viscosity<br>(Newton s/m <sup>2</sup> )         | 10 <sup>-5</sup> | 10 <sup>-6</sup> | 10 <sup>-4</sup> |
| Diffusion<br>Coefficient<br>(m <sup>2</sup> /s) | 10 <sup>-7</sup> | 10 <sup>-5</sup> | 10 <sup>-9</sup> |

sadvantage of this method is the high cost of solvent recompression. At temperatures in the range of  $1.0 \leq T_R \leq 1.5$  ( $T_R$  = Reduced temperature) and pressures in the range of  $1 \leq P_R \leq 3.0$  ( $P_R$  = Reduced pressure) a temperature increase at constant pressure causes a noticeable decrease of density of compressed gases. However, this temperature increase does not result in sufficiently high degree of regeneration. Addition of a third component, often referred as an entrainer or modifier, increases the temperature dependence of the solubility of the low volatile components in the supercritical phase. In the range of the critical temperature of the supercritical solvent and the entrainer, the solvency power is increased so much that effective regeneration of the supercritical solvent is possible by a temperature change only. Figure 3 illustrates the extraction and regeneration steps in ternary diagrams.

The current interest in SCE for separation and/or purification of solid and/or liquid mixtures results from:

1. Sensitivity to process variables

In liquid extraction, only temperature has a strong effect on equilibrium solubility. The existence of small amounts of trace components usually does not affect solubility significantly. However, in SCE the effects of temperature, pressure, and com-

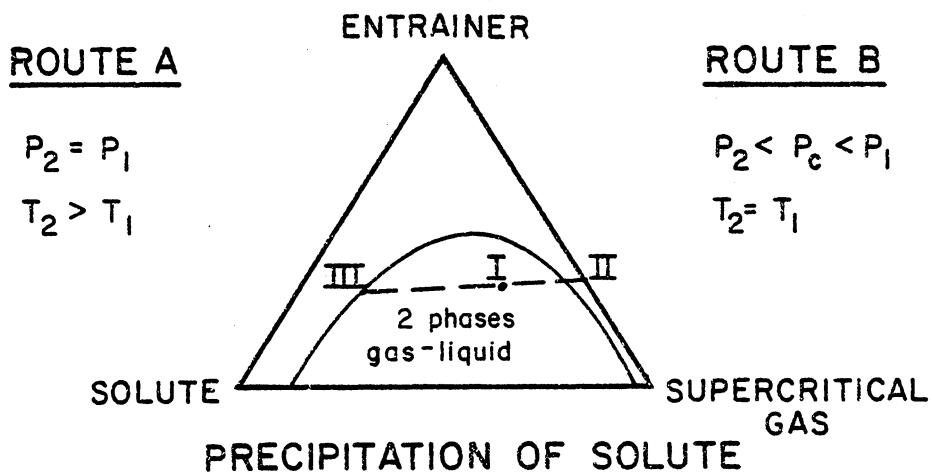
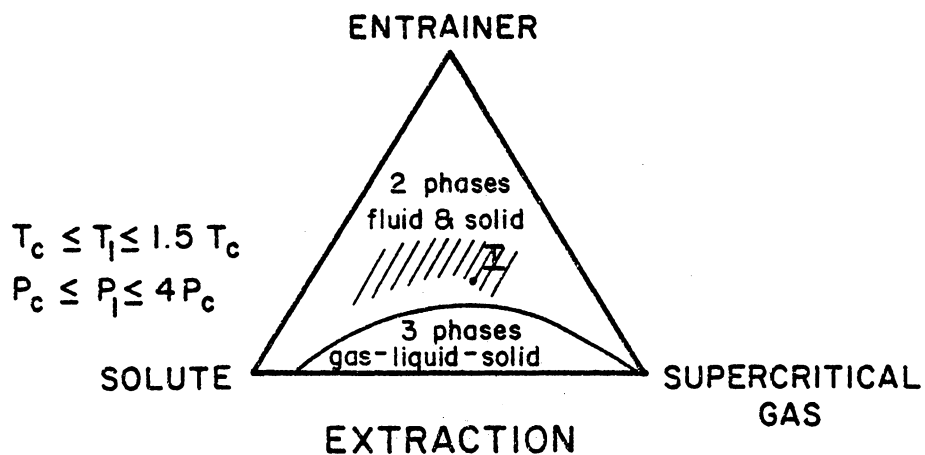


Figure 3: Ternary Diagrams for Representation of SCE in the Presence of an Entrainer

position on solubility are important. Furthermore, depending on whether or not conditions are near the critical pressure of the solvent, the solubility may increase or decrease several orders of magnitude with small changes in temperature (Figure 4 [4]). Sharp solubility changes with small perturbations of process variables ensure almost complete regeneration of solvents as well as fractionations which were not possible before. For example, addition of an entrainer increases the temperature dependence of the solubility of the low volatile components in the fluid phase as well as often increasing solubility and inducing selectivity. In the vicinity of the solvent critical temperature, the temperature dependence of the solvency power increases so much that the regeneration of the solvent gas is possible by only a slight temperature increase [5]. This sensitivity to process variables may lead to innovative and efficient process designs.

## 2. Energy saving

SCE can be more energy efficient than distillation especially for more difficult separations [6]. With better understanding of high pressure phase equilibria, the energy efficiency can be improved. For ex-

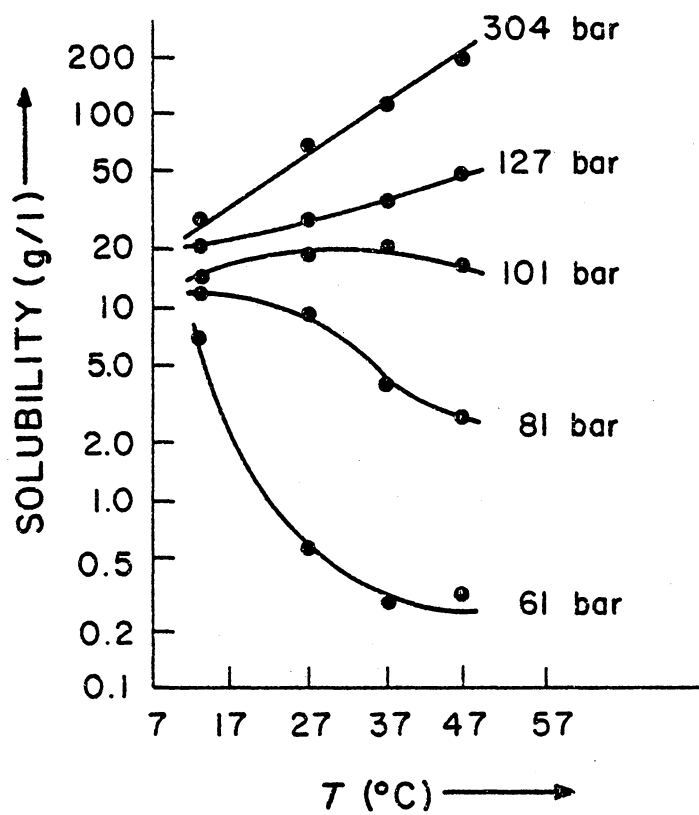


Figure 4: Solubility of Naphthalene in Compressed Ethylene

ample, one option which is only used in deashing of coal or heavy petroleum residua is the addition of a third component to agglomerate and precipitate the heavier fractions. Use of entrainers, which is a closely related phenomenon to deashing, may also be an efficient way of decreasing energy requirements as well as enhancing solubility and/or inducing selectivity in extraction steps.

3. Volatility enhancement for low volatile compounds.

As shown in Figure 2, the volatility of the low volatile solute is enhanced several orders of magnitude in the presence of a supercritical fluid. Thus, it is possible to fractionate low volatile compounds at temperatures much lower than in distillation. The low temperature operations ensure higher quality and safer heat-labile products. Solvent mixtures with nearly the same critical points, and solid and/or liquid entrainers are means of further enhancing the volatility of the low volatile components [7].

4. Good transport properties.

As shown in Table 1, low viscosities and high diffusivities of supercritical fluids make them attractive in heavy hydrocarbon processing. High mass transfer diffusivity coefficients suggest high mass

transfer coefficients and hence higher mass transfer rates than are possible in liquid extractions. Furthermore, liquid like densities enable supercritical fluids to carry significant amount of solute. Thus, supercritical fluids blend the favorable properties of both gases and liquids.

5. Potential for use of non-toxic, non-flammable, and inexpensive solvents

Probably the most widely used SCE solvent is carbon dioxide due to its low cost, non-toxicity, non-inflammability, and a critical temperature conveniently close to ambient temperatures (31.1°C). Such properties make carbon dioxide an ideal solvent for food and pharmaceutical processes.

2.2 CRITICAL STATES: STABILITY AND EQUILIBRIUM

Since supercritical extraction involves solvents above their critical points, definition and computation of critical phenomena are essential in prediction, modelling, and identification of various phases at high pressures. In this section, critical phenomena, state and stability requirements will be briefly reviewed. The review of the phase behavior will be the topic of the next section.

Gibbs presented the definition of critical state in his pioneering paper On the Equilibrium of Heterogenous Substances in 1876 [8] as:

It has been ascertained by experiment that the variations of two coexisting states of the same substance are in some cases limited in one direction by a terminal state at which the distinction of the coexisting phases vanishes. This state has been called the critical state.

He then proceeded to show the implications by deriving certain mathematical relationships between the thermodynamic properties at the critical point.

For a pure substance, the critical state is the state coincident with the highest pressure and temperature at which two phases coexisting in equilibrium become indistinguishable from one another with reference to all their intensive properties. The critical state of a pure compound is governed by following thermodynamic relations:

$$P > 0 \qquad \qquad \qquad \text{Eq. 2.1}$$

$$(\partial P / \partial V)_T = 0 \qquad \qquad \qquad \text{Eq. 2.2}$$

$$(\partial^2 P / \partial^2 V)_T = 0 \qquad \qquad \qquad \text{Eq. 2.3}$$

where  $T$ ,  $P$ , and  $V$  are temperature, pressure, and volume respectively.

The critical state for mixtures is defined in a similar manner as for pure substances. However, in general, for

mixtures it is neither the highest pressure nor the highest temperature at which two phases can coexist in equilibrium. The critical points found experimentally for "simple" binary mixtures have been conventionally put into two distinct categories. At temperatures well below the critical temperature of more volatile component, liquid-liquid critical points are observed, and at temperatures near the critical temperatures of both components gas-liquid critical points are seen. There is no absolute distinction between Liquid-Liquid (L-L) and Gas-Liquid (G-L) critical points for mixtures. They are both defined by the limits of "diffusional stability". For mixtures, mechanical and thermal stability criteria are not sufficient to describe the critical behaviour and diffusional (material) stability criteria, Eq. 2.4 and Eq. 2.5, are required.

$$U = \begin{vmatrix} \frac{\partial^2 G}{\partial x_1^2} & \cdot & \cdot & \cdot & \frac{\partial^2 G}{\partial x_1 \partial x_{n-1}} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \frac{\partial^2 G}{\partial x_{n-1} \partial x_1} & & & & \frac{\partial^2 G}{\partial x_{n-1}^2} \end{vmatrix} = 0 \quad \text{Eq. 2.4}$$

$$M = \begin{vmatrix} \frac{\partial U}{\partial x_1} & \cdots & \frac{\partial U}{\partial x_{n-1}} \\ \frac{\partial^2 G}{\partial x_1^2} & \cdots & \frac{\partial^2 G}{\partial x_1 \partial x_{n-1}} \\ \vdots & \ddots & \vdots \\ \frac{\partial^2 G}{\partial x_{n-1} \partial x_1} & \cdots & \frac{\partial^2 G}{\partial x_{n-1}^2} \end{vmatrix} = 0 \quad \text{Eq. 2.5}$$

where  $G$  is the Gibbs free energy and  $x$  is the component mole fraction.

Various other authors [9, 10] have transformed Gibbs' criteria to other variable sets and recently Reid and Beegle [11] have developed Gibbs' criteria in Legendre transforms. They derived the two necessary and sufficient conditions in terms of " $n$ " Legendre transforms, where  $n$  is the number of components present in the system.  $y^{(n)}$  is the  $n^{\text{th}}$  order Legendre transform, and  $y_{(n+1)(n+1)}^n$  is the second order partial derivative with respect to extensive variable  $x_{n+1}$ ; the derivative is obtained at constant value of  $\zeta_1, \zeta_2, \dots, \zeta_n, x_{n+2}$ .  $\zeta_1$  is an intensive variable and is the partial derivative of zero order Legendre transform, that is, the base function  $y^0 = f(x_1, x_2, \dots, x_{n+2})$  with respect to  $x_1$ .

$$y_{(n+1)(n+1)}^n = 0 \quad \text{Eq. 2.4a}$$

$$y_{(n+1)(n+1)(n+1)}^n = 0 \quad \text{Eq. 2.5a}$$

Furthermore, Reid and Beegle extend their approach to suggest modifications to overcome indeterminacy.

It is desirable to point out some phenomena which occur in mixtures which do not occur in pure substances. By far the most important of these is retrograde condensation [12, 13]. Another unusual phenomenon called the barotropic effect, occurs in some mixtures[14, 15]. When certain mixtures are compressed isothermally, the gaseous phase becomes more dense than the liquid phase and sinks to the bottom of the vessel; such inversion of phases is termed the barotropic effect.

### 2.3 PHASE EQUILIBRIA INVOLVED IN SCE OF HYDROCARBONS

Initial studies of mixtures revealed new phenomena that were not present in pure fluids. The most important of these were the additional types of phase equilibria that arose from the extra degrees of freedom introduced by varying the number and proportion of the components. More systematic and intensive experimental study began by Gibbs' introduction of phase rule (1875) and lasted until about 1915. A revival of experimental thermodynamics of fluids took place during the second quarter of this century as a result of the growth of chemical engineering technology. The systematic application of pressure in the study of phase

equilibria, in particular the effects of pressure on the critical properties, brought new insights into the relations between the three types of two phase equilibria (L-L, L-G, and G-G). A picture of the unity and continuity of the critical phenomena in fluid mixtures has gradually emerged from the experiments of last two decades (especially those of G.M. Schneider [16]). The understanding of these phenomena is only very slowly assimilated into the current literature mainly because of the difficulties in interpretation of multi dimensional phase diagrams. In this section, the phase equilibria as related to supercritical extraction of hydrocarbons are reviewed.

In the classification of phase diagrams, one of the most important analytic papers is due to Scott and Van Konynenberg [17]. They demonstrated that most of the experimental observations can be described qualitatively by Van der Waals equation of state [17, 18]. Using pressure-temperature projections of their results of critical and three-phase lines, they initially grouped fluid phase equilibria into five groups and later added a sixth group, which occurs in some aqueous systems but is not predicted by van der Waals equation of state. These classes are shown in Figure 5 and are described by Street [19]. This classification scheme illustrates the principal lines (degrees of freedom=1) and points

(degrees of freedom=0) that form the boundaries in pressure-temperature space of the surfaces that describe equilibrium between two components. The types of boundary lines are:

1. Solid lines = Pure component vapor pressure curves
2. Dash-dot lines = Three phase lines
3. Dashed lines = Critical lines

The types of points are:

1. Open circles = Pure component critical points
2. Triangles = Critical end points.

The classes described by Scott illustrate only a few of the known types of fluid phase equilibria. There are many more possible classes, especially where azeotropic behaviour variations are involved, as discussed in the works of Rowlinson [20] and King [21].

Supercritical extraction often involves the separation of relatively nonvolatile components, often in the solid phase, through selective solubility in supercritical gases. Thus, the critical temperatures of the pure components are likely to be significantly different and the critical temperature of the solvent is likely to be less than the triple point temperature of the solute. The implication is that there is no common temperature range where both components will be liquid. The phase diagrams involved in cases where the critical temperatures are well separated is best explained by

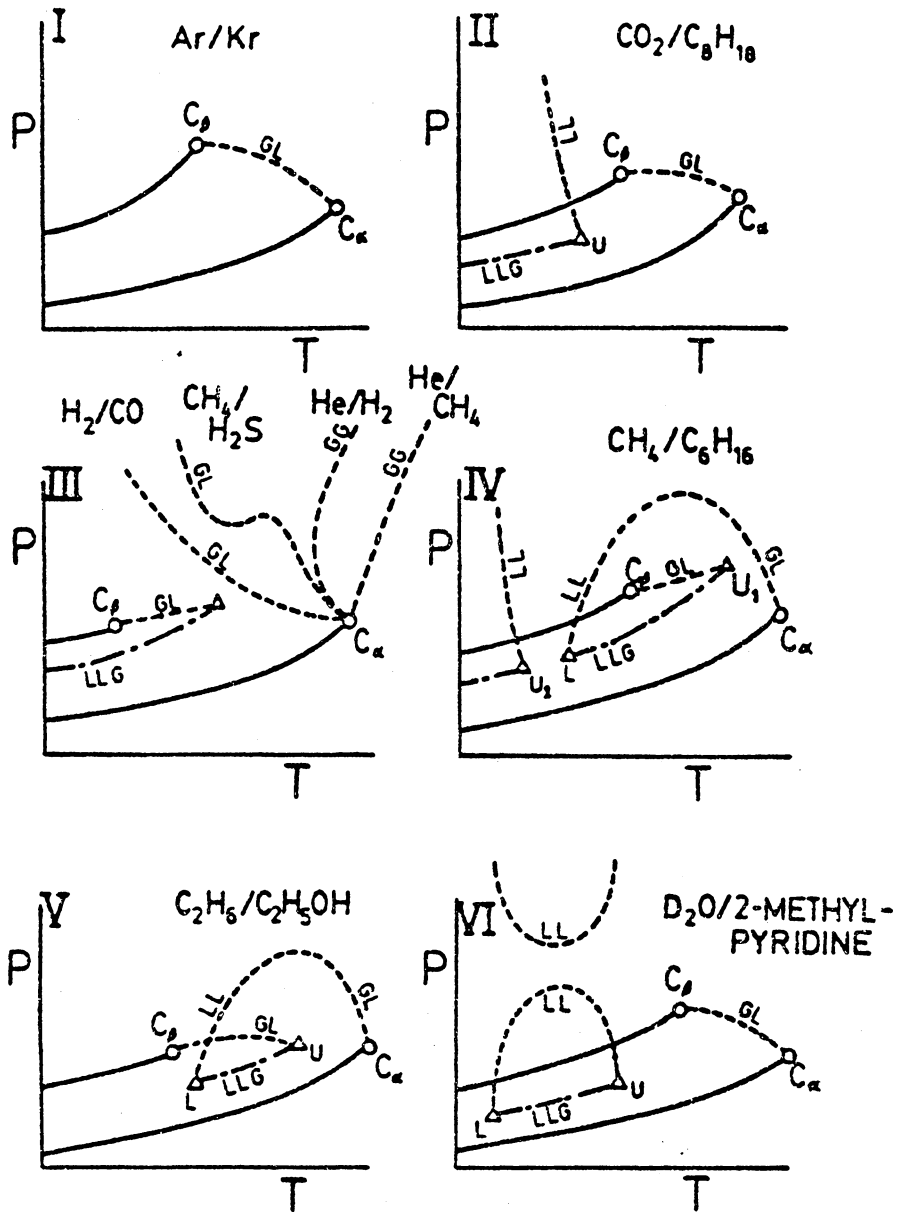


Figure 5: Classes of Fluid Phase Equilibria (Van Konynenberg and Scott)

Figure 6. The full lines are the sublimation, melting, and vapor pressure curves of the pure components  $\alpha$ , and  $\beta$ . Point Q is a quadruple point, where four phases  $S_1$ ,  $S_2$ , L, and G, are in equilibrium. If the temperature of  $C_\beta$  lies far below that of  $A_\alpha$  (triple point of  $\alpha$ ) the three phase region  $S_2+L+G$  curves upwards, and intersects the gas liquid critical line to form critical end points  $U_1$  and  $U_2$ . No liquid phase exists in the temperature range between of  $U_1$  and  $U_2$ . The three sided region  $A_\alpha C_\alpha U_1$  is a region of gas-liquid phase separation. At temperatures between this region and  $U_2$ , the solid phase of component  $\alpha$  is in equilibrium with a  $\beta$ -rich gas phase. If the vapor pressure of  $\alpha$  is small at temperatures less than  $C_\beta$ , then  $U_2$  and Q are virtually coincident with  $C_\beta$  and  $A_\beta$ , respectively. If one looks at a pressure-composition (P-X) isotherm corresponding to a temperature which lies between  $U_1$  and  $U_2$ , it has the shape shown in Figure 7. The region just above the nose on the right of this diagram, where the slope of the gas-phase boundary is negative, illustrates a type of behaviour sometimes associated with enhanced solubility of a nonvolatile solute ( $\alpha$ ) in a supercritical solvent ( $\beta$ ). It has been shown, both experimentally and theoretically, that at much higher pressures this trend is reversed and the gas phase boundary takes on a positive slope.

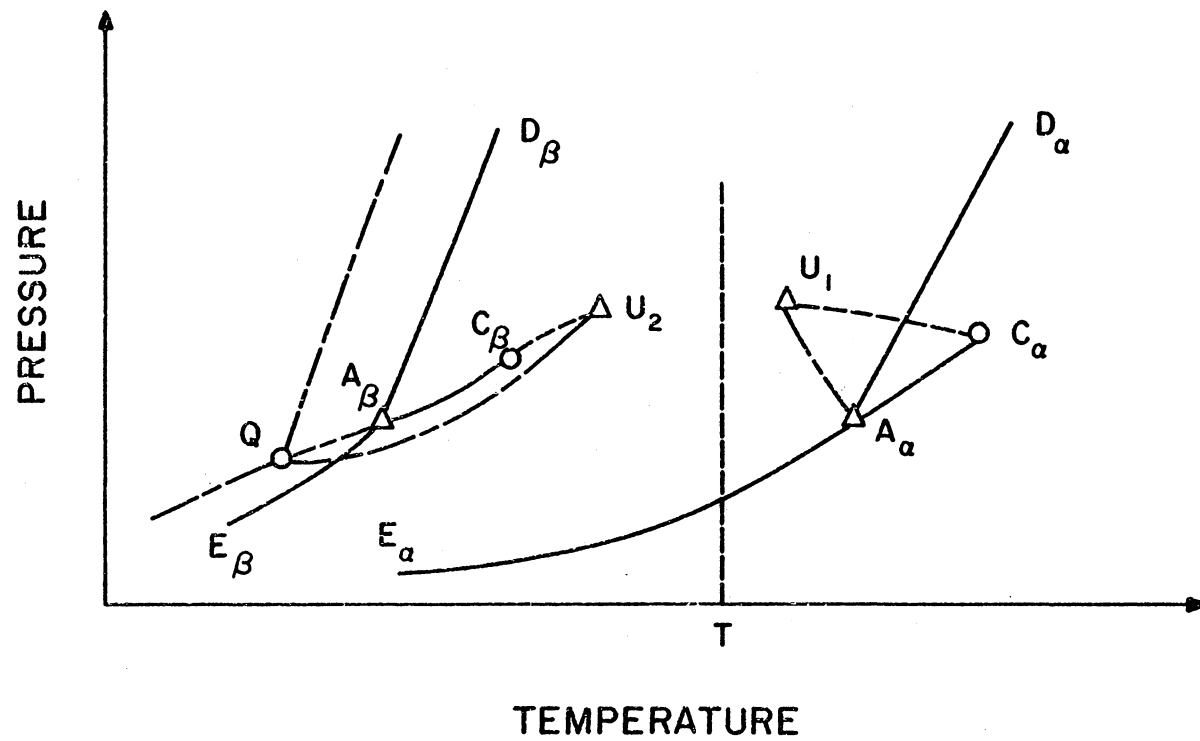


Figure 6: The Phase Diagrams if the Critical Temperatures of Pure Components are Well Separated (Street)

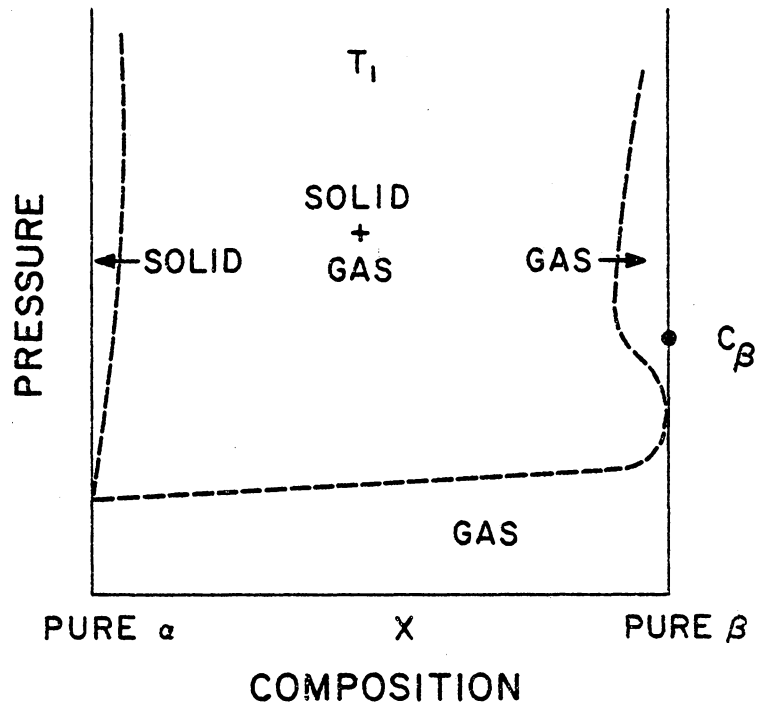


Figure 7: Pressure-Composition Diagram for an Isotherm where Solid-Fluid Equilibria Exists (Street)

There exist regions of temperature other than  $U_2 \leq T_1 \leq U_1$  where supercritical extraction is possible. Although there are upper and lower bounds on operating pressure, higher solubilities are possible in these regions. Solubilities approaching 100% solute are theoretically possible [22] (Figure 8).

The selective solubility of aromatic hydrocarbons in aqueous solutions at high temperatures and pressures has been known for some time. However, commercial exploitations of this phase behaviour were limited due to the high pressures and temperatures involved. The solubility of various hydrocarbons in aqueous phases are shown in Figure 9 and the topic reviewed by Schneider [23], Franck [25], and Irani [26].

Another application of supercritical solvents is to aid in the fractionation of liquid and/or solid mixtures. When either partially or completely miscible mixtures are mixed with supercritical fluids, the mutual solubility of the original mixture components are often reduced [27]. This phenomenon is analogous to addition a solid solute, normally an inorganic salt, to cause phase splits between the organic liquids and water (salting out). Critical solvent deashing, and deasphalting are typical terms used for describing the fractionation of hydrocarbons with the aid of supercritical

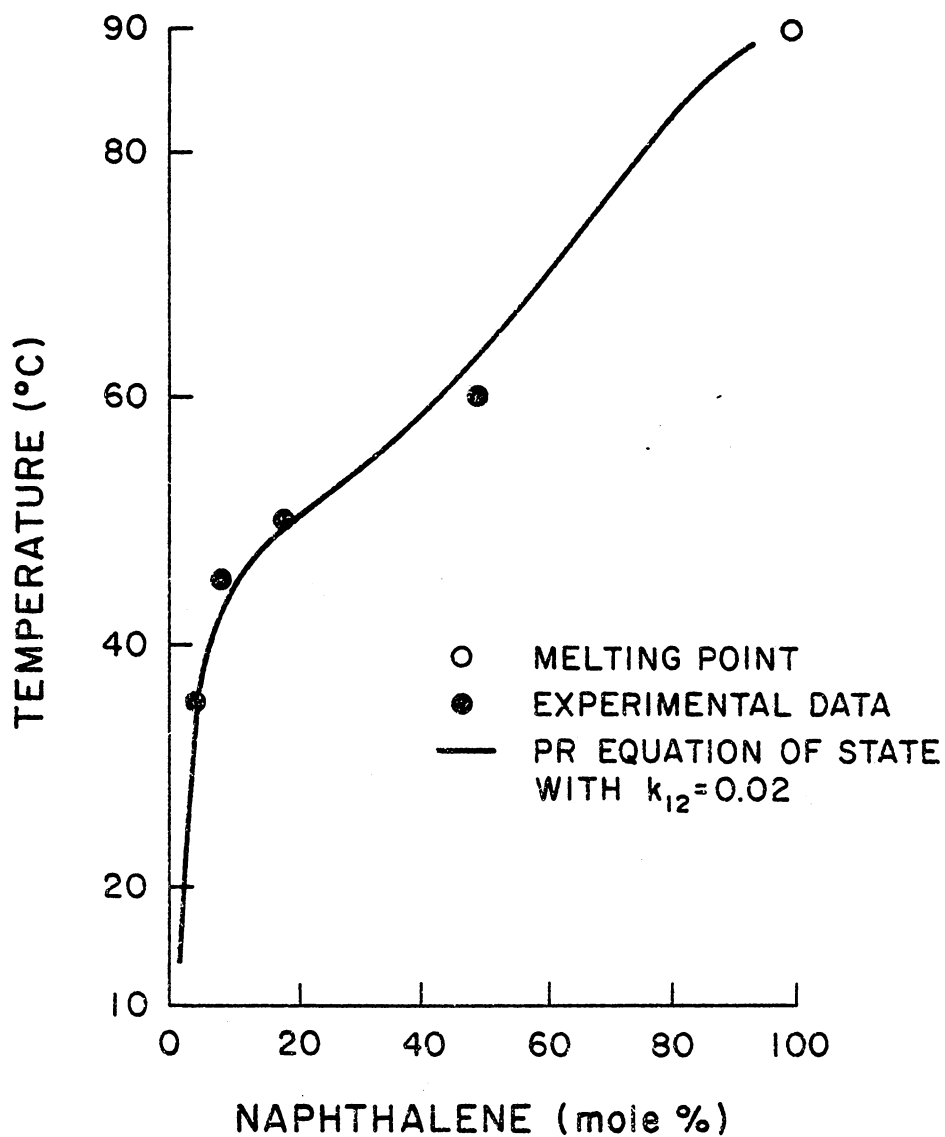
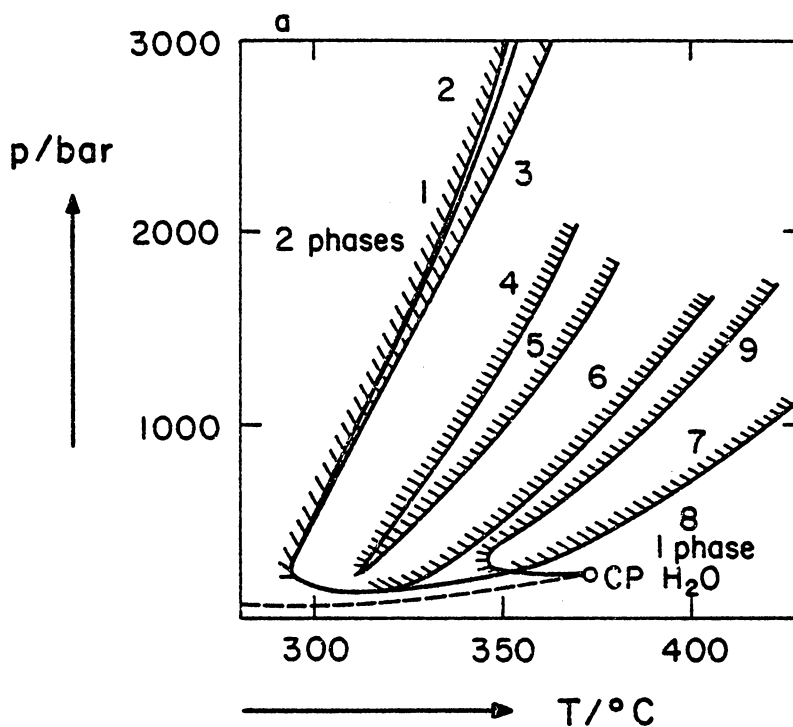


Figure 8: Temperature-Composition Projection of Ethylene-Naphthalene Above the Critical Locus (Kurnik)



### Legend

1 = 1,4-Difluorobenzene-Water  
 2 = Fluorobenzene-Water  
 3 = Benzene-Water  
 4 = Toluene-Water  
 5 = Naphthalene-Water

6 = Tetralin-Water  
 7 = Cis Decalin-Water  
 8 = Trans Decalin-Water  
 9 = Cyclo hexane-Water  
 C.P. H<sub>2</sub>O = Critical point of Water

Fig. 9: Phase Behaviour of Hydrocarbon-Water Systems [23]

fluids. A recent process, the Kerr-McGee Critical Solvent Deashing process, which separates coal liquids from solids in direct liquefaction processes, exploits such behaviour. The representation of phase behaviour of critical solvent deashing processes is best achieved by ternary diagrams and such a treatise is offered by Newsham and Stigset [28]. The use of entrainers and the phase equilibria involved in supercritical extraction in the presence of entrainers is a closely related topic. The ternary phase diagrams and their relation to component binaries is reviewed in a recent article [29].

#### 2.4 MODELLING PHASE EQUILIBRIUM OF SCE

The systems which involve supercritical fluids can be modelled using existing phase equilibrium relations. Typically, the SCE processes involve a supercritical solvent and a solute which can be solid and/or liquid at the conditions of extraction. The basic equilibrium relation involved in description of phase behaviour of supercritical fluids are;

$$T_i^S = T_i^F \quad \text{Eq. 2.6}$$

$$P_i^S = P_i^F \quad \text{Eq. 2.7}$$

$$\hat{\mu}_i^S = \hat{\mu}_i^F \text{ or } \hat{f}_i^S = \hat{f}_i^F \quad \text{Eq. 2.8}$$

where  $T$  is the temperature of component  $i$ ;  $P$  is the pressure of  $i$ ;  $\hat{u}_i$  is the chemical potential of component  $i$

$\hat{f}_i$  is the fugacity of component  $i$  in the solution. Superscript  $S$  refers solute phase while superscript  $F$  refers to fluid (supercritical fluid) phase.

#### 2.4.1 Approaches to Modelling of SCE

The approaches to modelling of phase behaviour of SCE processes change in the treatment of the supercritical phase and in modelling of the solvent-solute interactions. The supercritical fluids may be either treated as "expanded" liquids or as "compressed" gases. With the "compressed gas" approach, one can model the interactive forces between the solute(s) and the solvent(s) with the aid of an equation of state which may or may not use critical properties of the components. The modelling of the supercritical fluid phase and the resulting overall phase equilibrium relations is the topic of this section.

##### 2.4.1.1 Expanded Liquid Approach

In this approach, the fluid phase is treated as an "expanded liquid".

$$\hat{f}_i^F(y, P) = y_i \gamma_i(y_i, P^R) f_i^L(P^R) \exp \int_{P^R}^P \left( \frac{\bar{V}_i^L}{RT} \right) dP \quad \text{Eq. 2.9}$$

where  $P_R$  is a reference pressure and  $f_i^L$  is a hypothetical fugacity of pure liquid  $i$  at the system temperature and reference pressure. A similar approach for the solid phase leads to

$$\hat{f}_i^S = x_i \gamma_i^S(x_i, P^R) f_i^S(P^R) \exp \int_{P^R}^P \left( \frac{\bar{V}_i^S}{RT} \right) dP \quad \text{Eq. 2.10}$$

where  $f_i^S(P^R)$  is the fugacity of the pure solid at the system pressure and at a reference pressure. Eq. 2.10 could be simplified by the following assumptions.

1. The solid is incompressible
2. The solubility of fluid in the solid phase is so small that  $x_i = 1$  and  $\gamma_i^S = 1$
3. No solid solutions form.

Then,

$$\hat{f}_i^S = f_i^S(P^R) \exp \left( \frac{(P-P^R) \bar{V}_i^S}{RT} \right) \quad \text{Eq. 2.11}$$

Combining Eq.s 2.9 and 2.11 gives:

$$y_i = \frac{1}{y_i(y_i, P^R)} \cdot \frac{f_i^S(P^R)}{f_i^L(P^R)} \cdot \frac{\exp \left( \frac{(P-P^R) \bar{V}_i^S}{RT} \right)}{\exp \left[ \int_{P^R}^P \left( \frac{\bar{V}_i^L}{RT} \right) dP \right]} \quad \text{Eq. 2.12}$$

Furthermore, assuming a constant  $\Delta C_{p_i}$  over the temperature range  $T$  to  $T_{t_i}$ , it can be shown that

$$\ln \frac{f_i^L(P^R)}{f_i^S(P^R)} = \frac{\Delta H_i^F}{RT} \left[ 1 - \frac{T}{T_{t_i}} \right] - \frac{\Delta C_{p_i}}{R} \left[ \frac{T_{t_i} - T}{T} \right] + \frac{\Delta C_{p_i}}{R} \cdot \ln \left( \frac{T_{t_i}}{T} \right) \quad 2.13$$

where  $T_{t_i}$  is the triple point temperature and  $\Delta H_i^F$  is the enthalpy of fusion at the triple point. The last two terms in Eq. 2.13 are almost equal in magnitude and opposite in sign and hence can be eliminated. Also, for most substances melting temperatures and enthalpy of fusion at the melting temperature are close to those at the triple point. Thus the resulting relation is

$$y_i = \exp \frac{\left[ \Delta H_i^F \left[ \frac{T}{T_{t_i}} - 1 \right] \right]}{\gamma_i(y_i, P^R)} \cdot \frac{\exp \left( \frac{P - P^R}{RT} \right) v_i^S}{\exp \int_{P^R}^P \left( \frac{\bar{v}_i^L}{RT} \right) dP} \quad \text{Eq. 2.14}$$

Mackay and Paulatis [30] have used a reference pressure of

$$P^R = P_c \quad \text{Eq. 2.15}$$

where  $P_c$  is the critical pressure of the pure fluid phase.

They assumed

$$\gamma_i(y_i^i, P^R) \approx \gamma_i^\infty(P_C) \quad \text{Eq. 2.16}$$

$$\bar{V}_i(y_i, P^R) \approx \bar{V}_i^\infty(P_C) \quad \text{Eq. 2.17}$$

and treated  $\bar{V}_i^\infty$  as an adjustable parameter and calculated

$\gamma_i^\infty$  rigorously using the Peng Robinson equation of state.

Although the calculated  $\bar{V}_i^\infty$  values were unreasonably large, they correlated Carbon dioxide-Naphthalene and Ethylene-Naphthalene data.

#### 2.4.1.2 Compressed Gas Approach

Using the compressed gas approach it can be shown that

$$\hat{f}_i^F = y_i P \hat{\phi}^F \quad \text{Eq. 2.18}$$

If the gas approach is used the fluid phase equilibrium is obtained from Eq. 2.18 where  $\hat{\phi}^F$  can be obtained from an equation of state from the relation below.

$$\ln \hat{\phi}_i^F = \frac{1}{RT} \int_{\infty}^V \left[ \left( \frac{RT}{V} \right) - \left( \frac{\partial P}{\partial n_i} \right)_{T, V, n_j} \right] dV - \ln z \quad \text{Eq. 2.19}$$

Combining Eq.s 2.11 and 2.18 at a reference pressure of  $P_{VP_i}$

$$y_i = \underbrace{\frac{P_{VP_i}}{P}}_A \cdot \underbrace{\frac{1}{\hat{\phi}_i^F}}_B \cdot \exp \left( \underbrace{\frac{(P - P_{VP_i})V_i^S}{RT}}_C \right) \quad \text{Eq. 2.20}$$

Note that Eq. 2.20 is conveniently partitioned into three different terms. Term A is the equilibrium solubility assuming the ideal gas law to be valid; term B accounts for the non-ideality of the solute-solvent mixture in the fluid phase and is by far the most important term; term C is the Poynting correction and is a measure of the extent to which pressure enhances the solubility of the solid in the fluid phase.

Mole fraction of the solutes in the fluid phase,  $y$ , are often expressed as

$$y_i = P_{VP_i} / P E_i \quad \text{Eq. 2.21}$$

where  $E_i$  is called the enhancement factor.

#### 2.4.1.3. Approaches Which Do Not Require Critical Data

In both the "expanded liquid" or the "compressed gas" approach, the experimental solubility data have to be reduced and PVT (pressure volume temperature) behaviour of the existing phases are best expressed with the aid of an equation of state. The resulting solute-solvent mixtures in SCE pro-

cesses are often highly asymmetric, in terms of size and energy differences between the components. The prediction of the binary interaction coefficient,  $k_{ij}$ , becomes very difficult since solvent interacts with only part of the large solute. Solute-solute, and solvent-solvent interactions are no longer negligible. As important as choosing an equation of state is the handling of the mixture properties by proper choice and use of mixing rules. If an approach which uses critical properties is used, the individual critical properties must be combined with suitable mixing rules. The vastly different critical properties of the asymmetric components exacerbates the problem of choosing a corresponding state that can describe the unlike and the cross interactions. Furthermore, SCE often involves high molecular weight solutes. Reliable vapor pressure and critical data for such compounds seldom exist due to thermal decomposition of compounds at severe conditions approaching the critical point. Methods which do not require critical data aim to account for the difficulties mentioned above. More detailed discussions are presented by Kaul and Prausnitz [31], Kreglewski and Chen [32], and Henderson [33]. At present there are two approaches that do not require critical data to describe solute-supercritical fluid interactions. These are:

1. The augmented van der Waals treatment by Johnston et.al.[34]

Johnston et.al. use a perturbed hard sphere equation of state which does not require critical data to correlate their solid-fluid equilibrium data. They use an unlike pair energy parameter,  $\epsilon_{12}$ , which correlates with the enthalpy of vaporization of solute at the melting point. A second term based on square-well molecular dynamics increases the range of applicability of their approach to regions very close to the critical region. The availability of enthalpy of vaporization data at the melting point is one of the major drawbacks of their approach. Extensions of their approach to multicomponent mixtures is yet to be explored.

2. Approach due to Brunner and Hederer [35]

Brunner and Hederer correlated constants "a" and "b" of a modified Redlich-Kwong equation of state with molar liquid volume at different temperatures. They use a binary interaction coefficient which is correlative with molar excess volume of an equimolar mixture. However, this interaction coefficient is best calculated from binary data and is temperature dependent. Their approach is limited to solvents

which have critical temperatures less than 50°C. This approach is further developed and used by Wenzel et.al.[36]. Wenzel and coworkers' development included a bigger data base which extended the range of applicability of this approach and a new cubic equation of state which is particularly effective at supercritical conditions.

#### 2.4.2 Review of Equations of State as Applied to SCE

In the next section, the applicability of various classes of equations of state in description of phase behaviours of systems of dense gas phases is reviewed. These classes are:

1. Virial equation of state
2. BWR family of equations of state.

BWR equation of state can be visualized as an extension of Virial equation of state and can also be grouped accordingly.

3. Van der Waals family of equations of state

The virial equation was probably the first equation of state used to describe the phase equilibria of solid-fluid or liquid-fluid systems. Most of earlier studies [37] were based on the virial equation of state partly due to its theoretical basis and partly because high speed computers and extensive data banks were not yet available.

Although it may be helpful to model the phase equilibria of SCE using a virial equation of state, this approach is of limited practical use since third and fourth virial coefficients are necessary to represent regions of dense gas. This is illustrated in Figure 10 by Prausnitz [38]. However, one may use the virial approach to estimate the minimum solubility of low-volatile compounds in gases when a possible practical concern may be undesired solids precipitation to foul transfer lines. Reid et. al. [39] derived the minimum solubility requirements to be

$$y_{\min} = 2eB_{12}P_{VP_i}/RT \text{ and } P(y_{\min}) = -RT/(B_{22} + 2B_{12}) \text{ Eq. 2.22}$$

To represent higher densities one can express the compressibility factor,  $z$ , in a virial series followed by empirical terms:

$$z = PV/RT = 1 + B\rho + C\rho^2 + D\rho^3 + E(\rho, T) \quad \text{Eq. 2.23}$$

where the molar density,  $\rho$ , is the reciprocal of molar volume,  $v$ . For a pure fluid, all coefficients ( $B$ ,  $C$ , and  $D$ ) are functions of temperature only. The most well known example of Eq. 2.23 is Benedict-Webb-Rubin (BWR) [40]. Since its first introduction, BWR received considerable attention especially by the petrochemical industry due to its high accuracy resulting from the large number of constant param-

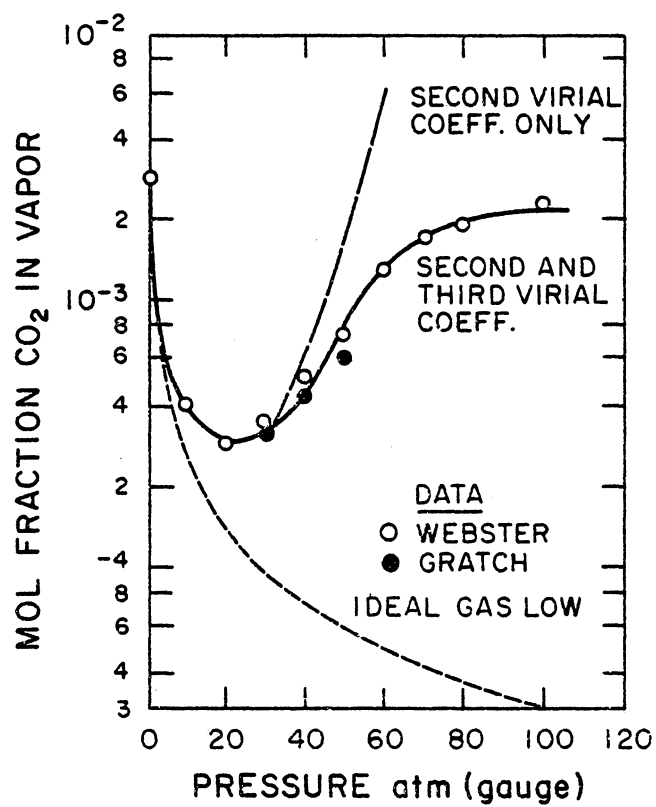


Figure 10: Solubility of Carbon Dioxide in Air at 143°K  
(Prausnitz)

ters. Later modifications by Starling [41] and the availability of new and better data improved the accuracy of BWR. However, due to its empirical nature and arbitrary mixing rules, the BWR family of equations of state does not adequately describe the critical region. Furthermore, possible implementation by introduction of an adjustable binary interaction coefficient is complicated by convergence problems especially around the critical region. Another difficulty is the pressure dependence of the binary interaction coefficients. Care must be taken to ensure pressure and composition independence of  $k_{ij}$  especially for mixtures with asymmetric components. Since BWR mixing rules are empirical, elimination of such dependence is difficult.

An ingenious combination of the correlative power of the BWR equation with the corresponding states theory resulted in the Lee-Kessler equation of state [42]. Plockner's implementation of Lee-Kessler equation [43] via new mixing rules enables one to be able to apply this equation of state to asymmetric mixtures. Since the binary correlation coefficients,  $k_{ij}$ , correlate reasonably well with  $T_{c_i} V_{c_i} / (T_{c_j} V_{c_j})$ , good predictions are possible. At present, the Lee-Kessler equation is not recommended for applications in vicinity of mixture critical loci due to the use of pseudocritical properties in mixing rules which tend to underes-

timate the true critical temperatures. However, with further research in mixing rules and use of different reference compounds for different classes of chemicals, extension of this promising approach may be possible.

Equations of state based on Van der Waals' model are alternative to the BWR family of equations of state. According to this model compressibility factor  $z$  is given by the sum of two parts:

$$z = z(\text{repulsive}) + z(\text{attractive}) \quad \text{Eq. 2.24}$$

The originally proposed form of repulsive forces which are more significant at low densities, is:

$$z(\text{repulsive}) = v/(v-b) \quad \text{Eq. 2.25}$$

where "b" is a constant proportional to the size of the molecules. The most satisfactory expression for repulsive forces is believed to be due to Carnahan and Starling [44].

$$z(\text{repulsive}) = 1 + \zeta + \zeta^2 - \zeta^3 / (1 - \zeta^3) \quad \text{Eq. 2.26}$$

where reduced density  $\zeta = b/4v$

There is less fundamental knowledge for attractive forces especially at low temperatures where van der Waals' fundamental assumption, negligibility of the liquid volume, is least justified. The general form of attractive forces is

$$z(\text{attractive}) = a/F(v)/T^{1/2} \quad \text{Eq. 2.27}$$

where  $F(v)$  is a simple function of molar volume  $v$ .

The first approximation of constant " $a$ " is independent of temperature. However, to achieve a better representation, especially at lower temperatures, " $a$ " must increase as temperature decreases. Reid et. al. proposed several empirical functions which were determined from vapor pressure data. These functions are not very reliable at temperatures above the critical.

Cubic equations of state denote equations of state which are cubic in molar volume. They typically represent van der Waals' model and most retain the original representation of repulsive forces and differ from each other primarily in representation of the attractive forces, both in the derivation of constants " $a$ " and " $b$ " and in mixing rules. Cubic equations can be solved analytically and are thus readily applied in chemical engineering. There are many excellent reviews [45, 46] on cubic equations of state. The use of cubic equations of state is most likely to decrease as computer specialists learn thermodynamics and/or as thermodynamicians learn more about computational sciences (collective name given to computer science, numerical methods and statistics). As thermodynamic data banks emerge and become readily available, more powerful equations of state may replace cubic equation of state.

The first successful cubic equation of state was van der Waals' equation of state. The next major improvement on cubic equations came with Redlich-Kwong Equation [47]. The third, and at present the last major improvement was introduced to cubic equations of state by the modifications of Soave to the Redlich-Kwong equation [48]. Today, the best cubic equation of state is believed to be the Peng-Robinson (P-R) equation [49] which is a slight modification and a better fit of Soave-Redlich-Kwong (SRK).

The cubic equations do surprisingly well around the critical region and are readily applied to describe solid-fluid and liquid-fluid equilibria by various investigators. This is partly due to the fact that the constants "a" and "b" are computed from critical points. The present cubic equations concentrate on attractive forces which are stronger in comparison to repulsive forces especially around the critical region. The resulting inaccuracies from less correct representations of repulsive forces are relatively small around the critical region. However, all the approaches lack practical predictive power and are thus limited for possible applications to multicomponent mixtures. Since, the importance of supercritical extraction has only been recently realized, there is need for much more data for process development purposes. The slight temperature dependence of

the interaction coefficient and the suspected incorrect use and/or inadequacy of the non-linear parameter estimation methods further complicate the issue. With the aid of more and better data, reliable predictive methods may be developed. Qualitative, but promising, results in describing the phase behaviour of selected mixtures for which extensive high pressure data is available are reported by Hong et.al. [50]. In their study, Hong et. al. used the P-R equation with constant  $k_{ij}$ 's to describe high pressure phase behaviour of Carbon Dioxide-Naphthalene, Benzene-Water, and Ethylene-Naphthalene binaries.

#### 2.4.3 Hildebrand Solubility Parameter

A more empirical approach to solubility predictions is to use the Hildebrand parameter. The Hildebrand solubility parameter,  $\xi$ , originally defined as the square root of molecular cohesive energy per unit volume (internal pressure), is admittedly a general quantity not based on a precise model [51]. However, it has been found to be quite useful for solubility predictions for a wide variety of compounds. Generally if a component solubility parameter values agree to within  $\pm 1$  (cal/cc)<sup>1/2</sup>, these components will be mutually soluble.

The internal pressure ( $P_i$ ) is given by :

$$P_i = (\partial E / \partial V)_T \quad \text{Eq. 2.28}$$

Thus for a van der Waals gas it can be shown that

$$P = RT/(v-b) - a/V^2 \quad \text{Eq. 2.29}$$

The parameter "a" in the van der Waals equation can be evaluated in terms of critical pressure,  $P_c$ , and critical volume,  $V_c$ . Upon substitution one obtains

$$\xi_g = (3P_c)^{1/2} \rho_g / \rho_c \quad \text{Eq. 2.30}$$

where

$\xi_g$  = The solubility parameter of the gas

$P_c$  = Critical pressure

$\rho_g$  = Gas density

$\rho_c$  = Critical density of the gas

Giddings et.al [52] found that

$$\xi_g = 1.25 P_c^{1/2} \rho_g / \rho_l \quad \text{Eq. 2.31}$$

where  $P_c$  is in atmospheres, and  $\xi_g$  is in  $(\text{cal/cc})^{1/2}$ .  $\rho_l$  is the critical density of liquid and is chosen so that  $(\rho_l / \rho_c)$  is 2.66. If we express Eq. 2.31 in terms of temperature (T), pressure (P), the molecular weight (Mw) and the compressibility factor (z) of the gas we get

$$\xi_g = \underbrace{1.25 P_c^{1/2}}_A \underbrace{P_{Mw} / (zRT \rho_c^{2.66})}_B \quad \text{Eq. 2.32}$$

where  $R$  is the gas constant, and  $\rho_g$  is critical density of the gas. A detailed derivation and use of Hildebrand parameter in SCE can be seen in another dissertation (53). Part A of Eq. 2.32 reflects the chemical effects on the solubility parameter while part B is the state effect. The second effect, state effect, is dominant in SCE.

The Hildebrand solubility parameter will be used as an index of solvent strength in this thesis. Solvents with  $\xi$  higher than  $4 \text{ (cal/cc)}^{1/2}$  will be called strong while the solvents with  $\xi$  less than  $2 \text{ (cal/cc)}^{1/2}$  will be referred as weak solvents.

### Chapter III

#### NATURE OF COAL

Coal is a generic term covering a range of complex, solid fossil fuels containing primarily organic material admixed with smaller quantities of mineral matter. The organic components are derived from complex plant material by complicated chemical and biochemical reaction processes and are mainly composed of large "polymeric" molecules whose chemical structures are variable and non-repetitive. The physical structure represents the spatial arrangement of these molecules. Most physical properties of coal are a consequence of physical structure and thus many facets of physical structure can be studied and used to develop processing schemes without detailed knowledge of the chemical structure of the large coal molecules. Unlike chemical structure, physical structure of coals seem to vary systematically with coal rank and thus physical structure of various coals can be reasonably predicted from the carbon content or the volatile matter content of the coal. This systematic dependence, however, is not monotonic with respect to coal rank and most physical properties show maximum or minimum values at carbon contents of 85-90%, near the point of transition from bituminous to anthracitic coals [54].

Many properties and aspects of coal behaviour have been studied over the past several decades. In this chapter, however, the properties coal affecting the understanding of SCE of coal are reviewed and discussed. Two such properties are the porous structure of coals and the effect of temperature on the coal structure.

### 3.1 COAL PROPERTIES AND THEIR SIGNIFICANCE IN SCE OF COAL

Statements about composition or structure of coal mean little unless one specifies their application domain as macroscopic, microscopic or sub-microscopic (molecular).

#### 1. Macroscopic level

Macroscopic domain refers to bands of alternating layers of differing composition and appearance. These irregularly alternating layers are generally called lithotypes. Lithotypes are composed of vitrain, clarain, durain, and fusain. This banded appearance is less apparent in less mature coals.

#### 2. Microscopic level

At microscopic level lithotypes are found to be complex aggregates. These aggregates are called macerals and subdivided as vitrinite, exinite, and inertinite. Of the three groups, vitrinite is by far the most studied and most important one because of

its reactivity in converting into coal liquids. Furthermore, vitrinites are usually the biggest fraction of the macerals.

### 3. Molecular level

At the molecular level macerals consists of organic macromolecules. The detailed chemical structure of such macromolecules is unknown. The identification of much smaller volatile or easily extractible molecules constitute a much simpler problem, and considerable information exists about them [55, 56, 57, 58].

The binding forces among macromolecules have been ascribed to molecular entanglement, to weak non-covalent associative forces (such as hydrogen or acid base interactions) or to the highly cross linked structure [59, 60]. One of the evidences for the existence of entangled molecules is that the coal residua exhaustively extracted with pyridine can be further extracted with pyridine in an ultrasonically vibrated environment.

#### 3.1.1 The Porous Nature of Coal

The porous nature of coal has been known for many years. The properties of the delicately structured pore system of coal, such as the void volume, internal surface, and the

pore size distribution, are more responsible in influencing the behaviour of coal than any other property. Most studies suggest that the coal is a visco-elastic solid [61] (neither rigid nor fluid) and is deformable to the extent permitted by the cross linkages from their equilibrium configurations. Thus, the porosity of coal can be appreciably altered by adsorption of the fluids used to measure the porosity. Moreover, the interconnecting pores are far from cylindrical and are more like thin slits of considerable width. There are portions so thin that more than a monolayer of adsorbate is not possible without distortion.

#### 3.1.1.1 Porous Structure of Coal

Hirsch [62] has demonstrated that broadly three types of porous structure are present in a wide range of coals:

1. The 'open structure' characteristic of low rank coals with high porosity
2. The 'liquid structure' of the coking coals with very little porosity
3. The anthracite structure of the high rank coals with high porosity

The pores can be divided into three groups according to sizes:

1. Macropores (300-30,000 Å)

2. Transitional pores (12-300 A)

3. Micropores (4-12 A)

In the low rank coals ie. lignites, porosity is primarily due to macropores while for high volatile bituminuous coals about 80% of the pore volume is due to micro and transitional pores [63].

The internal capillary structure of coal is of considerable importance. Blayden [64] found that interatomic distances in coal are approximately 2-3 times greater in one dimension than other. Solvents are influenced by the restrictions imposed by the narrow channels in a coal.

### 3.1.1.2 Measurement of Pore Structure

The total void volume of coals and solid coal products is generally determined from absolute density measurements made using helium and mercury as displacement fluids or from measurement of capacity bed moisture. Helium with its very small atomic radius and lack of sorption was believed to penetrate the entire coal structure [65] till recent x-ray studies suggested that anthracites have some blind pores impenetrable by helium [66]. Since mercury does not penetrate into pores less than 10 microns at atmospheric pressures, the total pore volume in that pore diameter range is calculated from differences in specific volume in mercury and in helium.

The internal surface area of coal can be determined by:

1. Measurement of heat generated when coal is treated with liquids. (Heat of wetting)
2. Adsorption of gases and vapors.
3. Small Angle X-ray Scattering (SAXS).

Most initial studies used measurements of heats of wetting, especially using methanol, to determine the internal surface areas of coal. As methanol penetrates the coal matrix, pores swell and this swelling process is endothermic. The interactions between methanol and the coal surface is exothermic and the resulting difference, which is always exothermic is the heat of wetting [67]. The debatable implicit assumption that all pore surfaces are reached means that measured internal surface areas of coal are lower than the absolute areas. However, methanol is imbibed by the coal, creating new surfaces. Furthermore, methanol reacts exothermically with some of the functional groups (e.g. phenols) in coal [68]. Thus, the measurements of internal surface area of coal by heats of wetting are higher than the absolute internal areas.

The measurements of internal surface area of coal by adsorption of gases and vapors are lower than the absolute areas. The earlier measurements at low temperatures (100°K) were an order of magnitude lower than the actual areas since

diffusion of adsorbed gases such as nitrogen or argon into very fine pores required considerable amounts of energies of activation which were not available at such low temperatures [69]. Recent studies with Carbon dioxide at 25°C seems to be the closest to the absolute values [71]. SAXS eliminates the interaction of the coal with the probe and has the best chance of development into an absolute method [71]. Surface areas of two American coals by several methods are compared in Table 2 [72].

### 3.2 THERMAL BEHAVIOUR OF COAL

All coal conversion technologies and almost all the end uses of coal require thermal treatment of coal and thus the structural changes upon heating are of significant importance in coal technology. All coals release volatile matter as heated and the quantities evolved depend on heating rate, temperature, pressure and the coal rank. At low temperatures and under vacuum, first loosely bound water and carbon dioxide and then the lower molecular weight hydrocarbons ( $C_2$ ,  $C_3$ , and  $C_4$ ) devolatilize. At around 180°C, lower molecular weight aromatic compounds and sulfur containing species follow. Above 350°C rapid (primary) devolatilization occurs and the low molecular weight gases, chemically complex liquids, and semi-solid tars evolve. This rapid devo-

TABLE 2

Surface Areas of Two American Coals by Different Methods

| <u>METHOD</u>               | <u>Surface Area of Coal (m /g)</u> |                     |
|-----------------------------|------------------------------------|---------------------|
|                             | <u>Illinois 6</u>                  | <u>St. Nicholas</u> |
| Methanol adsorption at 20°C | 175                                | 122                 |
| CO adsorption at -78°C      | 136                                | 165                 |
| CO adsorption at 25°C       | 160                                | 234                 |
| SAXS                        | 179                                | 275                 |

latilization rate passes through a temperature maximum which increases as rate of heating increases.

The rate of devolatilization decreases with increasing coal rank. The rapid devolatilization rate proceeds as a first order reaction with an average energy of activation of 50 Kcal. The rate determining step in devolatilization could be either

1. Rupture of covalent bonds such as C-C bonds.
2. Rate of diffusion of volatile matter out of the pores.

The thermal behaviour of coal in the presence of liquid solvents is of interest especially in direct liquefaction processes. Solvents which have the capability to hydrogenate the coal are called donor solvents. Hydrogen from donor components are abstracted to stabilize the thermally broken coal bonds. These reactions are often called progressive coal reactions and result in smaller molecular weight compounds. If the thermally broken bonds are not stabilized by either hydrogen from the donor solvent or molecular hydrogen, or hydrogen from coal itself, these bonds are stabilized by combining with other coal originated radicals resulting in larger macromolecules. This process is called coking and the reactions are known as regressive reactions. In the presence of nondonor solvents regressive reactions

are much more dominant than progressive reactions and the undesired coking process decreases the conversion and pyridine solubility significantly at prolonged reaction times. The competing regressive and progressive coal reactions in the presence of donor solvents and non donor solvents are shown in Figures 11 and 12 respectively [73] and discussed in the works of G.H. Beyer [74] and Tom Mason [tom.]. The reaction pathways in donor solvent liquefaction processes are discussed by Squires [75].

Another interesting thermal characteristic of some coals is that coals preheated to temperatures of 400°C give higher yields, when later extracted, at near ambient conditions, than the coals which have not been preheated. This phenomenon is called thermo-solvolysis. Improved yields in supercritical extraction of preheated coals can be achieved near ambient conditions because of thermo-solvolysis.

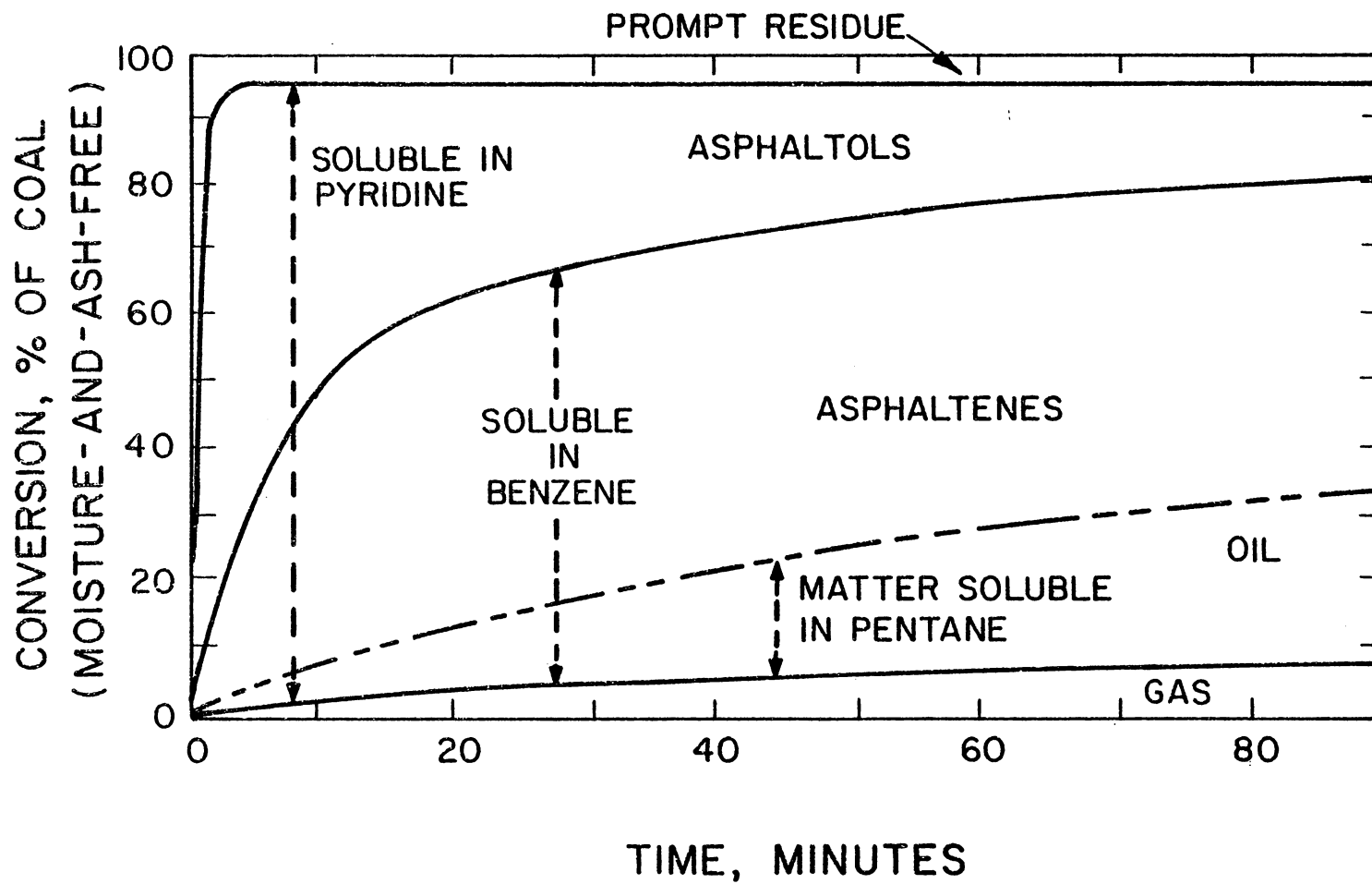


Figure 11: Conversion of Coal Reacted at 400°C in Tetralin

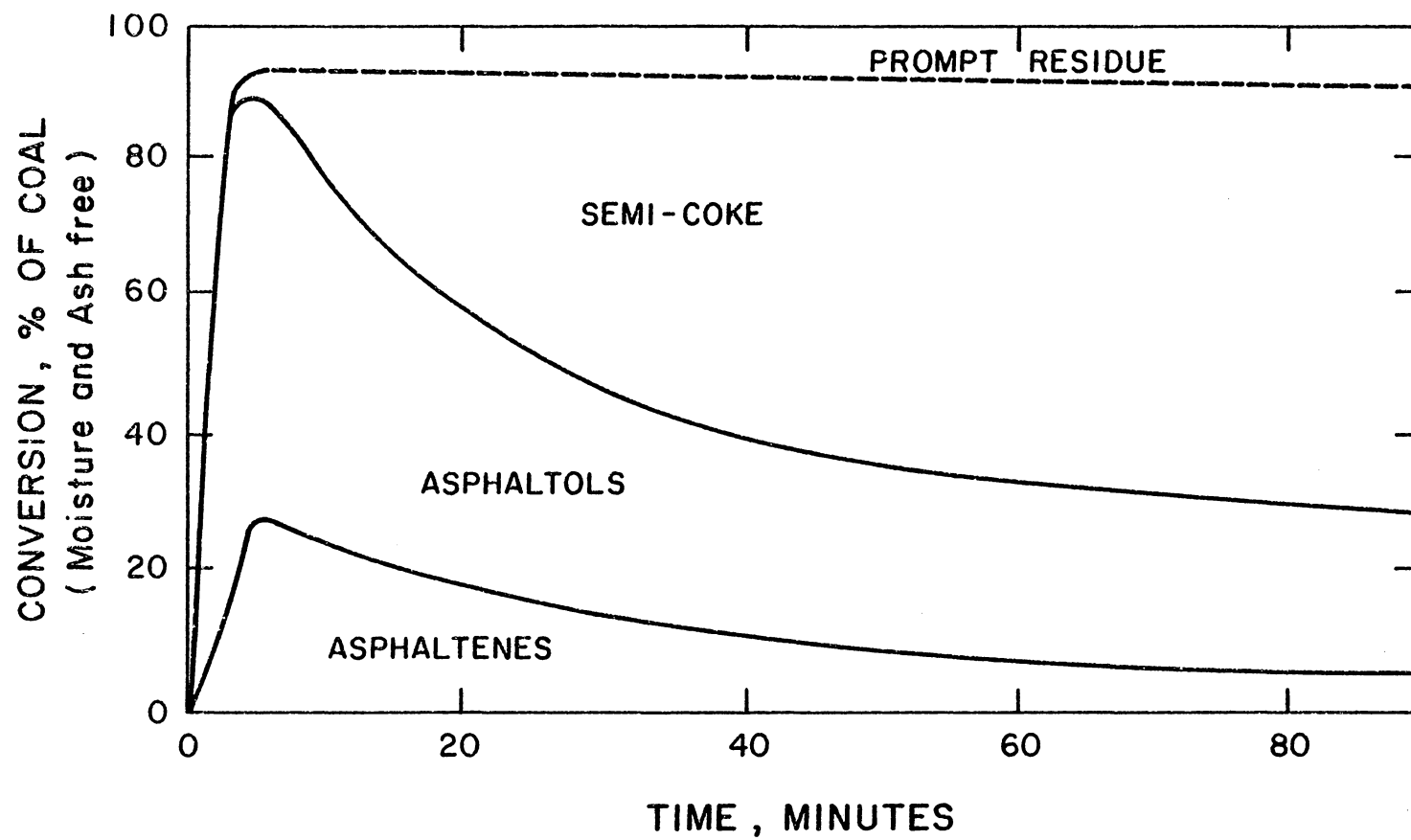


Figure 12: Conversion of Coal Reacted at 400°C in Naphthalene

## Chapter IV

### SOME PROCESSES WHICH USE SUPERCRITICAL FLUIDS

Development of techniques of separating substances using supercritical gases first began in the early sixties [76], though certain fundamental principles had already been known for more than 80 years [1] and experimental results seemingly anticipating the potential of this rediscovered principle were reported in the early fifties [77]. The sequence of events which led to development of SCE processes is described by Zosel [78].

The typical applications of supercritical gases are:

1. Application to natural products

- a) Decaffeination of green coffee beans, which is being used on an industrial scale in Germany by Kaffee HAG [79, 80].
- b) The extraction of hops for the brewing industry [81].
- c) The extraction of aromatics from spices [81].
- d) The extraction of oils from oil containing seeds [82].
- e) The deodorization of vegetable and animal oils [82].

- f) The fractination of high boiling mixtures such as cod-liver oil [79].
- g) The decaffeination of black tea [83].
- 2. Application to waste water treatment [84].
- 3. Application to chromatography [85]
- 4. Applications in the hydrocarbon processing area
  - a) De-asphalting of petroleum fractions [77].
  - b) The separations of paraffins from tar [86].
  - c) The regeneration of waste lubricants [87].

#### 4.1 DESCRIPTION OF KERR MCGEE CRITICAL SOLVENT DEASHING (CSD) PROCESS

Kerr-McGee Critical Solvent Deashing (CSD) process [88] is a continuous process which separates coal solids (mineral matter and unreacted coal) from coal liquids by solvent extraction near the critical point of the solvent. The CSD process evolved from another Kerr-McGee critical solvent process, the Residuum Oil Supercritical Extraction (ROSE) process [89].

A general flowsheet of CSD process is shown as Figure 13. The coal liquids are generally extracted from vacuum still bottoms produced in coal liquefaction processes. The stream going to the CSD process is typically 15 % coal liquids, 70 % deashing solvent, and 15 % coal solids. The light phase from extraction step contains about 80 % of the coal liquids

and the deashing solvent, while the heavy phase contains the coal solids (50-60 % of the stream), coal liquids, and the deashing solvent. There is very little mineral matter in the light phase and the separation of unreacted coal solids is sharper than the mineral matter separation. The coal liquids are precipitated from this light phase by decreasing the density of the deashing solvent in the subsequent stages. Initially reduction of density is accomplished by temperature increase as opposed to pressure reduction, implying that the pressure in the first stage is very close to the critical pressure of the solvent. The light phase can be fractionated further by addition of more stages. It is very likely that pressure reduction is used in the third stage since pressure reductions ensures sharper separations than temperature increases and thus product degradations due to higher temperatures are avoided.

The Kerr-McGee CSD process was tested in the Wilsonville SRC pilot plant. The plant was able to produce practically ash free product successfully. The on stream time of the CSD unit was around 80 %. Reliability of the CSD process is much higher than its competitors, e.g. filtration. However, it is short of typically desired reliabilities, e.g. 95 %.

The extent of recovery at the CSD unit depended on feed composition. As shown in Table 3, process conditions which

## Vacuum Tower Bottoms

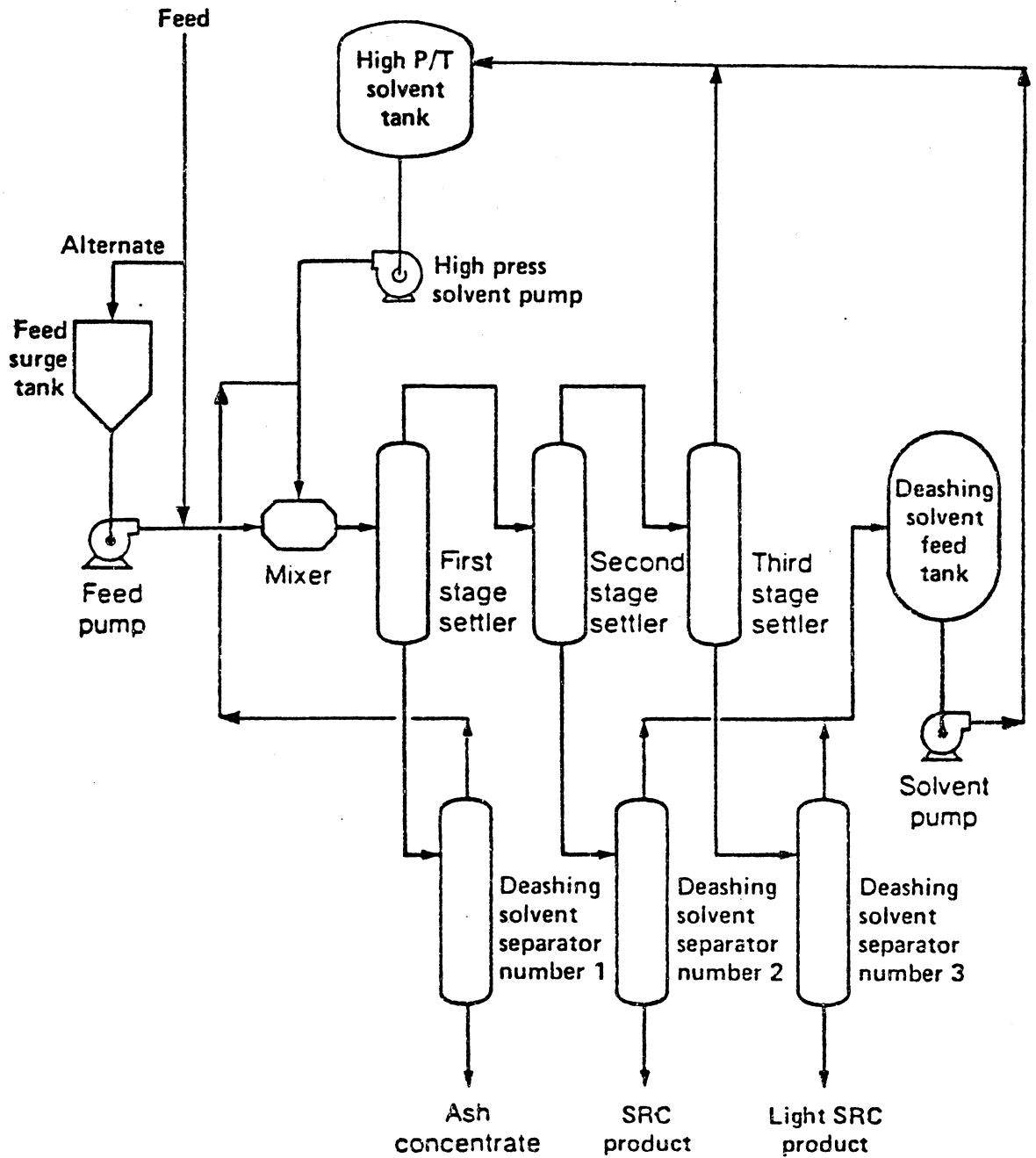


Figure 13: Kerr McGee Critical Solvent Deashing Process

resulted in polymerization of coal liquids prior to the CSD unit decreased the recovery trend.

Deashing solvent recovery in CSD process is around 80+ %. Unless solvent recovery factors around 95+ % are achieved, the magnitude of solvent losses will be very significant because the solvent makes up about 70 % of the CSD feed.

#### 4.2 DESCRIPTION OF SUPERCRITICAL GAS EXTRACTION PROCESS

The development of SGE process has been carried out mainly by the NCB where a 120 kg/d continuous pilot plant has been operational since 1977 [90]). The project is now sponsored by European Coal and Steel Community (ECSC) and a 15t/d pilot plant was scheduled for start-up by end of 1982.

The SGE process exploits the solubility power of compressed gases to extract the low-molecular-weight, decomposed volatiles, as they evolve at temperatures where such compounds normally would not distill. SGE can be viewed as a controlled pyrolysis process.

The solvents used for SCE of coal are supercritical hydrocarbon fractions derived from coal liquids or petroleum naphtha fractions and should preferably have a critical temperature slightly below the pyrolysis temperature of coal (300-400°C). Although most reported work is based on toluene as the solvent, the likely commercial solvents are narrow critical point aromatic mixtures. The extract from a

Table 3

The Effect of SRC Process Variables on Recovery of Coal  
Liquids with the CSD Unit

| <u>LIQUEFACTION PROCESS VARIABLE</u>     | <u>RECOVERY TREND</u> |
|------------------------------------------|-----------------------|
| INCREASE IN COAL SPACE RATE IN DISSOLVER | DECREASES             |
| INCREASE IN PRESSURE IN DISSOLVER        | INCREASES             |
| INCREASE SOLIDS CONC. IN DISSOLVER       | INCREASES             |
| INCREASE TEMPERATURE IN VACUUM STILL     | DECREASES             |
| INCREASE RESIDENCE TIME IN VACUUM STILL  | DECREASES             |

high volatile British bituminuous coal is a low-melting glassy solid, with a softening temperature of 70°C and represents the hydrogen-rich fraction of the coal. The extract is essentially free of ash and contains slightly less nitrogen and sulfur than the parent coal. The hydrogen/carbon ratio is highest in pentane solubles (oils) and lowest in benzene insolubles (asphaltols) [91]. The feed coal preferably has a high volatiles content and is non-caking. The residua from extraction are porous char (80-90 % of the original particle size is retained). Unlike normal pyrolysis products, the residua are highly reactive and has calorific values similar to that of the parent coal. The reactivity of the residua decreases as extraction depth increases.

The NCB investigation showed that the coal residence time was the variable which most influenced the extract yield. The influence of temperature and pressure was substantial. The effects of particle size (unless bigger than 10 mesh), moisture content (up to 15 %), and the solvent rate were found insignificant.

An American process design and construction company, Catalytic Inc., developed conceptual designs based on the development work of NCB [92]. Although subsequent commercial designs may be quite different, the SGE process as conceptu-

alized by Catalytic Inc. will be the used throughout this chapter for descriptive purposes. This design uses toluene as the solvent.

As seen in Figure 14, air dried and pulverized coal was preheated to 315°C prior to charging into a feed lock hopper. Hot pressurized recycle toluene was used to pressurize the feed lock hopper prior to charging of coal to the moving bed reactor. Low caking coals are desirable for this type of a reactor to avoid agglomeration and subsequent blockage of the equipment. A Wyodak subbituminous coal was used as the feed coal and the design was based on the few experiments carried out with this coal by NCB. The operating conditions were not optimized for this coal. Most NCB work was carried out with a high volatile bituminuous coal which is similar to Illinois No. 6 coal and conversions (percent extraction) as high as 47.5 % were reported to be feasible. The design basis was:

1. 10660 t/d feed coal (about 9000 t/d dried coal)
2. 8 moving bed reactors operating at:
  - a) Temperature = 440°C
  - b) Pressure = 10.4 MPa
  - c) Gas residence time of less than 2 minutes and coal residence time of at least 30 minutes.

3. The yields as a mass percent of dry coal were: 21.2 % extract, 67.5 % char, and 5.8 % gas.

The effluent from the top of the extractor was condensed and then depressurized to precipitate the extract as a liquid in the solvent, toluene. The extract, toluene, and water were separated by heating in a vessel.

The conceptual designs by Catalytic does not include hydrogenation in the flowsheets (See Figure 15). However, as shown in Figure 16, NCB designs include hydrogenation. A self sufficient plant design which has the product mix shown in Table 4 is reported to have thermal efficiency of about 68 % [93].

#### 4.3 MECHANISM OF SCE

The mechanism of supercritical extraction of coal can be visualized as follows:

1. Penetration by the supercritical fluid into the pore structure of the coal
2. Breakage of covalent bonds within the coal resulting in smaller molecular weight compounds. This breakage of bonds is primarily due to thermal cracking. However, depending on the solvent-coal interactions, extraction by physical means occurs as well. The physical forces becomes more dominant at lower

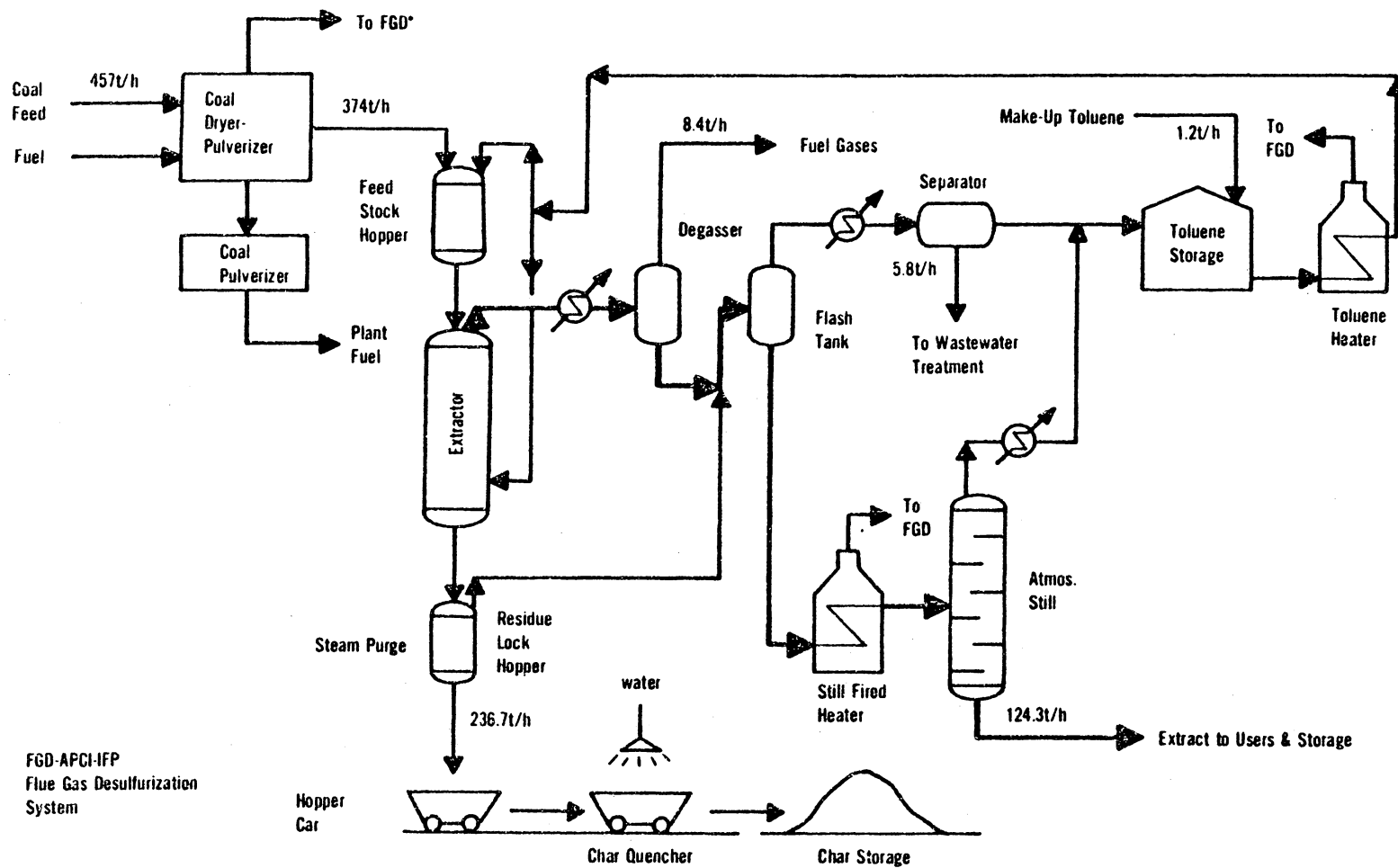


Figure 14: Conceptual Design of SGE by Catalytic Inc.

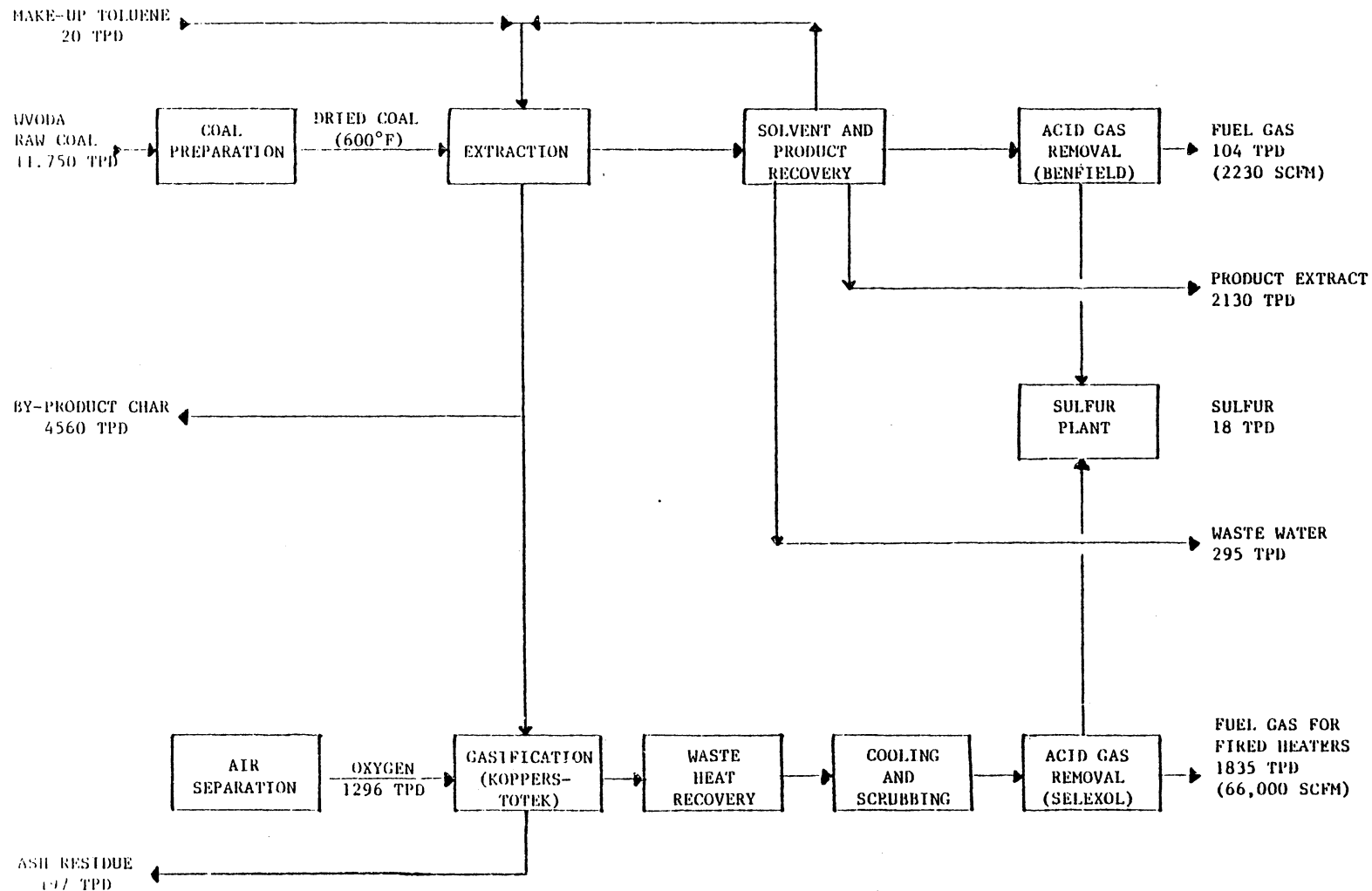


Figure 15: Conceptual Design of SCE Complex by Catalytic Inc.

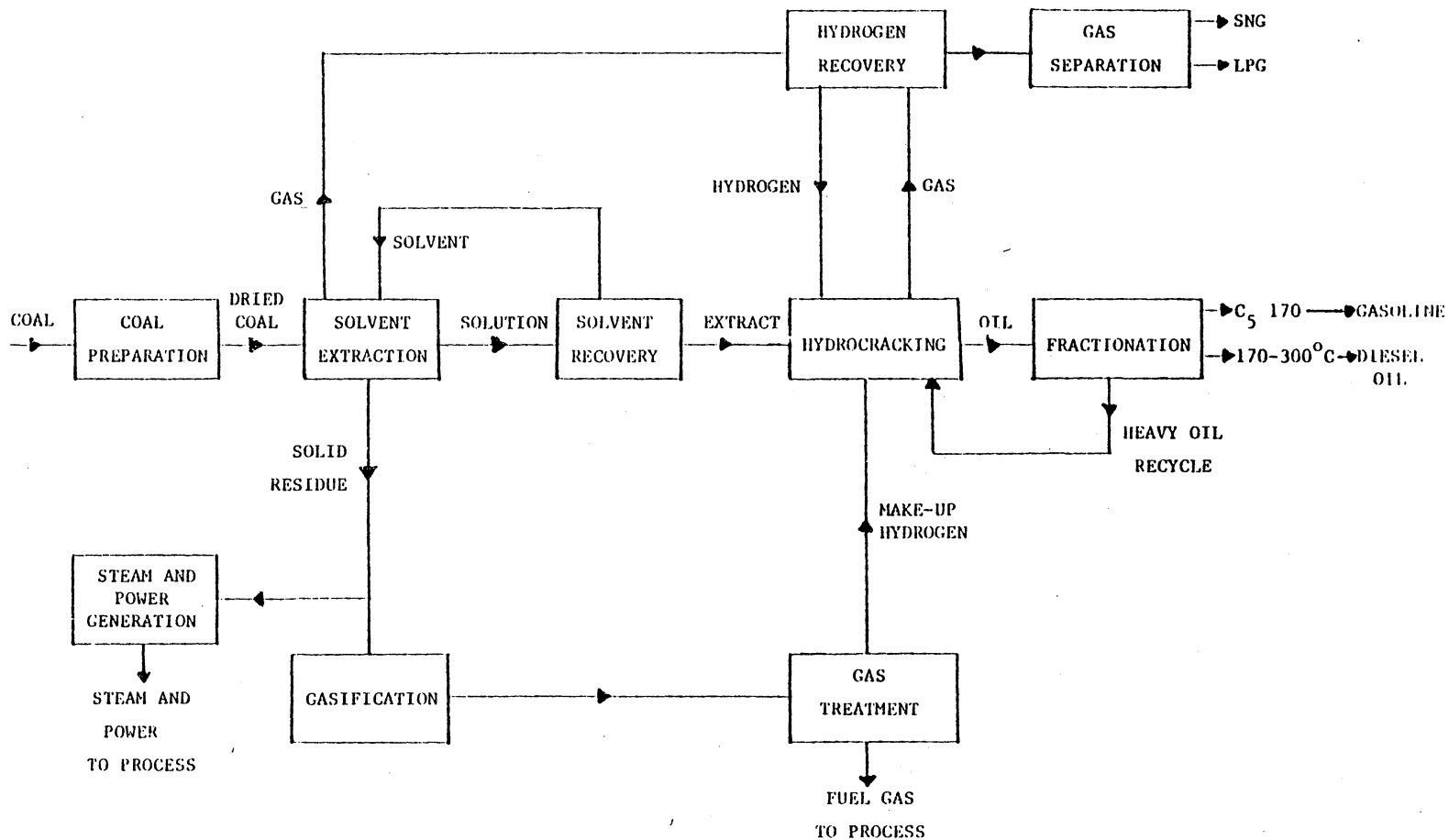


Figure 16: Conceptual Design of SCE Complex by NCB

TABLE 4  
The Product Mix of A Self Sufficient SGE Design<sup>1</sup>

|            | Material             | Fraction<br>(weight basis) | Fraction<br>(energy basis) |
|------------|----------------------|----------------------------|----------------------------|
| Input      | Raw Coal             | 100                        | 100                        |
| Output     | S.N.G.               | 4.0                        | 7.4                        |
|            | L.P.G.               | 1.2                        | 2.4                        |
|            | C <sub>5</sub> -473K | 16.9                       | 28.9                       |
|            | 473-523K             | 5.2                        | 8.9                        |
|            | 523-623K             | 11.8                       | 20.3                       |
| EFFICIENCY |                      | 39.1                       | 67.9                       |

<sup>1</sup>Based on 10000 t/d coal feed and 47.5% daf extract yield.

extraction temperatures and with coal specific solvents e.g. pyridine.

3. Creation of new pores.
4. Enlargement of pore structure.
5. Recombination of coal species.
6. Blinding of pores.
7. Dissolution of coal species in the supercritical solvent.
8. Diffusion of dissolved coal species out of the porous coal matrix. The diffusion is molecular within the micropores and primarily bulk in the macropores.

The rate of pore structure changes depends on the extraction severity (temperature, pressure, and coal residence time), the strength of the solvent, and the molecular size of the solvent. The rate of blinding of the pores is due to the absence and/or lack of solubilizing power of the solvent and this rate increases as the reaction temperature increases. The rate of recombination of coal species depends on the reaction severity and the strength of solvent. The steps 1 and 2 occur simultaneously, and are followed by steps 3 through 7 which proceed in a parallel fashion with respect to each other. The objective is to maximize steps 1-4, and 7-8 at the expense of steps 5-6.

#### 4.4 EXTRACTS FROM SCE OF COAL

A detailed chemical analysis of SCE extracts of low rank coals has been recently published by NCB [91]. In this section, their results will be summarized. The method of extract analysis used was discussed by Herod [94].

The extracts had a molecular weight range of 200-2000. The typical elemental analysis of the SCE streams and extract fractions can be seen in Table 5. The yields of n-pentane soluble material (oils) and asphaltenes each amounted to up to 10 % of the Dry Ash Free (DAF) coal while the yields of benzene insolubles were as high as 30 % DAF coal. The material extracted at the start of the run had a similar molecular weight to that extracted later.

The average molecular weights of extract fractions from SCE of coal with "weak or "strong" solvents at varying extraction temperatures and for a constant extraction period can be seen in Figure 17. The solvents used in this study were primarily aromatic mixtures which had critical temperatures very close to the extraction temperature. The solvent with the highest Hildebrand solubility parameter is referred as the "strongest" solvent (there was no definition of solvent strength in the original article and definition of solvent strength by Hildebrand solubility parameter is the author's interpretation). The "weak" solvents refer to

solvents which were paraffinic in nature and had low Hildebrand solubility parameters. Increased extraction temperatures decreased the average molecular weight of benzene insoluble fraction (asphalts) possibly because the high molecular weight material decomposed at higher temperatures before being extracted from the coal matrix. All but weak solvents extracted asphaltenes without any product degradation.

The statistical averages of chemical type and size of the large number of individual compounds present in supercritical extract fractions are shown in Figure 18. The average structures of the gas extracts contain benzene and naphthalene units joined by methylene bridges, ether bridges, and five membered rings. Methyl is the most common alkyl unit attached to aromatic rings. The liquid solvent extract is more condensed and contains phenanthrene and pyrene units. The liquid solvent extract contains more hydroaromatic rings possibly due to stabilization of its structure by hydrogen abstraction from the solvent. The analysis of the extract at different temperatures indicates that regressive and progressive reactions are minimized around 350°C while at higher temperatures, such as 450°C, product degradation is observed [91].

TABLE 5  
A Typical Elemental Analysis of SCE Feed and  
Products For a Low Rank British Coal

| Elements | Percent of Total<br>[Dry Moisture free basis] |      |         | Extract fractions<br>[Percent of Total] |             |          |
|----------|-----------------------------------------------|------|---------|-----------------------------------------|-------------|----------|
|          | Coal                                          | Char | Extract | Oils                                    | Asphaltenes | Asphalts |
| Carbon   | 81.2                                          | 87.4 | 83.6    | 83.5                                    | 81.7        | 79.8     |
| Hydrogen | 5.2                                           | 3.6  | 6.4     | 8.3                                     | 6.4         | 5.9      |
| Oxygen   | 11.4                                          | 6.7  | 8.0     | 6.4                                     | 9.1         | 9.5      |
| Nitrogen | 1.4                                           | 1.5  | 1.15    | 0.5                                     | 1.3         | 2.0      |
| Sulfur   | 1.65                                          | 1.1  | 0.95    | 0.9                                     | 1.0         | 1.1      |

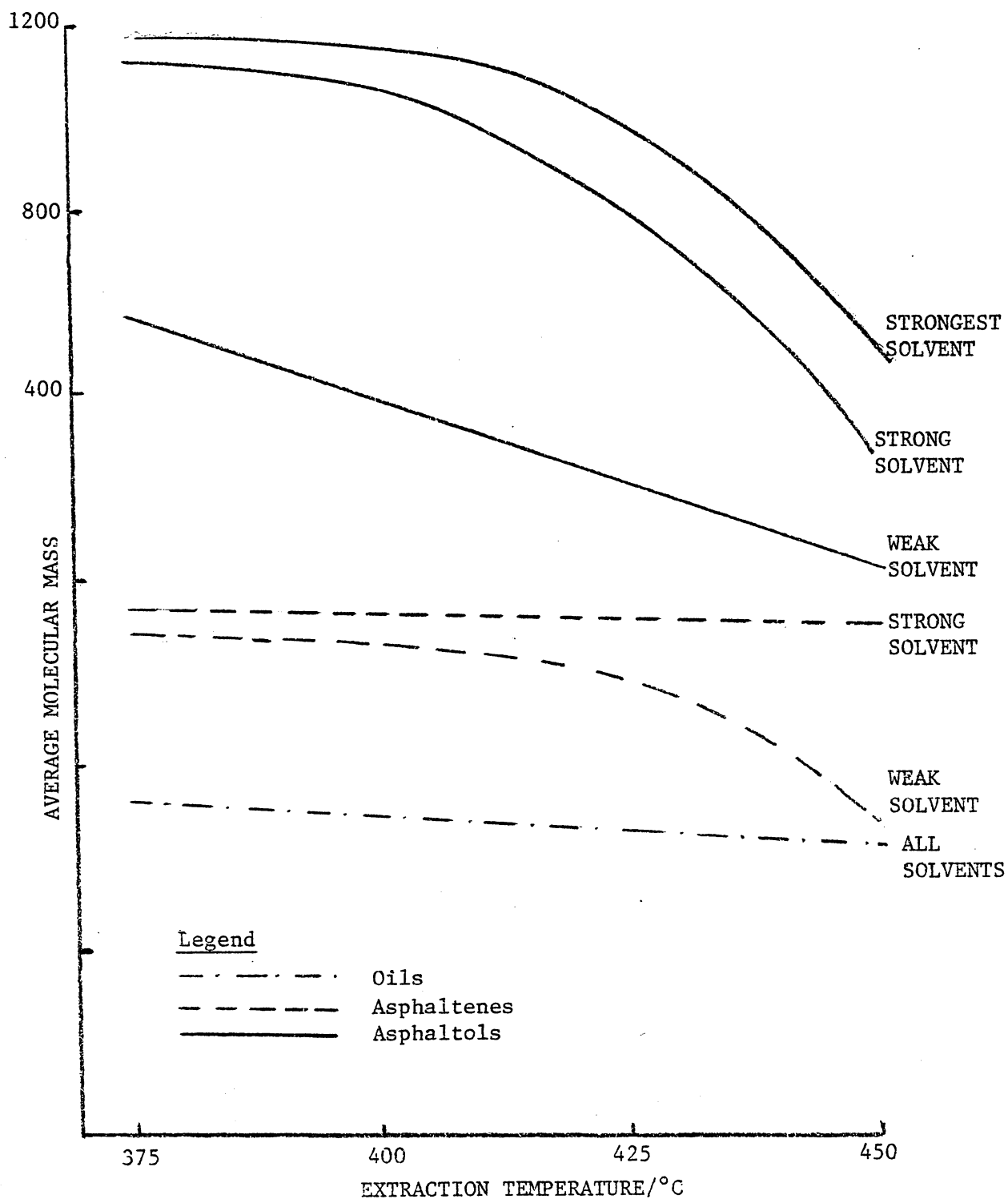
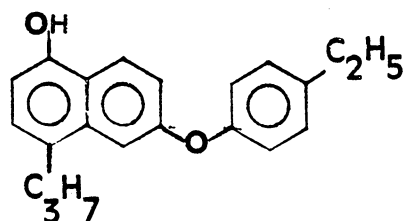
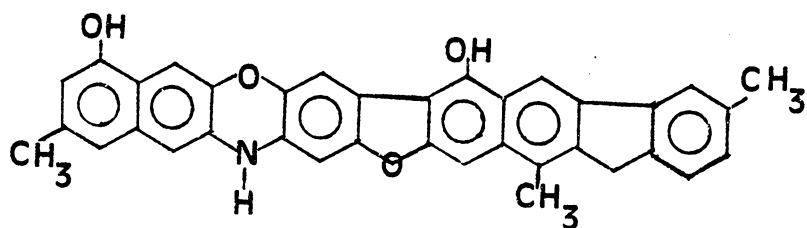


Figure 17: Average Molecular Weights of Extract Fractions From SCE of Low Rank British Coals for a Constant Time Period

## OILS



## ASPHALTENES



## ASPHALTOLS

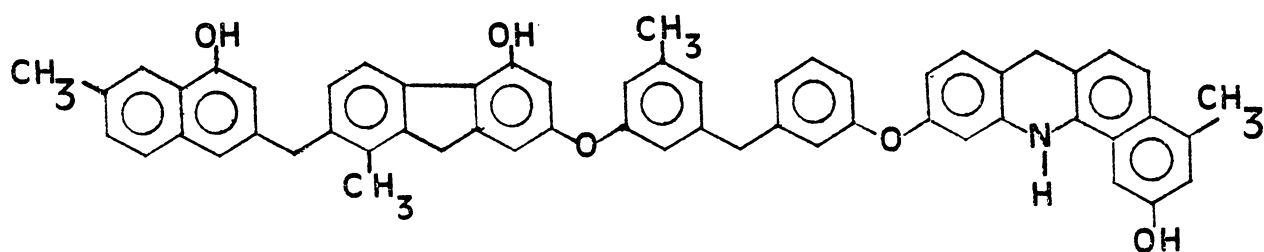


Figure 18: Average Structure of Extract Fractions from a SCE of a Low Rank British Coal

#### 4.5 PROBLEM AREAS AND NEEDED IMPROVEMENTS IN SCE OF COAL PROCESSES

There has been little reported in process design concepts of SGE process since 1979. Thus, the comments in this section are applicable to the initial design by Catalytic Inc. [92]. The suggested flowsheet raises concern on the following issues:

1. There are severe limitations on pressures when using lock hoppers to feed and remove solids feed from moving bed reactors. Use of slurry feed system may be less restrictive.
2. Use of moving bed reactors necessitates coal residence times of at least 30 minutes possibly in part due to slower heat and mass transfer rates. Transport reactors may be a viable alternative.
3. The separation train uses traditional hydrocarbon fractionation technology to separate the extract and the solvent. Pressure reduction prior to the condenser to separate the solvent from the extract would be more energy efficient. If the suggested separation step is to be used, this step has to be optimized simultaneously with the extraction step for solvent selection.

4. Partial hydrogenation of the extract should be done as soon as possible to stabilize the extract fractions.
5. The high cost of solvent requires almost complete solvent recovery.

## Chapter V

### EXPERIMENTAL WORK

This chapter describes experimental goals and equipment as well as analytical procedures and experimental designs. The data compilation and management will be the last section of this chapter.

#### 5.1 OBJECTIVES

The main experimental objective of this dissertation was to explore some of the phenomenological aspects of SCE of coal. More specifically the experimental objectives were:

1. To determine the potential of SCE of coal with the following types of solvents
  - a) An inexpensive solvent with a critical temperature close to ambient temperatures, i.e. carbon dioxide.
  - b) An inexpensive polar solvent with a critical temperature close to temperatures where pyrolytic coal conversion reactions occur, i.e. water.
  - c) An aromatic solvent with a critical temperature close to temperatures where the pyrolytic coal conversion reactions occur. Aromatic solvents are more likely to have the highest solubilizing power

for coal liquids, if the "like-dissolves-like" corollary applies. Furthermore, SCE studies of coal have traditionally employed aromatic solvents and their use enables the experimenter to validate the experimental system and procedure. Toluene is used as the aromatic solvent.

- d) A paraffinic solvent with a critical temperature close to the temperatures where the pyrolytic coal conversion reactions occur, i.e. n-decane. Although n-decane was chosen as the paraffinic solvent, n-pentane which has a much lower critical temperature was used due to availability. Paraffinic solvents, although dissimilar to coal, have some solubilizing power at supercritical conditions and may lead to easier extract-solvent, solid-fluid, and solvent-water separations.
- e) An alcohol, i.e. methanol. Alcohols are relatively small and polar molecules. Thus, they have a good chance of diffusing and attacking the porous coal matrix.
- f) Another aromatic solvent, i.e. xylene, in order to compare two similar solvents of a homologous series.

2. To analyze the coal reactions in extractions with toluene.
3. To develop and use a more informative SCE product and residua analysis procedure than conversion (percent conversion) or yield. The products are to be analyzed and grouped as gases, oils, asphaltenes, asphaltols, and pyridine insolubles. The residua are assumed to consist of asphaltenes, asphaltols and pyridine insolubles.
4. To study how the extraction of coal is affected by:
  - a) Temperature
  - b) Pressure
  - c) Coal/Solvent Ratio
  - d) Coal Residence Time
5. To choose coal/solvent ratios and coal residence times so that maximum information on thermodynamic solubility as well as the reaction kinetics can be obtained. At low residence times such as fifteen minutes and low solvent-to-coal ratios such as two, the solvent is assumed to leave saturated with the extract.
6. To select the extraction pressures so that at least one pressure is very close to the critical, such as 4.8 MPa (700psia), while there is at least one pres-

sure considerably higher than the critical, 13.8 MPa (2000 psia).

7. To study the effects of initial pyrolysis followed by SCE at ambient conditions.
8. To study the effects of entrainers on SCE at near ambient conditions.
9. To select the extraction temperatures to include temperatures where pyrolytic reactions are minimal, i.e. 375°C, and temperatures where such reactions are dominant, i.e. 425°C.

## 5.2 EXPERIMENTAL SYSTEMS

Following experimental arrangements were used to fulfill the experimental objectives set in the previous section:

1. A semi-batch high temperature SCE system
2. A semi-batch low temperature SCE system.
3. A Soxhlet extraction apparatus
4. A mini-autoclave system
5. Micro distillation apparatus
6. Thermogravimetric Analysis (TGA) equipment.
7. Filtration apparatus

The high temperature and low temperature SCE systems were used to extract the coal with supercritical solvents. The low temperature system used solvents which were gaseous at

feed conditions while the solvents used in the high temperature system were liquid at ambient conditions. The high temperature and low temperature SCE systems were built for this research and will be described in the next two sections because of their relative importance and the novelties of these experimental systems. The Soxhlet extraction apparatus was used in sequential extractions of the residua and the extract to further fractionate them into oils, asphaltenes, asphaltols, and insolubles. Distillations were used to separate the solvents from the extract fractions. Filtrations were used in some extract fractionations to replace Soxhlet extractions. The mini-autoclave was used to pre-condition the coal feeds prior to extraction with the low temperature unit. The Soxhlet extraction, micro distillation, and the TGA will be described in section titled "Analytical Procedures" while the mini-autoclave system was described in an other thesis [95].

#### 5.2.1 Description of High Temperature Semi-Batch SCE system

The high temperature Super Critical Extraction (SCE) system operated in a semi-batch fashion. The solid solute, dried coal particles (12-20 Mesh), was held between two wire mesh disks in the extractor and the solvent passed upward through it continuously. Some main design objectives and constraints were:

1. Safe operation
2. Ability to control the temperature history of the coal and avoid long heat-up and cooling times (heat up times of two minutes or less achieved).
3. Ensure small non-pulsating, constant, and controllable flow rates through the extraction column.
4. A system where multiple samples can be easily collected during an experimental run and where the extractor can be replaced rapidly in between experiments.
5. Avoid settling of the extract prior to sample collection flasks.
6. Recovery of the solvent and extract.
7. Constant extraction temperatures and pressures.
8. No entrainment of solid coal particles with the extract.
9. Ability to vent various sections of the unit independently.

All design criteria and constraints were met by the system illustrated in Figure 19. The control of the flow rate through the extraction section was the least successfully met criteria while all other constraints were met fully. The apparatus could be divided into following sections according to primary functions.

1. Feed section
2. Solvent pre-conditioning section
3. Extraction section
4. Extract reclaiming section

The feed system was rather involved due the overcapacity of the available feed pumps and consisted of a reciprocating pump (Pulsa feeder, 7126); a high pressure feed tank (Aminco Autoclave),  $A_1$ ; a high pressure nitrogen gas source and connecting tubing, fittings and valves.

A measured amount of solvent was pumped, usually before an experiment, to  $A_1$ . The Aminco autoclave,  $A_1$ , served as a storage tank and was under nitrogen pressure which was always higher than the SCE pressure during an experiment. Nitrogen pressure forced the feed through a ball valve (Whitey, SS-42SX4),  $M_1$ , and a metering valve (Whitey, SS-31RS4),  $M_2$ , to the pressurized solvent pre-conditioning section.

In the pre-conditioning section, the vapor pressure of the heated solvent was used to bring the solvent to the extraction pressure. The heating was done in a second autoclave (Autoclave Engineers, APF-150),  $A_2$ ,. The heating was accompanied with a pressure rise. The pressure in the second autoclave ( $A_2$ ) was a function of temperature. It was dependent on the heating and cooling (due to heat losses) rates and the solvent inventory. Above the critical point,

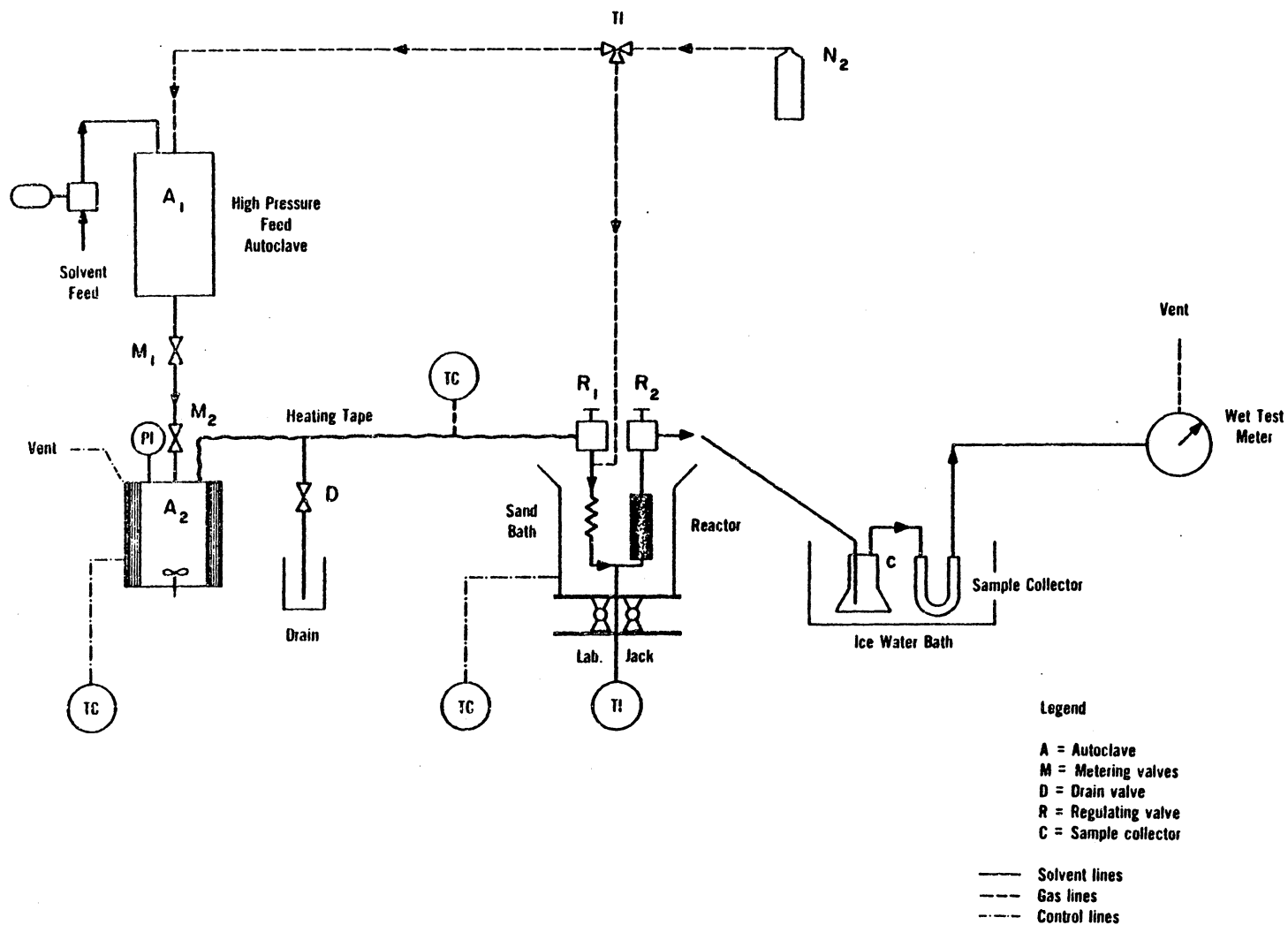


Figure 19: High Temperature Supercritical Extraction System

the solvent density can be calculated from an equation of state and the desired pressure can be reached and controlled by careful adjustment of the solvent inventory in the pre-conditioning section. This autoclave was connected through the bottom blow pipe to the extraction section with a regulating valve (Autoclave Engineers, SS-10V-4882 Ga ).<sup>1</sup> The regulating valve ( $R_1$ ) was basically a shut-off valve. Also in the transfer line of this section, there was a discharge valve (Nupro SS-8TG-HS), D. The discharge valve was for regulating the solvent inventory in order to control the system pressure. It was also used for emptying solvent in the system at the end of an experiment. The regulating valve ( $R_1$ ) was kept shut until solvent reached the desired pressure. The tubing and valves were heated by a heating tape. The temperature of the solvent, in the pre-conditioning section, was not necessarily at the extraction temperature since it is raised to the extraction temperature in a fluidized sand bath heater later. Although with higher temperatures at the pre-conditioning section the heat duty of the subsequent extraction section was lowered, higher temperatures decreased the life of valves  $R_1$  and D.

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<sup>1</sup> Sno-Trik valves as in ' $R_2$ ' were found to be much more reliable and were used after few initial runs

A preheating coil brought the solvent temperature within 1°C of the bath temperature. The length of this coil was kept short enough to minimize the solvent inventory in the extraction section, between two regulating valves ( $R_1$  and  $R_2$ ). The extractor was a stainless steel tube, 3/4 OD, 0.095 inch wall, and 15 cm. long, with wire mesh disk screens at both ends. The preheating coil and the connected extractor were immersible into a fluidized bath heater (Techam, SBL-2) which was controlled by a proportional-integral-differential temperature controller (PID) (Techam, TCA4). The bath was raised to immerse the coil and the extractor by two laboratory jacks (Precision Scientific Co., Big Jack). The extraction section was connected to the extract reclaiming section through stainless steel tubing and the necessary fittings. All tubing in the extraction section except the part immersed in the bath was heated with heating tape.

The system pressure was let down to atmospheric via a heated regulating valve (Sno-Trik SS-445 FPAR A1 STE ),  $R_2$ . This valve ( $R_2$ ) controlled the flow rate through the extraction section as well. The valve outlet was connected to a stoppered sample collection flask which was immersed in an ice-water bath. The extract and the solvent which were not collected in the flask were trapped in a U tube which was also immersed in the same ice-water bath. The level of the solvent in the graduated sample collection flask served as a

visual feedback for metering solvent rate through the extraction section via valve  $R_2$ . The noncondensables were metered by a wet test meter and vented.

The operating procedure is included as APPENDIX A part 1.

#### 5.2.2 Description of the Low Temperature Semi-Batch SCE System

The low temperature extraction system was limited by the back pressure regulator specifications to an extraction temperature of 95°C and a pressure of 20.7 MPa. This system was used for supercritical extraction coal and heat pre-treated coal with carbon dioxide. Figure 20 shows the details of the flow diagram for the system. This system was used for two purposes:

1. Studying the process conditions for SCE of various solid substances, e.g. coal and coal tar.
2. Getting solid-fluid thermodynamic equilibrium data. carbon dioxide-naphthalene solid-fluid equilibria was studied to gain experience with the system.

The pressurized solvent feed cylinder was connected to a compressor (Whitey, LC10). Whenever the solvent used was carbon dioxide, the feed to the compressor was preheated to avoid saturation in the compressor. The recycle loop at the feed to the system protected the system from undesired pressure build-ups. The recycle flow was controlled with a

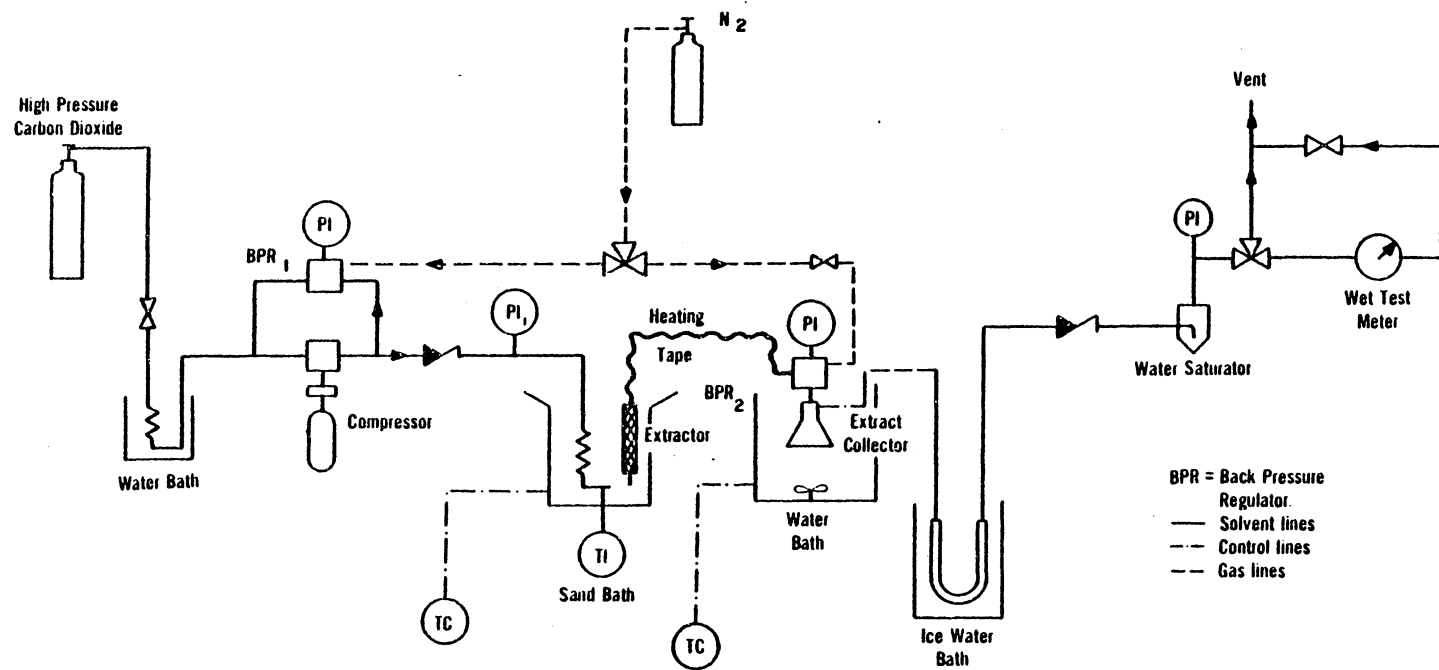


Figure 20: Low Temperature Extraction System

backpressure regulator (Mity-Mite Back pressure regulator, S-91XW), BPR<sub>1</sub>, which was usually set about 2 MPa higher than the system pressure. A second check valve in addition to the check valve at the compressor outlet eliminated backflow of gases to the compressor as well as to the recycle line.

The pressurized solvent was preheated through a coil immersed in the fluidized bath. This coil was sufficiently long to ensure solvent feed temperatures within 0.5°C of the extractor, but which at the same time minimized the volume between the compressor and a second back pressure regulator (BPR<sub>2</sub>), extraction section. Minimization of this volume was necessary for two reasons:

1. The amount of solvent used during start-up and shut-down had to be minimized.
2. The distance between the extractor and the BPR<sub>2</sub> should be kept to a minimum and controlled at the extraction temperature since the solvency power is highly sensitive to temperature fluctuations.

The extractors were made up of 15 cm. 3/4inch OD SS316 tubing with wire mesh screens at the bottom and either packed glass wool or wire mesh screens at the top.<sup>2</sup>

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<sup>2</sup> Wire mesh screens are used for coal runs.

A second back pressure regulator ( $BPR_2$ ) held the extraction pressure at a desired pressure. The inlet and outlet of  $BPR_2$ , were immersed in a water bath (Haake, E52). The temperature of the bath was kept close to the critical temperature of the solvent. If the bath temperature was too high, some extract precipitated at  $BPR_2$  inlet and if it was very low, dry ice formation at  $BPR_2$  outlet occurred. This arrangement gave smooth trouble free flows. The  $BPR_2$  outlet was connected to a stoppered flask through the top of the beaker. The flask's side arm outlet was packed with a preweighed amount of glass wool. The flask, the back pressure regulator ( $BPR_2$ ), and the connecting tubing were immersed in a water bath. After the precipitation of the extract, solvent left through the side arm of the flask and passed through an U-tube which was packed with glass wool. The U-tube was immersed in an ice-water bath to ensure complete precipitation of the extract.

The solvent then went through a water saturator which was primarily used to saturate the solvent, carbon dioxide, with water and also to observe flow patterns visually. The solvent flow rate was measured using a wet test meter. The wet test meter measurements were corrected to standard temperature and pressure prior to reporting. The solvent gases and non-condensibles were then vented.

### 5.3 DESCRIPTION OF ANALYTICAL FACILITIES AND PROCEDURE

In this section, the analytical procedures and facilities will be presented. Characterization of coal and coal products is complex. The analyses performed for this dissertation were modest but aimed to be informative and accurate. The analytical techniques used were:

1. TGA of the coal and the SCE residua
2. Scanning electron microscopy of selected coal and residua samples.
3. Micro distillation of the solvent from the extract.
4. Soxhlet extraction of the extract and the coal.
5. Filtration of the extracts from various solvents

The feed preparation method will be presented in this section as well as the the analytical procedures. Particular attention has been paid to minimize the oxidation of the coal.

#### 5.3.1 Feed Preparation

The coal used throughout the study was Wyodak 1 and was received and coded by Hydrocarbon Research Incorporated (HRI) as HRI 4176. The proximate and ultimate analyses of the coal are shown as Table 6.

The preparation of the feed coal is shown in Figure 21. The coal was stored under water to avoid oxidation. Shortly

TABLE 6

Analysis of the Feed Coal (Wyodak 1)

| <u>Proximate Analysis</u> |                 | <u>Ultimate Analysis</u> |                 |
|---------------------------|-----------------|--------------------------|-----------------|
| <u>Contents</u>           | <u>Weight %</u> | <u>Contents</u>          | <u>Weight %</u> |
| Ash                       | 4.7             | C                        | 65.81           |
| Moisture                  | 9.9             | H                        | 5.15            |
| Volatiles                 | 36.1            | N                        | 0.86            |
| Fixed Carbon              | 49.3            | O                        | 21.19           |
|                           |                 | S                        | 0.41            |

before an experiment, the coal was dried and sieved to a particle size range of 12-20 mesh. Investigators at NCB [90] had reported that the particle size did not affect the experimental results significantly under 8 mesh. Thus, 12-20 mesh particle size range was used to avoid any possible entrainment of the fines. The coal particles were then vacuum dried at 60°C. The drying was done to vent the gases trapped within the pores and to get rid of the moisture, but not the volatile matter. The dried coal particles were stored in closed jars within dessicators and were used after a TGA run.

#### 5.3.2 Post-treatment Analysis

The objectives of the post-treatment analysis were:

1. Determination of the exact amount of solvent used.
2. Fractionation of the extract and the residua into oils, asphaltenes, asphaltols, and insolubles so that distribution of such fractions can be found. Competing regressive and progressive reactions occur simultaneously with solvation and numerical results can not be taken as absolute values.
3. Determination of the volatiles and the fixed carbon contents of the residua with TGA. Examination of the pore structure of coal and extraction residua under electron microscope.

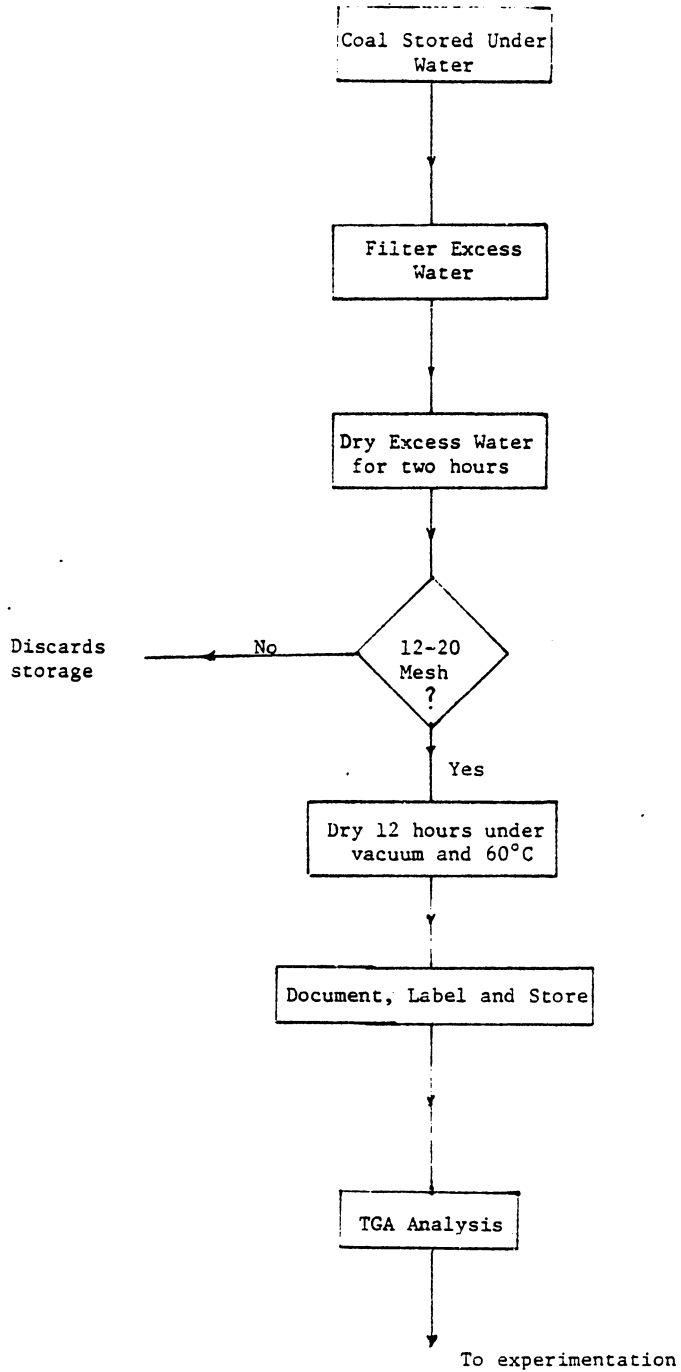
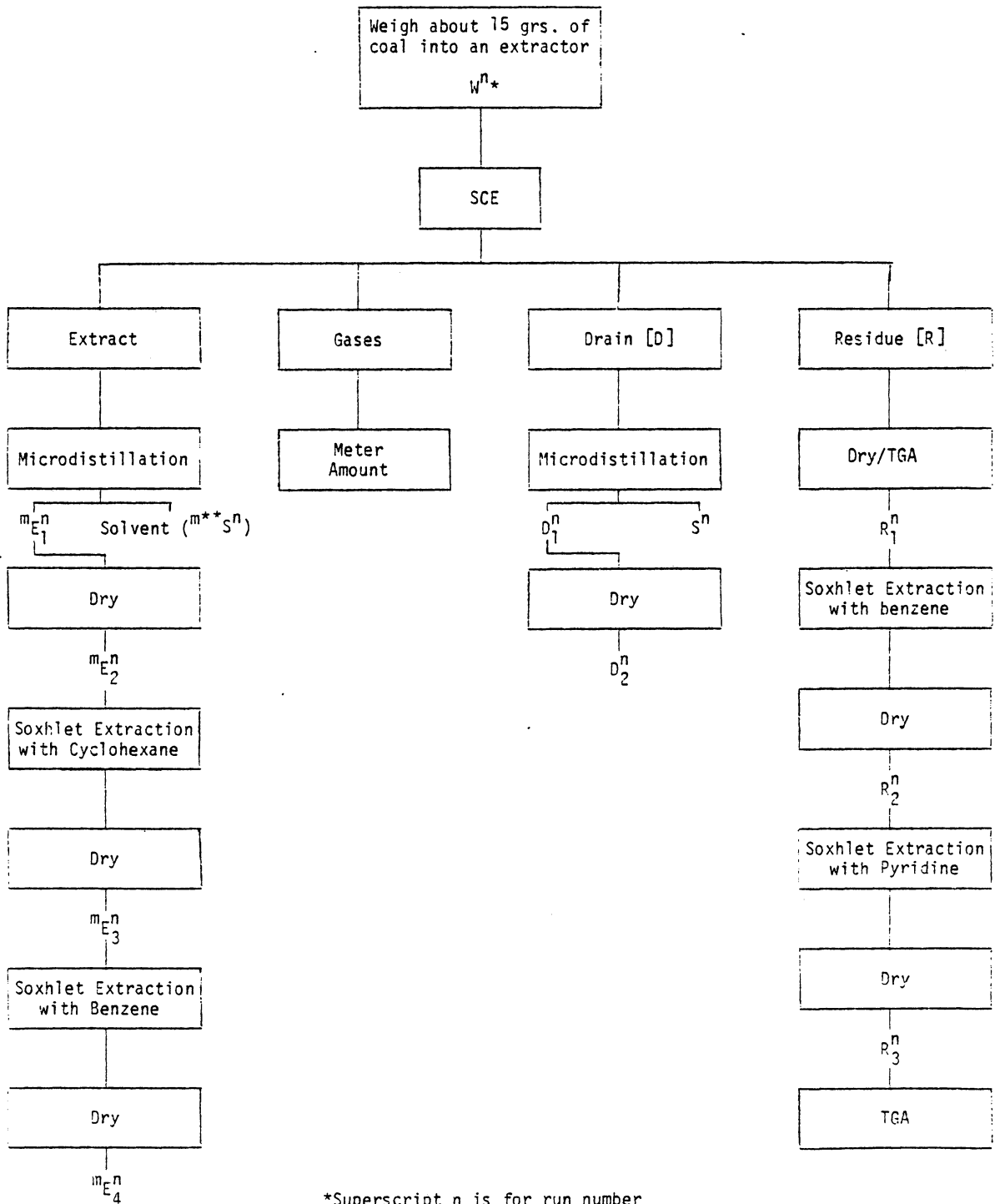


Figure 21: Feed Preparation

The schematic summary of the characterization sequence is shown as Figure 22. A sample analysis is included in APPENDIX B. Both the Soxhlet extraction and the distillation procedures are standard analytical methods and will not be discussed. The drying operations took about 12 hours. Soxhlet extractions continued approximately 12 hours while micro-distillations were done in 1-2 hours. Since the analytical procedures were lengthy (a sample was analyzed in 2-3 days), multiple trains were used. Six Soxhlet extractions and two micro-distillations were done at a time. During the later stages of the research extract analysis procedure was changed to the procedure outlined in Figure 23. This new procedure gave approximately the same breakdown as in Soxhlet extractions. However, more extract was recovered by this second method.

#### 5.4 EXPERIMENTAL DESIGN

The experimental conditions were chosen to meet the objectives described in the first section of this chapter. Temperature, pressure, time, and solvent-to-coal ratio were the design parameters. A different experimental design was used for each of the following areas:



\*Superscript n is for run number  
 \*\*Initial superscript is for sample number within a run

Figure 22: Product Analysis Procedure

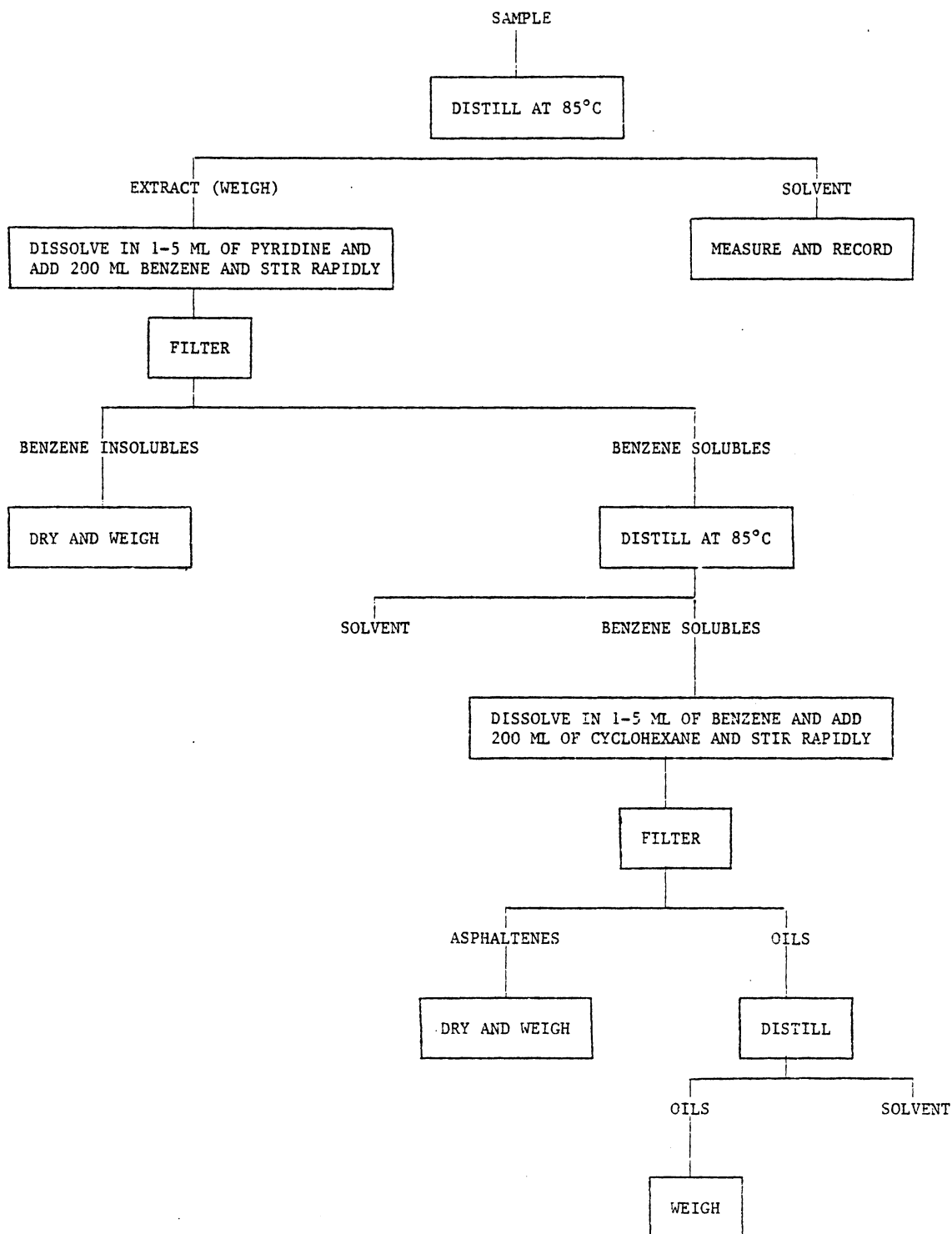


Figure 23: Alternate Extract Fractionation Procedure

1. Extraction of raw coal with carbon-dioxide (see Table 7).
2. Extraction of heat-pretreated coal with carbon-dioxide (see Table 8).
3. Entrainer-aided extraction of raw coal or heat-pretreated coal with carbon-dioxide (see Table 9).
4. SCE with the high temperature system (see Table 10).

The experimental designs used in this study is summarized in the next set of Tables.

#### 5.5 DATA COMPILATION AND MANAGEMENT

All data is recorded on data sheets, and labelling is done consistent with Figure 22. The summary of results are stored in a computer file in such a fashion that they are easily and efficiently accessible for computation and/or reporting purposes. The data sheets for typical runs are shown in Appendix B with sample analysis.

TABLE 7

## Extraction of Coal with Carbon Dioxide

| <u>Parameters:</u>         | <u>1</u> | <u>levels</u><br><u>2</u> |
|----------------------------|----------|---------------------------|
| Temperature (°C)           | 45       | 90                        |
| Pressure (Mpa)             | 10.4     | 17.3                      |
| Solvent amount (STD cu. m) |          | .43                       |

TABLE 8

Extraction of Heat-Pretreated Coal with Carbon Dioxide

Pretreatment Conditions

Temperature (°C) : 200, 300, 400, 450

Time (h ) : .25, 1

SCE condition

Temperature (°C) : 90

Pressure (MPa.) : 10.4

Solvent (STD cu. m) : 0.43

TABLE 9

Extraction of Coal with Carbon Dioxide After Pretreatment  
with Solvents

|                        |                                      |
|------------------------|--------------------------------------|
| Entrainers (Modifiers) | : Water, Toluene, Pyridine, Tetralin |
| Entrainer/Coal Ratio   | : 1/5, 1/2                           |
| SCE Temperature (°C)   | : 50, 75, 90                         |
| SCE Pressure (MPa.)    | : 10.4                               |
| Solvent (STD cu. m)    | : 0.43                               |
| Heat pretreatment      | : none, 1hr. at 400°C                |

TABLE 10

## SCE Extraction with High Temperature System

Solvents : Toluene, Xylene, Pentane, Methanol, Water  
Temperatures (°C) : 375, 425  
Pressure (MPa) : 4.8 - 24.  
Coal residence time (s) : 600 - 5400  
Solvent/Coal ratio : 2-20

## Chapter VI

### RESULTS OF EXPERIMENTAL WORK

In this chapter, results of the experimental work will be presented and discussed. The results and discussion of the experiments with the high temperature system will be followed by that of the low temperature system. The major difference between extractions with the low temperature and the high temperature system is that at high temperatures decomposition and recombination reactions within coal occur simultaneously with solubilization.

The supercritical solvents used in the high temperature system were toluene, xylene, water, methanol, and n-pentane. Supercritical carbon dioxide was used as the solvent in all the experiments with the low temperature system. In some of the low temperature experiments, liquid entrainers (modifiers) such as water, pyridine, toluene, and tetralin were used to aid the extraction. Entrainer-aided supercritical extraction of coals which were preheated at 400°C for one hour were also studied.

In supercritical extraction, the critical properties of the solvent dictates the experimental conditions because solvency power of the solvent is closely related to its critical properties. Thus, critical properties of solvents used in this research are show in Table 11.

TABLE 11

Critical Properties of Solvents Used in Supercritical Extractions

| Solvent        | M <sub>w</sub><br>[g/g-mole] | T <sub>c</sub><br>[°C] | P <sub>c</sub><br>[MPa] | Z <sub>c</sub> | ρ <sub>c</sub><br>[g/cc] |
|----------------|------------------------------|------------------------|-------------------------|----------------|--------------------------|
| Toluene        | 92.13                        | 319                    | 4.5                     | 0.25           | 0.292                    |
| Xylene         | 106.16                       | 357                    | 3.86                    | 0.26           | 0.284                    |
| Pentane        | 72.15                        | 169                    | 3.67                    | 0.262          | 0.237                    |
| Methanol       | 32.05                        | 240                    | 8.8                     | 0.224          | 0.272                    |
| Water          | 18.0                         | 374                    | 24.1                    | 0.229          | 0.315                    |
| Carbon dioxide | 44.0                         | 31.1                   | 7.3                     | 0.274          | 0.47                     |

## 6.1 SCE WITH THE HIGH TEMPERATURE SYSTEM

There were approximately forty experimental runs made with the high temperature system. The moisture content of the coal before and after an experimental run was determined with the aid of thermogravimetric analysis, TGA. Three samples were collected during a run. The first sample contained the extract and the solvent from the start to fifteenth minute of the experiment while the second contained the amount from fifteenth to forty-fifth minute. The third and final sample contained the amount collected during the last thirty minutes. The gas amounts passing through the wet test meter were recorded for each sampling period during a run. After the experimental run, the collected solvent and the extract were separated from each other via distillation. The extract and the residua char left from extraction were further analyzed.

Samples of only twenty-one experimental runs were successfully analyzed. In few runs, experimental conditions were changed due to operational problems. There were some experimental runs where at least one of the samples was destroyed during fractionation. These runs were excluded from this dissertation. Both the extracted coals (residua) and the extracts were fractionated using the procedures discussed in Chapter V. The residua were fractionated via suc-

cessive Soxhlet extractions (Figure 22). The extracts were fractionated either using Soxhlet extractions (Figure 22) or via sequential filtrations and distillations (Figure 23). Most of the discarded data were the ones from Soxhlet extractions. For the experimental runs, more than eighty percent of the weight loss of coal was accounted for as extract and gas.

Toluene was used as the solvent in thirteen of the experiments. A full  $2^3$  factorial design was used to study percent extraction of coal with toluene. In this design, effects of temperature, pressure and the flowrate were studied at two levels. Fractional extraction completion and extract component distribution were studied by  $2^4$  factorial designs where elapsed time was the additional parameter. This was possible because multiple (three) samples were taken during each run. Replication for all the experiments was not attempted. Instead two extreme conditions of the factorial design were replicated. The two extreme conditions were:

1. 13.8 MPa (2000 psia), 425°C, and 4.3 g Toluene/minute
2. 4.8 MPa (700 psia), 375°C, and 2.2 g Toluene/minute

Two additional experiments at 10.4 MPa (1500 psia) and 4.3 g Toluene/minute were performed for temperatures 425°C and 375°C to study the effects of pressure. One short residence time (coal residence time = 6 minutes) experiment with to-

luene was also performed. Solvents other than toluene were also used in accordance to objectives described in Chapter V. Three experimental runs with xylene, two with methanol, two with n-pentane, and one with water were done.

One suggested index for solvency power of supercritical solvents was Hildebrand solubility parameter (Theory discussed in Chapter II Section 4.3). The Hildebrand solubility parameter is very sensitive to the state of the solvent, i.e. temperature and pressure. Hence, Hildebrand parameter for all the operating conditions and for all the solvents are shown in Table 12. The state of the solvents at experimental conditions can be further illustrated in terms of reduced temperatures and pressures (Figure 24). At high temperatures, above 350°C, the extraction process depends on reaction kinetics as well solubility. Hence a direct correlation of percent extraction with the Hildebrand parameter is not suggested and should not be expected. Furthermore, Hildebrand solubility parameter is rather empirical and can not replace the more rigorous approaches discussed in Chapter II. Thus Hildebrand solubility parameter is used only as an index to quantify terms such as "strong solvent" and "weak solvent". Solvents with  $\xi$  higher than 4 (cal/cc)<sup>1/2</sup> will be called strong, while solvents whose  $\xi$  is less than 2 (cal/cc)<sup>1/2</sup> will be referred as weak.

Table 12

Hildebrand Solubility Parameter at Extraction Conditions  
of the High Temperature System

| Solvent   | T<br>[°C] | P<br>[MPa] | Z    | $\rho$<br>[g/cm <sup>3</sup> ] | $\xi_g$<br>[cal/cm <sup>3</sup> ] <sup>1/2</sup> |
|-----------|-----------|------------|------|--------------------------------|--------------------------------------------------|
| Toluene   | 425       | 13.8       | 0.56 | 0.39                           | 4.00                                             |
| Toluene   | 425       | 10.4       | 0.54 | 0.30                           | 3.11                                             |
| Toluene   | 425       | 4.8        | 0.75 | 0.10                           | 1.05                                             |
| Toluene   | 375       | 13.8       | 0.5  | 0.47                           | 4.82                                             |
| Toluene   | 375       | 10.4       | 0.42 | 0.42                           | 4.31                                             |
| Toluene   | 375       | 4.8        | 0.63 | 0.13                           | 1.33                                             |
| Xylene    | 425       | 13.8       | 0.53 | 0.48                           | 4.7                                              |
| Xylene    | 375       | 4.8        | 0.30 | 0.32                           | 3.12                                             |
| Xylene    | 360       | 13.8       | 0.48 | 0.58                           | 5.68                                             |
| n-Pentane | 375       | 13.8       | 0.77 | 0.24                           | 2.75                                             |
| n-Pentane | 375       | 4.8        | 0.86 | 0.075                          | 0.86                                             |
| Methanol  | 425       | 13.8       | 0.86 | 0.089                          | 1.37                                             |
| Methanol  | 375       | 13.8       | 0.72 | 0.115                          | 1.77                                             |
| Water     | 425       | 24.0       | 0.61 | 0.13                           | 2.87                                             |

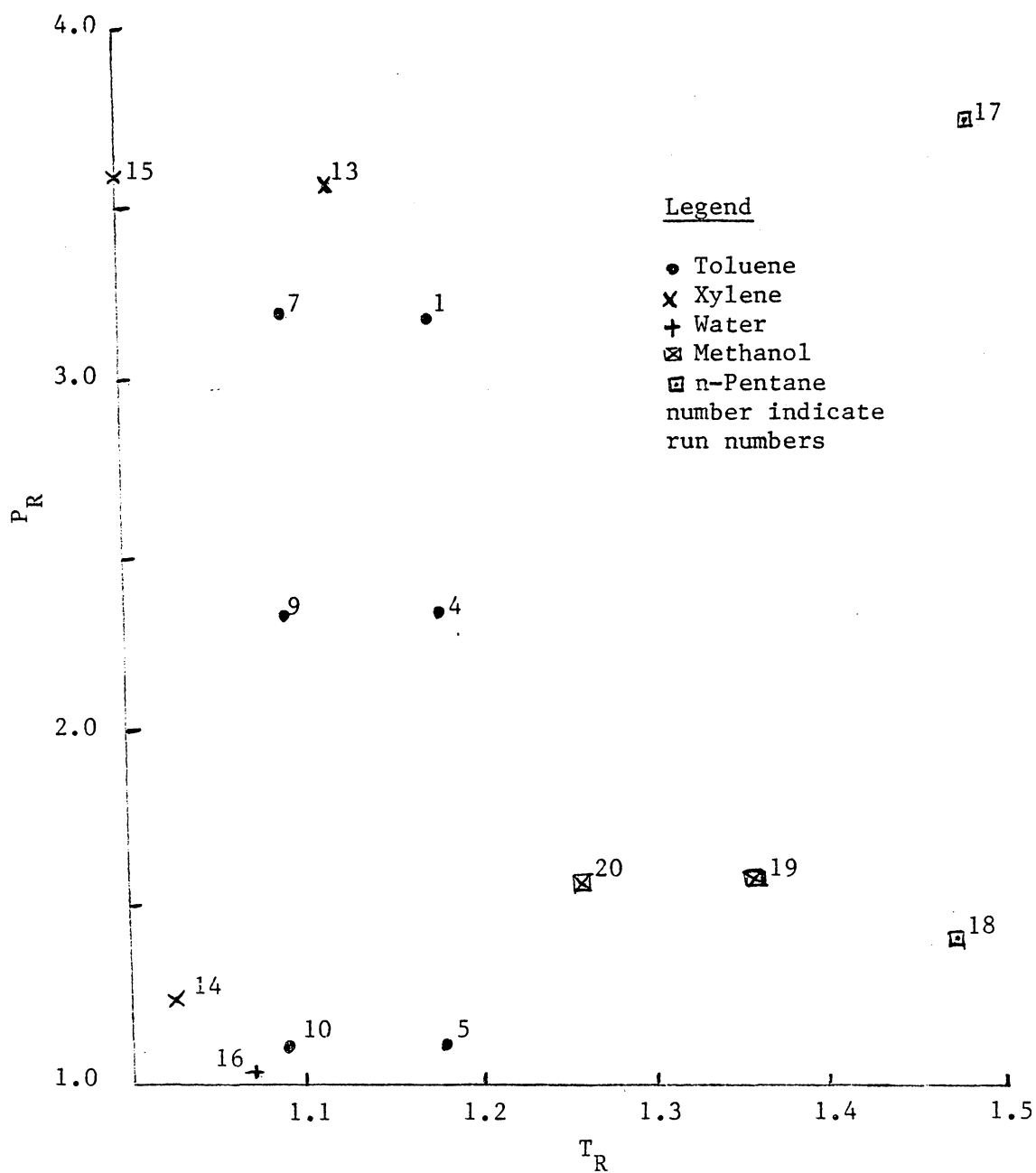


Figure 24: Experimental Conditions in Terms of Reduced Temperatures and Pressures of the Solvent

In this section, first the experimental results will be presented, and then the analysis and discussion of results will follow.

#### 6.1.1 Results of the Experimental Work

The twenty one experiments, parameters, and percent extraction (weight loss on dry basis) are summarized in Table 13. The order of experiments in the summary is not same as the order experiments were performed. The total amount of extract collected during each period was measured after the extract and the solvent were separated. Table 14 summarizes the distribution of extract amount among different periods for each run. Each extract sample was fractionated into oils, asphaltenes, and oils using the procedures discussed in Chapter V and shown in Figure 22 and Figure 23. A sample analysis for fractionation can be found in Appendix B. In most of the reported experiments, filtration procedure was used as opposed to Soxhlet extractions (unless specified). A comparison of procedures can be seen from Table 15. The absolute amounts of extract fractions for each sampling period of all the experiments is exhibited in Appendix B.4. while the relative amounts of extract components with respect to the total amount of extract are shown, for each period of all the experimental runs, in Table 16.

The gas analysis was based on wet test meter readings on noncondensables. The gas analysis results can be seen in Table 17, which summarizes overall material balance results. For samples where there were no reliable gas amount, 5% gas (dry coal feed basis) was used in material balance calculations. Relatively high gas yields are due to the nature of coal. Wyodak 1 has 21% elemental oxygen which cause the relatively high gas production. Some of the data on gas amounts was discarded because of solvent loss through the gas line. The trends of residuals of extent of recovery was checked to possibly correlate the unrecovered fraction with gas amount. However, no such trend was observed.

The coal residua from extraction were analyzed with TGA for determination of volatile content. The volatiles content ranged from fifteen to twenty-five percent of residua char depending on percent extraction. This may be due to inaccessibility of certain fraction of volatiles which were trapped in blind micropores. The residua were also subjected to sequential Soxhlet extractions with benzene and pyridine, respectively, to determine whether or not any extractable material was left in the residua char. The results of residua fractionation showed that very little benzene-soluble matter existed in extracted coal samples. Benzene-soluble matter was left only in chars from supercritical extrac-

Table 13

## Summary of Experimental Conditions and Percent Extraction

| Run No. | Solvent              | Temperature<br>[°C] | Pressure<br>[MPa] | Amount of Solvent used [cc] |             |             | Percent <sup>1</sup><br>Extraction |
|---------|----------------------|---------------------|-------------------|-----------------------------|-------------|-------------|------------------------------------|
|         |                      |                     |                   | [0-15 min]                  | [15-45 min] | [45-75 min] |                                    |
| 1       | Toluene              | 425                 | 13.8              | 58                          | 110         | 121         | 31.0                               |
| 2       | Toluene              | 425                 | 13.8              | 67                          | 102         | 117         | 31.8                               |
| 3       | Toluene              | 425                 | 13.8              | 41                          | 77          | 71          | 29.5                               |
| 4       | Toluene              | 425                 | 10.4              | 70                          | 118         | 111         | 27.1                               |
| 5       | Toluene              | 425                 | 4.8               | 71                          | 109         | 120         | 26.0                               |
| 6       | Toluene              | 425                 | 4.8               | 29                          | 64          | 61          | 25.7                               |
| 7       | Toluene              | 375                 | 13.8              | 58                          | 128         | 131         | 19.1                               |
| 8       | Toluene              | 375                 | 13.8              | 37                          | 66          | 64          | 18.8                               |
| 9       | Toluene              | 375                 | 10.4              | 68                          | 137         | 119         | 17.5                               |
| 10      | Toluene              | 375                 | 4.8               | 71                          | 127         | 118         | 16.3                               |
| 11      | Toluene              | 375                 | 4.8               | 34                          | 63          | 67          | 16.2                               |
| 12      | Toluene              | 375                 | 4.8               | 29                          | 67          | 54          | 15.8                               |
| 13      | Xylene               | 425                 | 13.8              | 64                          | 121         | 113         | 34.2                               |
| 14      | Xylene               | 375                 | 4.8               | 30                          | 118         | 125         | 21.0                               |
| 15      | Xylene               | 360                 | 13.8              | 37                          | 63          | 69          | 26.2                               |
| 16      | Water                | 425                 | 24.6              | 61                          | 112         | 127         | 43.2                               |
| 17      | n-Pentane            | 375                 | 13.8              | 41                          | 71          | 59          | 13.0                               |
| 18      | n-Pentane            | 375                 | 4.8               | 64                          | 114         | 119         | 11.8                               |
| 19      | Methanol             | 425                 | 13.8              | 25                          | 59          | 63          | 21.1                               |
| 20      | Methanol             | 375                 | 13.8              | 41                          | 71          | 62          | 12.1                               |
| 21      | Toluene <sup>2</sup> | 375                 | 4.8               | 66+                         |             |             | 12.1                               |

<sup>1</sup>Weight loss of dried coal (dry basis)<sup>2</sup>Run lasted 6 minutes

TABLE 14

## Amount of Extract Collected During Each Sampling Period

| Run No. <sup>1</sup> | Solvent   | Amount of extract collected<br>during the sampling period [g] |             |             | Relative fraction of extract<br>collected |             |             |
|----------------------|-----------|---------------------------------------------------------------|-------------|-------------|-------------------------------------------|-------------|-------------|
|                      |           | [0-15 min]                                                    | [15-45 min] | [45-75 min] | [0-15 min]                                | [15-45 min] | [45-75 min] |
| 1 <sup>2</sup>       | Toluene   | 1.9697                                                        | 0.3693      | 0.1231      | 0.80                                      | 0.15        | 0.05        |
| 2                    | Toluene   | 2.5627                                                        | 0.5809      | 0.2734      | 0.75                                      | 0.17        | 0.08        |
| 3                    | Toluene   | 2.2320                                                        | 0.4281      | 0.3975      | 0.73                                      | 0.14        | 0.13        |
| 5                    | Toluene   | 1.9079                                                        | 0.4088      | 0.4101      | 0.70                                      | 0.15        | 0.15        |
| 6                    | Toluene   | 1.6009                                                        | 0.4540      | 0.3345      | 0.67                                      | 0.19        | 0.14        |
| 7                    | Toluene   | 1.4912                                                        | 0.2577      | 0.2762      | 0.74                                      | 0.13        | 0.14        |
| 8                    | Toluene   | 1.2487                                                        | 0.3438      | 0.2172      | 0.69                                      | 0.19        | 0.12        |
| 9                    | Toluene   | 1.3165                                                        | 0.1984      | 0.2885      | 0.73                                      | 0.11        | 0.16        |
| 10                   | Toluene   | 1.3385                                                        | 0.4169      | 0.4388      | 0.61                                      | 0.19        | 0.20        |
| 11                   | Toluene   | 0.6761                                                        | 0.2272      | 0.2050      | 0.61                                      | 0.205       | 0.185       |
| 13                   | Xylene    | 2.5960                                                        | 0.4623      | 0.4979      | 0.73                                      | 0.13        | 0.14        |
| 14                   | Xylene    | 1.8168                                                        | 0.2952      | 0.1590      | 0.80                                      | 0.13        | 0.07        |
| 15                   | Xylene    | 1.9850                                                        | 0.3389      | 0.0968      | 0.82                                      | 0.14        | 0.04        |
| 16                   | Water     | 1.3607                                                        | 0.9293      | 1.0288      | 0.41                                      | 0.28        | 0.31        |
| 17                   | n-Pentane | 0.8499                                                        | 0.5377      | 0.3469      | 0.49                                      | 0.31        | 0.2         |
| 19                   | Methanol  | 0.7704                                                        | 0.2430      | 0.1755      | 0.65                                      | 0.20        | 0.15        |
| 20 <sup>2</sup>      | Methanol  | 0.2776                                                        | 0.1955      | 0.1577      | 0.44                                      | 0.31        | 0.25        |

<sup>1</sup>Extract is not fractionated for missing runs.

<sup>2</sup>Fractionation based on Soxhlet extractions.

tions with weaker solvents. The pyridine solubility of the char is much lower than that of original coal and increases with decreasing supercritical extraction solvent strength (Table 18).

#### 6.1.2 Analysis and Discussion of Results of High Temperature System

In this section, the data will be analyzed and a qualitative model for SCE will be developed. At first, accuracy of the data and the material balance closure will be studied. Then percent extraction results will be analyzed. The distribution of extract components were summarized in the previous section as Table 14 and Table 16. Their analysis will follow. In the analysis of extract fraction and their time distributions, statistical tools will be used. A review of the statistical tools and sample calculations are presented as Appendix F. Then residua and their characteristics will be studied. Finally, the summary of the analyses will be presented.

##### 6.1.2.1 Accuracy of Material Balance Results

The present practice by most other researchers is to measure percent extraction (weight loss of coal on dry basis) with very little concern for what happens to the extracted material. However, the material balance closure is very im-

TABLE 15

Comparison of Analyses from Soxhlet Extraction and  
Filtration Procedures

Run History

Temperature = 425 °C  
Pressure = 13.8 Mpa  
Solvent = Toluene

|              | <u>Soxhlet</u> | <u>Filtration</u> |
|--------------|----------------|-------------------|
| Run number   | 1              | 2                 |
| % Extraction | 31.0           | 31.8              |

Comparison

|            | <u>%<br/>Recovery</u> | <u>Asphaltols</u> | <u>Fraction<br/>Asphaltenes</u> | <u>Oils</u> |
|------------|-----------------------|-------------------|---------------------------------|-------------|
| Soxhlet    | 71                    | 0.28              | 0.39                            | 0.32        |
| Filtration | 91                    | 0.31              | 0.39                            | 0.30        |

TABLE 16

Extract Fractions Distribution for each Sampling Period

| Run # | Solvent   | Sampling Period |      |      |             |      |      |             |      |      |
|-------|-----------|-----------------|------|------|-------------|------|------|-------------|------|------|
|       |           | [0-15 min]      |      |      | [15-45 min] |      |      | [45-75 min] |      |      |
|       |           | A               | B    | C    | A           | B    | C    | A           | B    | C    |
| 1     | Toluene   | 0.26            | 0.41 | 0.33 | 0.39        | 0.32 | 0.29 | 0.42        | 0.30 | 0.28 |
| 2     | Toluene   | 0.27            | 0.42 | 0.31 | 0.40        | 0.31 | 0.29 | 0.49        | 0.27 | 0.23 |
| 3     | Toluene   | 0.27            | 0.45 | 0.28 | 0.42        | 0.32 | 0.26 | 0.37        | 0.31 | 0.31 |
| 5     | Toluene   | 0.22            | 0.45 | 0.32 | 0.42        | 0.30 | 0.27 | 0.35        | 0.23 | 0.42 |
| 6     | Toluene   | 0.20            | 0.42 | 0.38 | 0.44        | 0.29 | 0.26 | 0.56        | 0.26 | 0.18 |
| 7     | Toluene   | 0.38            | 0.34 | 0.28 | 0.51        | 0.27 | 0.21 | 0.54        | 0.28 | 0.28 |
| 8     | Toluene   | 0.36            | 0.34 | 0.29 | 0.63        | 0.21 | 0.16 | 0.39        | 0.29 | 0.32 |
| 9     | Toluene   | 0.41            | 0.34 | 0.24 | 0.57        | 0.24 | 0.19 | 0.51        | 0.27 | 0.22 |
| 10    | Toluene   | 0.38            | 0.34 | 0.28 | 0.48        | 0.28 | 0.24 | 0.42        | 0.27 | 0.31 |
| 11    | Toluene   | 0.37            | 0.38 | 0.25 | 0.41        | 0.29 | 0.30 | 0.40        | 0.22 | 0.29 |
| 13    | Xylene    | 0.36            | 0.40 | 0.24 | 0.62        | 0.22 | 0.16 | 0.59        | 0.22 | 0.19 |
| 14    | Xylene    | 0.48            | 0.32 | 0.19 | 0.61        | 0.25 | 0.14 | 0.62        | 0.26 | 0.12 |
| 15    | Xylene    | 0.46            | 0.38 | 0.16 | 0.59        | 0.23 | 0.18 | 0.63        | 0.23 | 0.14 |
| 16    | Water     | 0.17            | 0.41 | 0.42 | 0.44        | 0.26 | 0.29 | 0.35        | 0.32 | 0.33 |
| 17    | n-Pentane | 0.18            | 0.39 | 0.43 | 0.28        | 0.31 | 0.31 | 0.31        | 0.28 | 0.40 |
| 19    | Methanol  | 0.27            | 0.34 | 0.38 | 0.47        | 0.24 | 0.29 | 0.31        | 0.34 | 0.36 |
| 20    | Methanol  | 0.26            | 0.33 | 0.40 | 0.38        | 0.27 | 0.35 | 0.35        | 0.27 | 0.38 |

A = Asphaltols, B = Asphaltenes, C = Oils

TABLE 17  
Overall Material Balance

| Run No.         | Coal [Dry Basis] |       | Gas <sup>1</sup> | Extract | % Recovery |
|-----------------|------------------|-------|------------------|---------|------------|
|                 | IN               | OUT   |                  |         |            |
|                 | [g]              | [g]   | [g]              | [g]     |            |
| 1 <sup>2</sup>  | 14.48            | 9.99  | -                | 2.46    | 71         |
| 2               | 14.27            | 9.73  | -                | 3.42    | 91         |
| 3               | 14.38            | 10.14 | -                | 3.06    | 89         |
| 5               | 14.16            | 10.48 | .71              | 2.73    | 93         |
| 6               | 14.18            | 10.54 | -                | 2.39    | 85         |
| 7               | 14.16            | 11.46 | .57              | 1.84    | 89         |
| 8               | 14.28            | 11.60 | -                | 1.81    | 94         |
| 9               | 14.34            | 11.83 | .43              | 1.80    | 89         |
| 10              | 14.17            | 11.86 | -                | 2.20    | 95         |
| 11              | 14.21            | 11.91 | -                | 1.11    | 79         |
| 13              | 14.17            | 9.32  | .71              | 3.56    | 88         |
| 14              | 14.20            | 11.22 | .57              | 2.27    | 95         |
| 15              | 14.23            | 10.50 | -                | 2.42    | 84         |
| 16              | 14.17            | 8.05  | 1.70             | 3.32    | 82         |
| 17              | 14.19            | 12.35 | -                | 1.73    | 94         |
| 19              | 14.20            | 11.20 | .86              | 1.19    | 68         |
| 20 <sup>2</sup> | 14.21            | 12.49 | -                | 0.63    | 78         |

<sup>1</sup>Average gas molecular weight is taken as 30. For runs where there were no reliable gas data, 5% gas (by weight) was assumed.  
[Solvent vapor escaping with the noncondensables.]

<sup>2</sup>Extract analysis by Soxhlet Extraction.

TABLE 18  
Extraction Residua Analysis

| Run No. | Extraction Solvent | % Benzene Solubles | % Pyridine Solubles |
|---------|--------------------|--------------------|---------------------|
| 1       | Toluene            | .04                | 2                   |
| 2       | Toluene            | .13                | 3                   |
| 3       | Toluene            | -0.05              | 2.2                 |
| 5       | Toluene            | .21                | 3.2                 |
| 6       | Toluene            | -.32               | 1.7                 |
| 7       | Toluene            | .2                 | 2.7                 |
| 8       | Toluene            | .15                | 3.1                 |
| 9       | Toluene            | .17                | 4.1                 |
| 10      | Toluene            | .21                | 2.8                 |
| 11      | Toluene            | .1                 | 1.7                 |
| 13      | Xylene             | .1                 | 1.2                 |
| 14      | Xylene             | .2                 | 1.4                 |
| 15      | Xylene             | .1                 | 1.3                 |
| 16      | Water              | 1.0                | 5.1                 |
| 17      | n-Pentane          | .8                 | 4.7                 |
| 19      | Methanol           | 1.8                | 3.5                 |
| 20      | Methanol           | 1.5                | 4.1                 |

portant in validation of the experimental apparatus, experimental procedures and the analytical procedures. Furthermore, characteristics of the extract and its variation with processing conditions is of utmost importance for process development purposes. The overall material balance closure was shown as Table 17 in the previous subsection of this chapter.

Percent extraction can be measured by weighing the coal before and after an experiment. The possible sources of measurement error in percent extraction values were:

1. Spills or adhesion of coal to containers.

Spills were easy to visually observe, especially with the narrow mesh size used. Adhesion to the weighing paper were eliminated by reweighing the containers after the transfer of the coal to the extractor. Adhesion the extractor were minimized by ensuring a dry residue.

2. The accuracy of TGA readings which were used in determining the dry coal weight.

The moisture content of the coal was determined within  $\pm 0.5\%$  of the whole sample. Assuming that the errors were cumulative (i.e.  $\pm 0.005$  in initial coal sample and  $\pm 0.005$  in the final sample), this was roughly equivalent to  $\pm 1.0\%$  conversion. Any solvent

left within the coal residua did not present any loss of accuracy since they were detected as moisture during the TGA.

3. Sufficient time was allowed to the extract and the residua to cool prior to weighing.

More significant errors usually result as limitations of the experimental procedures and apparatus (system errors). As will be discussed later, temperature profile and time are two very significant parameters in SCE of coal at temperatures above 350°C. In the present set-up, the coal and the solvent were brought to extraction temperatures in two minutes. During this two minute period, neither solvent nor extract left the system since outlet (regulating) valve R<sub>2</sub> was closed. The possible error due to sedimentation in transfer lines and/or the outlet valve R<sub>2</sub> did not contribute to error in percent extraction directly, because percent extraction was measured by coal balance only. However, it probably contributed indirectly, because flow fluctuations from line or valve blockage affect the extraction process within the extractor.

In summary, percent extraction values are good within 1%. The conversion (percent extraction) in the replicated runs 1&2 (31.0% and 31.8%) and 11&12 (16.2% and 15.8%) support such a trend [See Table 13 for the values].

The tracking of the extracted material is a harder task since it involves lengthy post-run analytical work. This task becomes harder as the samples get smaller. The extract amounts collected during the initial periods were around 2 grams while the extract amounts collected in later periods sometimes were as low as 0.3 grams. Further fractionation of the extract into three fractions as asphaltols, asphaltenes, and oils involved multiple steps and many transfers of the extracts in various solvents. Thus, the accuracy of the extract component amounts are least for samples from the second and third periods. As could be seen from the sample calculations for extract fractionation, Appendix B.4, tare weight differences were not included in calculation of asphaltols and asphaltenes. These quantities were calculated from extracts collected during filtrations. Inclusion of tare weight differences into determination of these extract component amounts would have been misleading since they would have reflected the solvents dissolved in the extract and the solvent layer on the walls of the containers. More importantly, judgment on relative distribution of different extract components would have been necessary (e.g. How much of it is asphaltols as opposed to oils or asphaltenes ?). This judgment would have introduced bias. Furthermore, tare weight differences were usually less than 0.02 grams. Thus,

the omission of tare weight differences was not a major error source especially for samples where extract component amounts involved were higher than 0.2 grams. If tare weight differences were included, overall material balance closures would have been slightly higher than the presented 80+ %.

The originally planned method of extract fractionation method, sequence of Soxhlet extractions (Figure 22), was not reliable. Only very few runs were successfully analyzed using this procedure. The state of the vacuum pump and lack of a dry-box contributed to the lack of success in this area. More importantly, the nature of extract was also responsible for the unreliable analyses. Historically, a sequence of Soxhlet extractions were used on coal residua. However, extracts are not as dry. The particle size distribution and the character of the coal residua is different from extract. The comparison of the runs where extract fractionation by both methods were successfully completed, show that the relative fractions of extract components are comparable and the absolute extract amounts measured by filtration procedure were higher (See Table 15 for comparison).

The system errors due to the experimental set-up or operation result from extract precipitation in transfer lines and/or at the outlet valve. Although the transfer lines were kept as short as possible, the operating experience

showed that there was some temporary sedimentations around the outlet valve  $R_2$  during the initial periods. Furthermore, during sample changes, the flow through  $R_2$  was temporarily stopped for 1-2 minutes. These transient behaviours were averaged out in rather long sampling periods.

In summary, accuracy of extract component amounts and their time distributions were not as high as that of percent extraction. Most of the error was due to measurement error and the accuracy was least for samples collected in second and third periods. The system errors were not very high. They were highest during the initial sampling period.

The amount of non-condensable gases were measured during each run with a wet test meter. As could be seen from Table 17, in most of the runs there is no gas data reported. During these runs, flow fluctuations resulted in surges, through the collectors immersed in a water bath, and solvent vapor escaped through the wet test meter. A second but minor system error resulted from the transient behaviour and lag caused by the temporary shut-offs during collector changes. In converting the measured gas amounts from cubic feet to grams, an average gas molecular weight of 30 was assumed (For Sample calculations see Appendix B.8). During SCE with water a higher amount of gas was measured. This, in part, was due to the severe extraction conditions ( $425^{\circ}\text{C}$ ,

24.6 MPa). The data collected on gas amounts was not very reliable.

An overall material balance closure over eighty percent is gratifying and all but gas amount measurements are accurate enough to warrant their further analysis.

#### 6.1.2.2 Analysis of Effects of Design Parameters on Supercritical Extraction

Factorial designs were used to study the mechanism of SCE with toluene. In this subsection, implications and interpretation of these results will be given. However, the reader can find a review of the techniques involved in Appendix E. Appendix E is structured as follows:

1. Why factorial designs are chosen over other experimental designs ? (Appendix E.1)
2. Calculation of main effects of parameters (Appendix E.2)
3. Calculation of interaction effects (Appendix E.3)
4. Quicker methods of calculating the effects, Yates Algorithm (Appendix E.4)
5. Calculation of standard deviation of factorial designs (Appendix E.5)
6. Diagnostic checks (Appendix E.6)

Table 19 summarizes the effect analysis for percent extraction of dried coal with toluene. The parameters were

temperature (T), pressure (P), and toluene flow rate (Q) while the measured response was percent extraction (y). The level of experimental design which resulted in less severe extraction conditions was denoted "-" while the higher severity level for each parameter was denoted as "+". For example, T=375°C was "-" while T=425°C was "+".

The average percent extraction for the study was 22.85. If we convert the analysis into an empirical model, percent extraction (y) can be given at the vertices of design by

$$y = 22.85 + (10.6/2)T + (3.7/2)P + (0.9/2)TP + (0.7/2)Q + (0.4/2)(TQ+PQ+TPQ) \quad \text{Eq. 6.1}$$

where all the independent parameters take the values of -1 or +1. Notice that the coefficients that appear in Eq. 6.1 are half of the calculated effects. This is because, a change from x=-1 to x=+1 is a change of two units along the x-axis. The occurrence of cross product terms in this expression suggest that quadratic terms (e.g. T<sup>2</sup>) might be needed in a model which adequately represented the percent extraction at interpolated levels of the variables. Such terms can not be estimated using two-level designs and require more sophisticated experimental designs. Since our purpose was a rather qualitative description, such experi-

Table 19

Effect Analysis for Percent Extraction of Dried Coal With Toluene

Legend

| Variable              | -   | +    |
|-----------------------|-----|------|
| Temperature [°C]      | 375 | 425  |
| Pressure [MPa]        | 4.8 | 13.8 |
| Toluene rate [ml/min] | 2.2 | 4.1  |

Analysis

| T | P | Q | % Extraction | Effect  | Estimate |
|---|---|---|--------------|---------|----------|
| - | - | - | 16.0         | Average | 22.85    |
| + | - | - | 25.7         | T       | 10.6     |
| - | + | - | 18.8         | P       | 3.7      |
| + | + | - | 29.5         | TP      | 0.9      |
| - | - | + | 16.3         | Q       | 0.7      |
| + | - | + | 26.0         | TQ      | 0.4      |
| - | + | + | 19.1         | PQ      | 0.4      |
| + | + | + | 31.4         | TPQ     | 0.4      |

mental designs were not necessary. The effect analysis results incorporate experimental error (noise) and diagnostic checks, such as the one described in Appendix E.6, are necessary to detect such noise. The effects of temperature (T), pressure (P), flow rate (Q) and the temperature-pressure interaction are attributable to noise. They have meaningful contributions to percent extraction.

The parameter which affected the percent extraction most was temperature. The effect of temperature on conversion is positive, 10.6, meaning that conversion increases significantly when extraction temperature is raised from 375°C to 425°C. Percent extraction is on average 17.5 for 375°C and 28.1 for 425°C (average conversion was 22.85). As temperature increased, extraction severity (i.e. rate of coal reactions) increased resulting in a higher fraction of extractable material.

The increase in percent extraction with increase in pressure was primarily due to the increase in solvency power of toluene. For a given temperature, as pressure increases solvency power increases. For example, at 425°C and 4.8 Mpa, the density ( $\rho$ ) of toluene is 0.1 g/cc. and the Hildebrand solubility parameter ( $\xi$ ) is  $1.05 \text{ (cal/cc)}^{1/2}$ . However, at the same temperature but 13.8 MPa,  $\rho$  is 0.39 while  $\xi$  is 4.0. As a result, percent extraction increased from 26% to 31.4% (31.4% is average of two replicated runs). A strong

solvent is required to extract decomposition products as they are formed so that the amount of extractable material does not decrease because of repolymerization. Furthermore, as pressure increases extraction severity increases and also more of the smaller pores becomes accessible.

The analysis of temperature-pressure interaction is important in understanding SCE of coal. The interaction is due to the following phenomena:

1. For a given pressure, solvency power of the solvent is higher at lower temperatures which are closer to the critical temperature of the solvent. For example, at 13.8 MPa and 425°C,  $\xi$  is 4.0 (cal/cc)<sup>1/2</sup> while at 375 °C and same pressure  $\xi$  is 4.82. Near critical pressure, the solubility decreases as supercritical temperatures are increased. The rate of this solvency power decrease, with increases in temperature of the solvent, decreases at higher pressures (See Figure 4). This phenomenon results in negative interaction.
2. At a given temperature, reaction rates are higher at higher pressures and a higher fraction of pores are accessible. The effect is positive interaction.

The effect of second interaction is more dominant in analysis of percent extraction since it is 0.9.

The solvent flow rate,  $Q$ , was included as the third parameter. However, solvent-to-coal ratio was the intended parameter. Since the experimental set-up was semi-continuous, the coal batch size was fixed at approximately 15 grams. Then, the solvent flow rate is directly indicative of the solvent-to-coal ratio. The solvent flow rate of 2.2 cc/min is equivalent to a ratio of 2.5 (solvent-to-coal ratio in weight basis) for the initial 15 minute period. The solvent-to-coal ratio for the second flow rate level, 4.1 cc/min., is about 5. Both of these solvent-to-coal ratios are rather high. Experimental difficulties due to valve clogging from precipitated extract resulted in high solvent-to-coal ratios. The slight increase of percent extraction as flow rate (equivalently solvent-to-coal ratio) increased was not surprising since there was more solvent available to extract the decomposed coal products. However, the magnitude of this increase was low because both of the flow rates were high.

Very often, significance of solvent is not reflected accurately if only percent extraction is studied. If the decomposition products are not extracted, the thermally ruptured bonds get capped by recombination to other products and this is reflected in percent extraction. However, there are also progressive reactions yielding smaller products

which can be extracted in later times when there is more solvent or when they are small enough to solubilize in the solvent. It is this second phenomenon that can not be easily seen from percent extraction results. Based on the analyses of extract fractions and their time distributions, role of the solvent can be understood better. Thus, highly nonlinear behaviour of responses (i.e relative amounts of asphaltols, asphaltenes and oils and their variation with time) in SCE were studied using four  $2^4$  designs. The parameters for the analyses were temperature (T), pressure (P), toluene flow rate (Q) (more correctly solvent to coal ratio), and time ( $\Delta t$ ). Since samples were averages for the time periods they are collected in, time had to be introduced into analysis in a rather unique fashion. The first period, from start to fifteenth minute, was assigned "-" while the second period, fifteenth to forty-fifth minute, was denoted as "+". The legend used in these four factorial designs are shown in Table 20. Results of the third period are very similar to that of second and are thus excluded. The responses used in the analyses were fractional extraction completion in each period and relative fractions of asphaltols asphaltenes, and oils. A separate  $2^4$  design was used for each response. First fractional extraction completion will be studied.

TABLE 20

Nomenclature Used in the Effect Analysis of Fractional Extraction  
Completion and Extract Component Distribution

| Variable                | -    | +     |
|-------------------------|------|-------|
| Temperature [°C]        | 375  | 425   |
| Pressure [MPa]          | 4.8  | 13.8  |
| Toluene Rate [ml/min.]  | 2.2  | 4.1   |
| $\Delta$ time (minutes) | 0-15 | 15-45 |

The study on fraction of extraction completion for the first two periods is summarized in Table 21. The parameters (i.e. T, P, Q, and  $\Delta t$ ), and the responses are shown in standard  $2^4$  design order. The standard deviation of the effects are calculated from third and fourth order interactions. A sample calculation for standard deviation estimation is shown in Appendix E.5. One very significant point to realize in interpretation of the effects is that every response, fractional extraction completions ( $y$ ), is dependent to one other response. For example, 9<sup>th</sup> response is 0.205 and it is dependent on the 1<sup>st</sup> response which is 0.61. They are dependent, because what happens in the second period is, in part, dictatated by the first period. The highly nonlinear time interactions are, in part, generated from this dependence among responses, but mostly it is due to fast nonlinear kinetics of the first period which is coupled with solubility relations. Once again, it is important to remember that 2-level factorial designs can do no more than show existing trends. This dependence also results in strong time interactions with less physical meaning. For example, rather significant effect of  $TP\Delta t$  is attributed to this dependence.

Time is the parameter that effects the fractional extraction completion most. The effect of time is -0.54. Thus,

TABLE 21

## Effect Analysis For Fractional Extraction Completion

| No. | T | P | Q | $\Delta t$ | Fractional<br>Extraction | Effect        | Estimate |
|-----|---|---|---|------------|--------------------------|---------------|----------|
| 1   | - | - | - | -          | 0.61                     | Average       | 0.435    |
| 2   | + | - | - | -          | 0.67                     | T             | 0.084    |
| 3   | - | + | - | -          | 0.69                     | P             | 0.04     |
| 4   | + | + | - | -          | 0.73                     | TP            | -0.13    |
| 5   | - | - | + | -          | 0.61                     | Q             | -0.02    |
| 6   | + | - | + | -          | 0.70                     | TQ            | 0.11     |
| 7   | - | + | + | -          | 0.81                     | PQ            | 0.024    |
| 8   | + | + | + | -          | 0.80                     | TPQ           | 0.10     |
| 9   | - | - | - | +          | 0.205                    | $\Delta t$    | -0.54    |
| 10  | + | - | - | +          | 0.19                     | $T\Delta t$   | -0.14    |
| 11  | - | + | - | +          | 0.19                     | $P\Delta t$   | -0.08    |
| 12  | + | + | - | +          | 0.14                     | $TP\Delta t$  | 0.13     |
| 13  | - | - | + | +          | 0.19                     | $Q\Delta t$   | 0.03     |
| 14  | + | - | + | +          | 0.15                     | $TQ\Delta t$  | 0.07     |
| 15  | - | + | + | +          | 0.14                     | $PQ\Delta t$  | 0.02     |
| 16  | + | + | + | +          | 0.15                     | $TPQ\Delta t$ | 0.13     |

Average Fractional Extraction Completion =  $0.435 \pm 0.05$

Standard Deviation of Effects =  $\pm 0.1$

(Computed from Higher-Order Interactions)

the average fractional extraction completion for each period are

$$y_{\Delta t_1} = 0.435 + 0.54/2 = 0.705 \quad \text{Eq. 6.2}$$

$$y_{\Delta t_2} = 0.435 - 0.54/2 = 0.165 \quad \text{Eq. 6.3}$$

This sharp decrease in the amount extracted in the second period was because there was little left to be extracted.

The interactive TP effect is negative, -0.13. As discussed in the analysis of percent extraction results, there are two opposing effects that determine temperature-pressure (TP) interactions. Positive one is due to reaction kinetics while the negative one is due to solubility relations. In responses which reflect the role of solvent more, as opposed to extraction severity, negative temperature-pressure interactions are to be expected. In the effect analysis of fractional extraction completion, temperature-pressure interaction was negative. The temperature-pressure interaction is negative because solvent can't keep extracting as fast and/or as much and/or as large molecules at higher temperatures. A similar reasoning can account for the significantly negative temperature-flow rate (TQ) interaction, -0.11. The flow rate has to be higher at higher temperatures since

1. There is more to be extracted due to the severity of reactions
2. The solvency power of the solvents are less at higher temperatures.

Table 22 summarizes three analyses on relative extract component distributions. Since there is no dependence between the responses within the analysis (e.g. asphaltols fraction in run number 3 is independent of all other run number asphaltols fractions), unlike the responses in fractional extraction completion, a more comprehensible analysis can be made. Although the responses are independent within the same analysis, they are dependent to each other since

$$Y_{\text{asphaltols}} + Y_{\text{asphaltenes}} + Y_{\text{oils}} = 1.0 \quad \text{Eq. 6.4.}$$

By far the most important parameters which affect the relative fraction of extract components are time and temperature. The effect of pressure and the temperature-pressure effect are significant in asphaltols content. The effects of other parameters are within the standard deviation of the effects. The standard deviations are calculated from higher order interactions and the calculation of standard deviation for effect analysis of asphaltols content is included in Appendix E.5 as sample calculation. Furthermore, diagnostic checks support these findings. Diagnostic check for the asphaltols content is shown in Appendix E.6 as a sample.

TABLE 22

Effect Analysis of Extract Component Distribution

| No.   | Effect        | Asphalts |          | Asphaltenes |          | Oils     |          |
|-------|---------------|----------|----------|-------------|----------|----------|----------|
|       |               | Fraction | Estimate | Fraction    | Estimate | Fraction | Estimate |
| 1     | Average       | 0.37     | 0.38     | 0.38        | 0.34     | 0.25     | 0.27     |
| 2     | T             | 0.20     | -0.11    | 0.42        | 0.06     | 0.38     | 0.05     |
| 3     | P             | 0.36     | 0.04     | 0.34        | 0.01     | 0.29     | -0.02    |
| 4     | TP            | 0.27     | -0.04    | 0.45        | 0.02     | 0.28     | 0.01     |
| 5     | Q             | 0.38     | -0.01    | 0.34        | ~0       | 0.28     | ~0       |
| 6     | TQ            | 0.22     | ~0       | 0.45        | ~0       | 0.32     | ~0       |
| 7     | PQ            | 0.38     | -0.03    | 0.34        | ~0       | 0.28     | 0.02     |
| 8     | TPQ           | 0.265    | -0.04    | 0.415       | -0.02    | 0.32     | 0.01     |
| 9     | $\Delta t$    | 0.41     | 0.16     | 0.29        | -0.11    | 0.30     | -0.05    |
| 10    | $T\Delta t$   | 0.44     | 0.02     | 0.29        | -0.02    | 0.26     | ~0       |
| 11    | $P\Delta t$   | 0.63     | 0.01     | 0.21        | 0.01     | 0.16     | -0.01    |
| 12    | $TP\Delta t$  | 0.42     | -0.03    | 0.32        | 0.01     | 0.26     | 0.04     |
| 13    | $Q\Delta t$   | 0.48     | -0.02    | 0.28        | 0.01     | 0.24     | ~0       |
| 14    | $TQ\Delta t$  | 0.42     | ~0       | 0.3         | -0.01    | 0.27     | 0.01     |
| 15    | $PQ\Delta t$  | 0.51     | -0.02    | 0.27        | 0.01     | 0.21     | 0.01     |
| 16    | $TPQ\Delta t$ | 0.39     | ~0       | 0.32        | ~0       | 0.29     | -0.03    |
| $S_d$ |               |          | 0.024    |             | 0.011    |          | 0.024    |

The effect of time period on asphaltols fraction is positive (0.16). It means that the asphaltols fraction of the sample changes significantly between the first and the second period. That is, the asphaltols fraction, is on average 0.30 for the first period and 0.46 for the second (average asphaltols fraction of the whole 16 responses was 0.38). This increase in the asphaltols content occurs at expense of asphaltenes and oils. This result supports the hypothesis that the during the initial period solvent can't keep up with the rate of extractable material generation and extract degradation occurs. The effect of time on asphaltenes fraction was -0.11 while the effect on oils fraction was -0.05. Thus the asphaltols fraction increase in the later periods results mainly at expense of asphaltenes fraction.

The study of temperature effects show a reverse trend. As temperature increases the asphaltols content of the extract decreases creating more oils and asphaltenes. The asphaltols fraction of extract changes from an average of 0.38 to 0.35 at 375°C and to 0.325 at 425°C. This decrease in asphaltols content with temperature increases is due to following reasons:

1. At higher temperatures, the decomposition rates are higher and increase the rate of asphaltols consumption.

2. Solvent is less effective and can not extract as much and as large molecules as at lower extraction temperatures which were closer to solvent critical temperature. Hence, asphaltols stay in the extractor longer either repolymerizing or decomposing into smaller molecules. These smaller molecules get extracted later whenever the solvent is strong enough to solubilize them.

This decrease in asphaltols fraction result in about equal increases of oils (0.05) and asphaltenes (0.06) fractions. The asphaltols fraction increase with pressure (0.04) and a negative (-0.04) temperature-pressure interaction show that higher asphaltols content are to be expected with stronger solvents.

#### 6.1.2.3 Comparison of SCE Results for Different Solvent Strengths

If the analyses made on factorial designs on supercritical extractions with toluene are extended to other solvents, factorial designs can not be used. However, an analysis can be made if supercritical extractions were categorized according to solvent strength as:

1. Supercritical extraction with strong solvents ( $\xi \geq 4.0 \text{ (cal/cc)}^{1/2}$ )

## 2. Supercritical extraction with poor solvents ( $\xi \leq 2.0$ (cal/cc)<sup>1/2</sup>)

The average values of extract components and their distribution for each group of solvents are shown in Table 23. With stronger solvents extraction is faster and larger molecules can be extracted. However, even with good solvents average asphaltols fraction, 0.35, for the first period is less than the average in second period, 0.52. This is most probably due to product degradation during the initial minutes. The extract component distributions in the second and third periods are about same for a solvent. Furthermore, different solvents have different relative extract fractions (e.g. average asphaltols fraction with strong solvents in second period is 0.53 while with weak solvents, it is 0.43). These two observations suggest that all the material which becomes small enough to be extracted gets extracted in the vast amount of solvent in late periods.

### 6.1.2.4 Residua Analysis

The coal residua from extraction was analyzed with TGA for determination of volatile content. The volatiles content ranged from fifteen to twenty-five percent of residua char depending on percent extraction. This may be due to inaccessibility of certain fraction of volatiles which were trapped in blind micropores.

TABLE 23  
Time Distributions of Average Extract and Extraction Fractions  
for Two Solubility Ranges

|               | $\xi_g \geq 4 \left( \frac{\text{cal}}{\text{cm}^3} \right)^{\frac{1}{2}}$ |                 |                 | $\xi_g \leq 2 \left( \frac{\text{cal}}{\text{cm}^3} \right)^{\frac{1}{2}}$ |                 |                 |
|---------------|----------------------------------------------------------------------------|-----------------|-----------------|----------------------------------------------------------------------------|-----------------|-----------------|
| Period        | [0-15 min]                                                                 | [15-45 min]     | [45-75 min]     | [0-15 min]                                                                 | [15-45 min]     | [45-75 min]     |
| Fraction A    | 0.35 $\pm$ 0.06                                                            | 0.52 $\pm$ 0.08 | 0.49 $\pm$ 0.08 | 0.28 $\pm$ 0.08                                                            | 0.43 $\pm$ 0.04 | 0.4 $\pm$ 0.09  |
| Fraction B    | 0.39 $\pm$ 0.04                                                            | 0.27 $\pm$ 0.04 | 0.27 $\pm$ 0.03 | 0.38 $\pm$ 0.05                                                            | 0.28 $\pm$ 0.02 | 0.27 $\pm$ 0.04 |
| Fraction C    | 0.27 $\pm$ 0.04                                                            | 0.22 $\pm$ 0.05 | 0.25 $\pm$ 0.05 | 0.34 $\pm$ 0.06                                                            | 0.29 $\pm$ 0.04 | 0.32 $\pm$ 0.09 |
| T.E. Fraction | 0.75 $\pm$ 0.04                                                            | 0.15 $\pm$ 0.02 | 0.11 $\pm$ 0.04 | 0.61 $\pm$ 0.10                                                            | 0.21 $\pm$ 0.06 | 0.18 $\pm$ 0.04 |

Fraction A = Average Asphaltols fraction of the extract for the sampling period

Fraction B = Average Asphaltenes fraction of the extract for the sampling period

Fraction C = Average Oils fraction of the extract for the sampling period

T.E. Fraction = Average Total Extract fraction

All Values are within 95% Confidence Limits

The residua was also subjected to sequential Soxhlet extractions with benzene and pyridine respectively to determine whether or not any extractable material was left in residua char. The results of residua fractionation showed that very little benzene-soluble matter existed in extracted coal samples. Benzene-soluble matter was left only in chars from supercritical extractions with weaker solvents. The pyridine solubility of the char is much lower than that of original coal and increases with decreasing supercritical extraction solvent strength (Table 18).

Another desirable property of the solvent is its accessibility to fine pores. It is also important to keep the porous structure intact after the extraction. The pore volume distribution and surface area determinations are necessary to study the porous structure. However, electron scanning microscope studies enable us to comment qualitatively. Three SCE residua samples and a raw coal sample were studied using electron scanning microscope. The micrographs shown in Figure 25 are for enlargement of 5000 times. The four pictures in the figure correspond to the following samples :

1. Above left: Dried raw coal.
2. Above right : Toluene extracted at 425°C and 4.8 MPa.
3. Below left : Xylene extracted at 360°C and 13.8°C.
4. Below right : Water extracted at 425°C and 24.6 MPa.

The magnifications enable us to comment on the surface rather than the micropores. The enlargements enable us to see above 500 A. The pictures of the residua from toluene and xylene extracts show cleaner surfaces than that of water extraction residua and raw coal. The surface of the coal extracted with water is most interesting. It seems that residua surface is destroyed by high pressures as well as high temperatures.

#### 6.1.2.5 Summary of Analyses on SCE at High Temperatures

In the previous section, the effects of parameters on SCE was studied. Each of the three responses, by design, emphasized a different aspect of SCE mechanism. Percent extraction showed the overall trend. Fractional extraction completion emphasized the interactive effects of kinetics vs. solubility. Solubility considerations were studied through component distributions.

The conversion (percent extraction) was affected by extraction condition severity most. This was true even if the solvent may not be as strong at such conditions. The effect of reaction severity was more dominant in the initial periods of extraction. Thus, a significant fraction of coal, mainly volatiles, is converted to asphaltols, asphaltenes, and oils during the initial period of exposure to high temperatures. Then, these unstable products are either solubi-

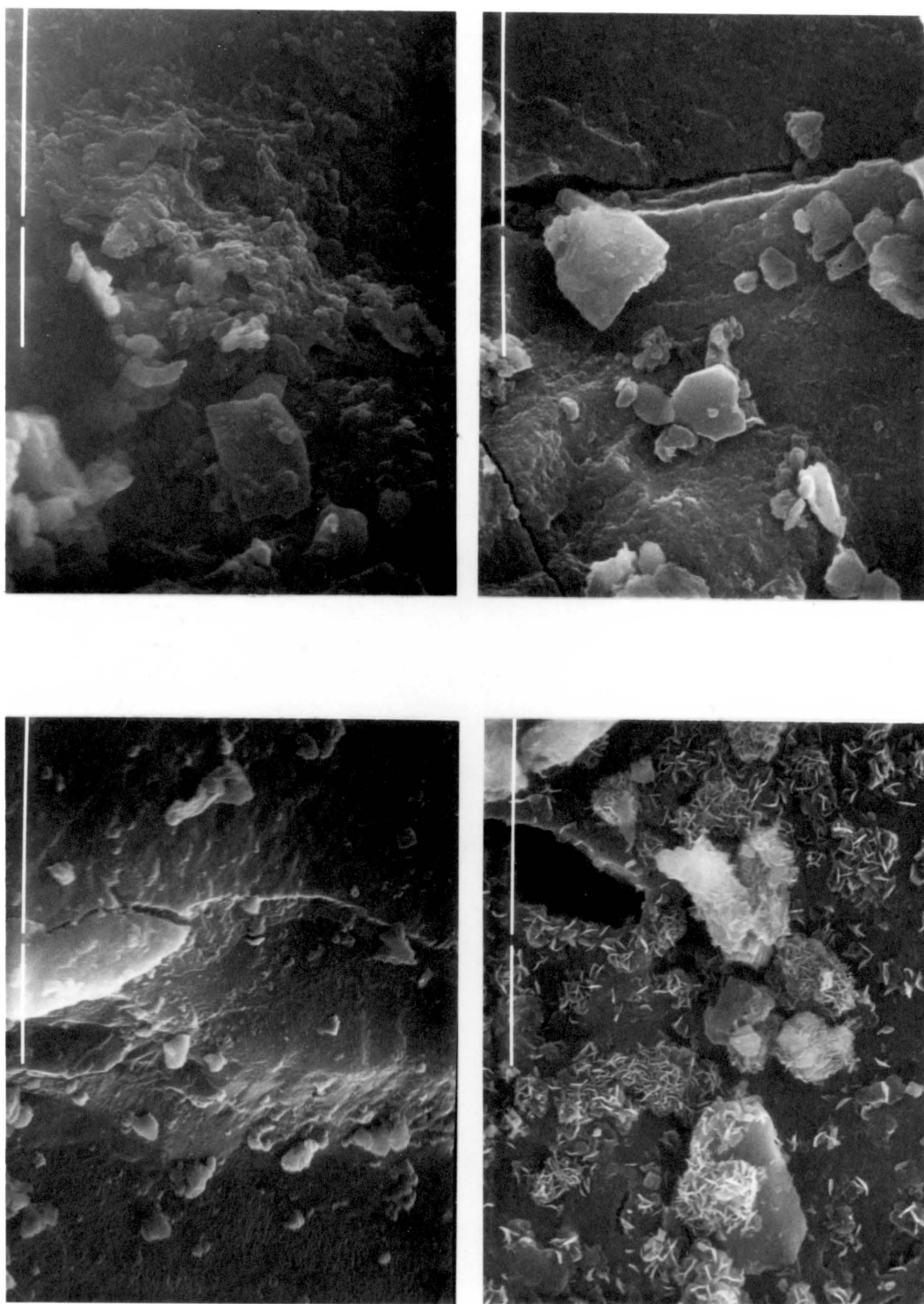


Figure 25: Micrographs of Dried Raw Coal and Residua from Extractions with Supercritical Solvents

lized or react at slower rate than that of initial decomposition reactions. The products from these slower reactions are smaller molecular weight compounds and repolymerization products, e.g. semi-coke. The smaller compounds can get extracted later as the solvent becomes abundant and/or as they become small enough to solubilize. The fate of repolymerization products is not known. Since extraction continues even after the initial forty-five minutes, it is possible that the repolymerization products can contribute to extract amount by re-decomposing in a later time. There is a second reason to avoid repolymerization. Repolymerization products can blind some of the smaller pores trapping the otherwise extractable material.

Strong solvents are needed in order to reduce the extraction time, decrease the amount of solvent used, and minimize repolymerization and degradation. Excessive product degradation is believed to increase the gas formation. However, such a trend was not observed, except in extractions with water, because of unreliable gas data.

Because of the strong response to reaction conditions, if maximization of the percent extraction is the objective, provided that other parameters are same (e.g. solvent cost, recoverability), the extraction conditions dictate the solvent selection.

## 6.2 SCE WITH THE LOW TEMPERATURE SYSTEM

Coal and heat-pretreated coals were extracted at near ambient temperatures using supercritical carbon dioxide. About 0.43 standard cubic meter of carbon dioxide was passed continuously through the extractor which was packed with approximately 15 grams of coal. One experimental run took approximately 90 minutes. Since relatively small amounts were extracted, percent extraction was defined as the weight loss of solute (coal or heat treated coal) on dry basis. Some samples were heated in a mini-autoclave at 400°C for 1 hour. After the heat-pretreatment, the quenched, vented, and weighed samples were extracted with supercritical carbon dioxide.

Near ambient temperatures, coal and heat-pretreated coals are not extractable with supercritical carbon dioxide. Although there are low molecular weight components in coal, their amount and extractability with supercritical solvents are limited. This limitation may be due to following reasons:

1. The components are so large that they are insoluble in carbon dioxide. The solubility of a component in a supercritical gas is given by Eq.2.20. The low ideal gas solubility which is due to the low vapor pressure of compound is enhanced by the non-ideal forces. The non-ideal part of Eq.2.20 is the reci-

procal of the fugacity coefficient of low volatile component in the "compressed gas" phase. The ideal solubility of coal components is a function of the vapor pressure of its components. If these ideal solubilities are several orders of magnitude lower than the enhancement due to non-ideal forces, the solubility of coal components will be negligible.

2. The low molecular weight coal components are dispersed in the coal pores and are attached to the coal matrix with physical forces. These physical forces are due to van der Waals forces or hydrogen bonding. The solvent should have enough activation energy to overcome these physical forces in order to solubilize low molecular weight components.

Liquid entrainer-aided supercritical extraction of coal and heat-pretreated coal were also studied. Weighed amounts of solute (coal or heat-pretreated coal) and entrainer were added into the extractor in three or four alternating batches. Then, they were extracted as in extractions with no entrainer. The results of these extractions are summarized in Table 24. The following observations were made:

1. Since the error band in TGA readings used in determining the dry weight of coal is equivalent to approximately 1% conversion, it may be concluded that

water does not aid the supercritical extraction of coal.

2. Both toluene and tetralin aid in SCE of coal with carbon dioxide.
3. If coal is treated at high temperatures, 400 °C, for a hour, the percent entrainer-aided extraction improves significantly. In part the improved extraction is due to thermosolvolyysis discussed in Chapter IV. Some of the covalent bonds are broken during the heat treatment and more extractable components than nontreated coals are available for extraction.
4. Strong solvents which are usually classified with respect to their electron donor and electron acceptor numbers have traditionally been found effective in extracting coal at low temperatures. Pyridine is such a solvent and was used as an entrainer. Even at a modest entrainer-to-coal mass ratio of 1/5, pyridine extracted 11.7%. Amount extracted was approximately equal to the amount extracted in Soxhlet extraction with pyridine. However, about 10% of the initial pyridine was unrecovered from the coal.

Although the yields from entrainer-aided supercritical extractions at low temperatures are not very significant, the potential implications are exciting. One of the most

encouraging observations was that the entrainer was completely extracted from coal along with the extract within 10 minutes and the extraction of coal ceased as entrainer depleted. The percent extractions were approximately equal to the amount extractable via Soxhlet extractions. Even if extraction yields do not improve with a continuous supply of entrainer, the supercritical gas ensures near complete recovery of the liquid entrainer. Thus low temperature liquid extraction processes which were not possible due to solvent recovery problem are now possible. Furthermore, if a particular temperature is not suitable, the extraction temperature can be increased. Different supercritical solvents are necessary for different extraction temperature ranges. This is due to the fact that supercritical solvents are more effective near their critical temperatures.

TABLE 24

The Summary of Extractions with the Low Temperature System

| Run # | Entrainer            | Entrainer/coal<br>[mass ratio] | T<br>[°C] | % Weight Loss of Coal<br>[dry basis] <sup>1</sup> |
|-------|----------------------|--------------------------------|-----------|---------------------------------------------------|
| 1     | Water                | 1/2                            | 90        | 1.7                                               |
| 2     | Water                | 1/2                            | 50        | -0.2                                              |
| 3     | Water                | 1/5                            | 90        | 1.1                                               |
| 4     | Water                | 1/5                            | 50        | 1.8                                               |
| 5     | Toluene              | 1/2                            | 90        | 3.2                                               |
| 6     | Toluene              | 1/2                            | 50        | 3.1                                               |
| 7     | Toluene              | 1/5                            | 90        | 1.9                                               |
| 8     | Toluene              | 1/5                            | 50        | 3.4                                               |
| 9     | Tetralin             | 1/2                            | 90        | 4.3                                               |
| 10    | Tetralin             | 1/2                            | 50        | 3.44                                              |
| 11    | Tetralin             | 1/5                            | 90        | 2.0                                               |
| 12    | Tetralin             | 1/5                            | 50        | 1.9                                               |
| 13    | Pyridine             | 1/2                            | 50        | 11.7                                              |
| 14    | Toluene <sup>2</sup> | 1/5                            | 75        | 7.6                                               |
| 15    | Toluene <sup>2</sup> | 1/2                            | 75        | 9.8                                               |

Other parameters:

$P = 10.4 \pm .5 \text{ MPa}$       Solvent =  $\text{CO}_2$        $Q_{\text{CO}_2} = 0.43 \text{ STD m}^3$

Extraction Time =  $90 \pm 15$  minutes

<sup>1</sup>TGA reading accuracy equivalent to  $\pm 1.0\%$  conversion

<sup>2</sup>Dried Coal Heat pretreated at  $400^\circ\text{C}$  for 1 hour.

## Chapter VII

### PROCESS DESIGN AND ECONOMIC CONSIDERATIONS OF SCE OF COAL

Capital requirements and operating expenses for synthetic fuels are much higher than that of fuels from crude oil and natural gas. Crude oil prices are determined by OPEC policies and reflect the market conditions. Crude prices are at least an of order magnitude higher than the production costs. The synfuel prices are a complex function of crude prices and unless crude oil reserves rapidly deplete, an economic displacement of crude oil or natural gas by synthetic fuels is highly unlikely. However, since development of a reliable process will involve years, research and development and possibly commercialization of promising synfuel conversion processes will keep oil prices from rapidly escalating. Furthermore, development of combustion equipment and engines which use synfuels is only possible as synfuels become available. Thus, synfuels and/or chemicals from coal should be explored, but in a competent manner. The commercialization efforts of chemicals or fuels from coal will be slow and they will be limited to special cases in the near future. These efforts and choice of conversion technology will be determined by infrastructure demand as well as factors such as cost, efficiency, and pollution potential.

In this chapter, process design alternatives for supercritical gas extraction (SGE) will be explored. The technical and economic feasibility of SGE will be compared with other alternative processing routes.

### 7.1 METHOD OF ECONOMIC ANALYSIS

Economic projections are usually the most important and final criteria in selecting among alternative processes. The accuracy and reliability of these projections often depend on factors beyond the control of the estimator. Hence cost analysis typically begins while a process is at bench scale and is continually revised and refined throughout development.

The method of economic comparison used in this thesis is the method developed by Engineering Societies Commission On Energy Inc. (ESCOE). The costing guidelines and recommended parameters are set forth in an ESCOE report [96]. The method is applied to coal conversion processes in another report [97]. The ESCOE method uses both private and utility financing with then-current money units and a product value technique as opposed to cost per unit energy basis. The product value technique assumes constant ratio product prices with respect to each other throughout the project life. Since all production costs must be recovered, the sum of all

product sales in a particular time period must equal all costs plus profit attributed to that time period. Thus

$$\sum P_i B_i = F + M + kC \quad \text{Eq. 7.1}$$

where

$P_i$  = Individual product price in \$/Million BTU

$B_i$  = Annual production for product i in Million BTU.

$F$  = Annual coal cost in \$.

$M$  = Total annual cost for labor and all other operating expenses in \$

$k$  = Capital factor which allows for all interest, taxes, profit, and recovery of capital investment.

$C$  = Total capital invested for the project in \$.

For each individual product, the value factor,  $f$ , is defined as:

$$f_i = P_i / P_R \quad \text{Eq. 7.2}$$

where

$P_R$  = The price of the reference product.

Therefore,

$$P_R = (F + M + kC) / (\sum f_i B_i) \quad \text{Eq. 7.3}$$

Thus, the necessary market price for the reference product,  $P_R$ , can be obtained from Eq. 7.3 using the  $f_i$  values calculated from the existing market conditions. Then, the prices

for each product of the process can be computed through Eq. 7.2. A sample calculation which illustrates the procedure is in Appendix H.

Although, ESCOE method combines efficiency of practical cost estimation methods with more elaborate capital recovery factor estimation techniques, it has serious drawbacks. Some of the more important disadvantages of ESCOE's, method are:

1. Whenever then-current money is used inflation discounting has to be used as well. Otherwise the resulting capital recovery factors are unrealistically small and the capital costs are very much under weighted. This introduces a major bias if the capital cost of projects compared are very dissimilar. Although the procedure presented is traditionally used by the utilities, the synfuel processes are very different and the use of low capital factors is dangerously misleading. Capital recovery factors around .24 are more realistic than the proposed capital factors of 0.08-0.12.
2. Different processes have different features i.e. different coal feeds, different process complexity, different economic plant sizes, and a forced common base introduces bias in itself.

3. Constant  $f_i$ , the value factor, is unrealistic. Since 1978 (time the ESCOE analysis was done), the price of liquid fuels tripled while the solid fuel prices (i.e. coal price) were nearly constant. Implication of this assumption is that analysis based on this assumption will tend to favor projects with low value solid products.

In summary, the ESCOE method has positive bias for projects which use expensive feed and which are capital intensive. Fortunately, most capital intensive synfuel projects are the ones which produce more higher value products and some of the biases are counter balanced.

#### 7.1.1 Implementation of ESCOE method

The ESCOE method, described in the previous section, is implemented and updated to November 1981 in the following manner:

1. The desired value of products based on the reference product (premium gasoline) are calculated for three capital recovery factors; 0.08, 0.16, 0.24
2. All value factors,  $f_i$ , are updated to November 1981 market conditions. The summary of these factors and their comparison to mid. 1978 factors are shown in Table 25 The method of capital cost estimation and

updating, operating cost estimation, product streams of processes, and more important assumptions are in Appendix D.

3. Three different supercritical gas extraction (SGE) plant designs are analyzed: SGE I, SGE II, and SGE III

a) SGE I is SGE without extract hydrogenation (Figure 15)

b) SGE II is SGE with product hydrogenation to high value fuels and with no char (Figure 16).

c) SGE III is SGE with extract hydrogenation and use of char as feed to M-gasoline process (Figure 26).

In this design, gases, SNG and LPG, are used as the hydrogen source.

The economic comparison based on the implementations discussed above will follow the technical comparison SGE of with other liquefaction processes.

## 7.2 COMPARISON OF SUPERCRITICAL GAS EXTRACTION (SGE) PROCESS WITH OTHER LIQUEFACTION PROCESSES

Liquefaction processes which are currently being developed have significant differences in design concepts, product mixes, and various measures of efficiency. In this section, an attempt will be made to compare SGE processes with other liquefaction processes. A more comprehensive

TABLE 25

## Value Factors for Selected Synfuel Conversion Products

| Item                   | Market Price<br>\$    | Heating Value          | Energy Price<br>\$/10 <sup>6</sup> kJ | Value Factor |        |
|------------------------|-----------------------|------------------------|---------------------------------------|--------------|--------|
|                        |                       |                        |                                       | Nov 81       | Mid 78 |
| Coal                   | 35/ton                | 26000kJ/kg             | 1.35                                  | .15          | .38    |
| SGE Char <sup>1</sup>  | 35/ton                | 30000kJ/kg             | 1.16                                  | .13          | .30    |
| SRC Solid <sup>2</sup> |                       | 37300kJ/kg             | 3.53                                  | .4           | .5     |
| Fuel Oil               | 164/m <sup>3</sup>    | 41800MJ/m <sup>3</sup> | 3.92                                  | .45          | -      |
| (No. 6, high sulfur)   |                       |                        |                                       |              |        |
| Fuel Oil               | 199/m <sup>3</sup>    | 41800MJ/m <sup>3</sup> | 4.76                                  | .54          | .56    |
| (No. 6, low sulfur)    |                       |                        |                                       |              |        |
| No. 2 Oil              | 260/m <sup>3</sup>    | 34500MJ/m <sup>3</sup> | 7.53                                  | .86          | .82    |
| Naphtha                | 266/m <sup>3</sup>    | 34500MJ/m <sup>3</sup> | 7.71                                  | .88          | .82    |
| LPG                    | 179/m <sup>3</sup>    | 26600MJ/m <sup>3</sup> | 6.73                                  | .77          | .86    |
| Gasoline               | 280/m <sup>3</sup>    | 33200MJ/m <sup>3</sup> | 8.43                                  | .96          | .9     |
| Premium Gas            | 291/m <sup>3</sup>    | 33200MJ/m <sup>3</sup> | 8.77                                  | 1.0          | 1.0    |
| SNG <sup>3</sup>       |                       |                        | 5.75                                  | .62          | 1.0    |
| Butane                 | 164/m <sup>3</sup>    | 23200MJ/m <sup>3</sup> | 7.07                                  | .81          | 1.07   |
| Propane                | 128/m <sup>3</sup>    | 21250MJ/m <sup>3</sup> | 6.02                                  | .69          | 1.08   |
| Benzene                | .46/kg                | 35.4J/kg               | 12.9                                  | 1.47         | -      |
| Toluene                | .37/kg                | 35.4J/kg               | 10.5                                  | 1.20         | -      |
| Ethylene               | .53/kg                | 44.0J/kg               | 12.0                                  | 1.37         | -      |
| Electricity            | 50/10 <sup>6</sup> wh | 3580/M wh              | 14.7                                  | 1.59         | 2.60   |

<sup>1</sup>Valued 10% less than parent coal on energy basis.

<sup>2</sup>SRC solid - valued 10% less than high sulfur #6 fuel.

<sup>3</sup>Severe price regulations valued 10% less than propane on energy basis.

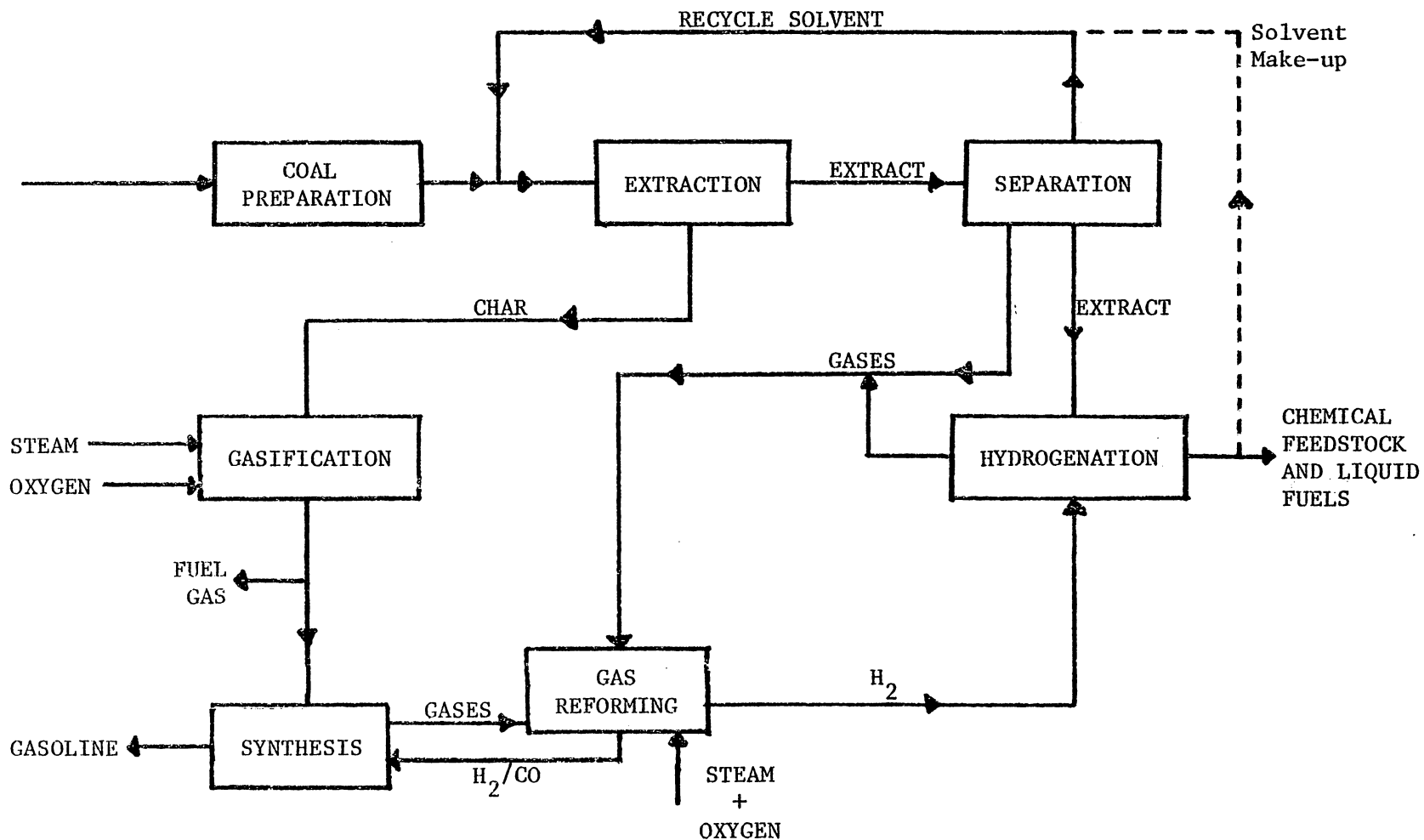


Figure 26: A Synfuel Complex Where SGE Char is Fed to an Indirect Liquefaction Process

comparison of coal conversion processes excluding the SGE process can be found in a report by ESCOE [96]. The comparison in this section will be in part based on ESCOE report, but will reflect the author's implementations and interpretations. The comparisons will be between Exxon Donor Solvent (EDS), Solvent Refined Coal (SRC-I, and SRC-II), H-COAL, SGE, Fischer Tropsch (F-T), and M-GASOLINE processes on three general areas of process comparison, products, and economics. The process comparisons will be in the areas of process complexity, process efficiency, and process development status. Sections on liquefaction products and economics will follow the section on process comparisons.

#### 7.2.1 Process Comparisons

##### 7.2.1.1 Process Complexity

Process complexity affects the technical feasibility of a process directly and the economic feasibility of the process indirectly. Process complexity is directly related to reliability and hence on-stream time of a process. The measures taken to achieve desired levels of on-stream-time are reflected in the process economics. The reliability of a processing step will affect processing steps to come and, in order to achieve a desirable overall on-stream time, multiple parallel units of a processing step must be used. Eco-

nomics of scale is the other major contributory factor in decisions regarding the number of parallel units to be used. Actual plant maintenance logs are required in order to derive concrete and quantitative process complexity indices. However, such data rarely exists even if made available. Thus the contributory items to process complexity and their relative weights are subjective. The developers' ability to handle the process complexities is also included in process complexity indices since different contributory factors can affect different processes at different levels. As can be seen from the analysis which is summarized in Table 26, SGE of coal is less complex than other direct liquefaction processes and is about as complex as indirect liquefaction processes.

#### 7.2.1.2 Efficiency

The efficiency measures commonly used are based on product and/or energy. Indirect liquefaction processes are less energy and product efficient (around 50 %) than direct liquefaction processes (around 70 %). The energy efficiency of SGE is comparable to other direct liquefaction processes while the product efficiency depends on the desirability of the residual char. If char is credited as feed coal, the product efficiency is more favorable in comparison to other direct liquefaction processes because:

TABLE 26

## Comparative Complexity of Different Liquefaction processes

| PROBLEM AREAS                        | IMPORTANCE   | HANDLING OF DIFFICULTIES |         |         |         |         |                       |
|--------------------------------------|--------------|--------------------------|---------|---------|---------|---------|-----------------------|
|                                      |              | SGE                      | SRC I   | SRC II  | EDS     | H-Coal  | Indirect Liquefaction |
| Solids/Fluid handling and separation | Major        | Good                     | Average | Average | Average | Problem | Good                  |
| Fired heater use                     | Minor        | Good                     | Good    | Good    | Good    | Good    | Excellent             |
| Complex reactor                      | Intermediate | Good                     | Problem | Problem | Average | Problem | Good                  |
| High Temperature and Pressure        | Minor        | Good                     | Good    | Good    | Good    | Average | Average               |
| TOTAL PENALTY POINTS                 |              | 10                       | 32      | 32      | 25      | 44      | 11                    |

$$\text{Penalty points} = \sum_{i=1}^6 \text{Importance}_i \times \text{Handling}_i$$

where  $i$  is process number

## Penalty Points

Importance

Major 5 pts.  
Intermediate 3 pts.  
Minor 1 pt.

Handling

Excellent 0 pts.      Problem 5 pts.  
Good 1 pt.          Fatal 10 pts.  
Average 3 pts.

1. Less gas is produced.
2. Less hydrogen is consumed since the extract is the hydrogen rich fraction of the coal.

#### 7.2.1.3 Development Status

The development status is an important factor in comparative studies since it indicates economic and technical reliability. However, by the same token less developed or explored processes may have a higher chance of improvements and breakthroughs. The F-T process is the only commercial liquefaction process. However, its low product and energy efficiency, as well as its wide product slate raise questions of doubt for employment in the United States. Other indirect liquefaction processes have a narrower product slate, but are not as efficient. All of the direct liquefaction processes included in this study have been tested in pilot plants and have significant technical problems. H-Coal has significant technical problems due to solids handling. EDS process is unlikely to be economic unless the coking scheme used to recover more liquids and separate the solids from the coal liquids is replaced with a more attractive alternative. Viability of the SRC processes depend on their solids handling and control problems in the dissolver as well as the performance of the Kerr-McGee deashing units.

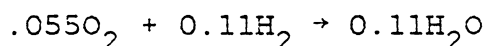
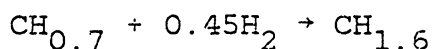
SGE extraction is less developed in comparison to the others included in this study. However, supercritical solvents reduce the solid-liquid separation problem as well as allowing, but not ensuring, virtually complete solvent recovery.

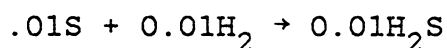
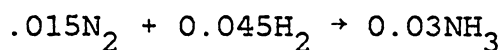
### 7.2.2 Liquefaction Products

The extract yield of SGE process is between 30-45%. The feasibility of the process depends on the value of residua char. Provided that the residua char is utilized wisely, extracts from SGE processes are more desirable than the products from other direct liquefaction processes because:

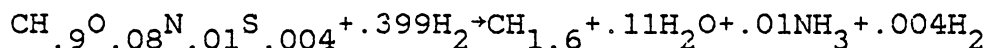
#### 1. They require less hydrogen

About 30% of the original coal feed is normally required to meet the hydrogenation requirements. Any reduction in this amount will affect the liquefaction economics favorably. In all direct liquefaction processes, hydrogen is manufactured by using some of the carbon source to upgrade the original feed. This reduces the amount of carbon available for upgrading. Coal can be described as  $\text{CH}_{0.7}\text{O}_{0.11}\text{S}_{0.01}\text{N}_{0.03}$  and complete conversion to  $\text{CH}_{1.6}$ ,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$  via following reactions





require 0.615 mole hydrogen per mole carbon in coal. The low hydrogen consumption of the SGE process is due to the higher hydrogen to carbon ratios of the extract, to less condensed molecular structure, and to the lower gas yields. As seen from the stoichiometry below



conversion of extract to premium products require 33% less hydrogen than that of raw coal.

## 2. They are less condensed

The SGE products are less condensed in comparison to other direct liquefaction products. This was shown in Figure 18. Thus the SGE products are more easily hydrogenatable to chemical feedstocks than direct liquefaction products.

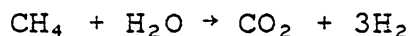
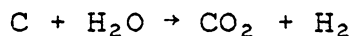
### 7.2.3 Comparative Economics of Coal Liquefaction Processes

Synfuel conversion processes, at this stage, should aim to maximize the weighted energy output,  $\sum f_i B_i$ . This can be best achieved by minimizing the hydrogen consumption, and by

maximizing the products which have high value. Although product value depends on the rather unpredictable market conditions, present trends are not likely to change.

$$f_{\text{chemicals}} > f_{\text{fuels}} > f_{\text{SNG}} > f_{\text{heavy fuels}} > f_{\text{solid fuels}}$$

As shown in Table 27, the marginal benefits of hydrogenation diminishes after  $\text{CH}_2$ . In most conceptual direct liquefaction designs, hydrogen is produced from raw coal or the liquefaction residua, while in indirect liquefaction processes it may be produced by steam reforming of gases. As shown in the reactions below, more hydrogen per carbon can be formed from methane reforming than coal.



However, since one of the aims of synfuel projects is to produce high BTU gases, most designers shy away from this option. The choice depends on the value factors of these light gases, availability of light gases in abundance, and value and use of liquefaction residua. For example, all direct liquefaction processes except SGE have high conversions, and relatively less valued residua (unreacted coal, unrecovered coal liquids, and mineral matter) and thus these processes use their residua as the hydrogen source. Howev-

er, SGE char is as good a carbon source as raw coal and economics of gasifying the char only to generate hydrogen and fuel is questionable. As shown in Figure 26 in a possible synfuel complex SGE char is fed to an M-Gasoline process and steam reforming is used to supply the hydrogen. Such a complex maximizes the product value and efficiency by minimizing hydrogen use and maximizing the percent carbon converted to high value liquid products. The economic comparison summarized in Table 29 and high value of aromatic feedstocks such as benzene, toluene, and xylene suggest that one attractive alternative use of coal would be SGE followed by indirect liquefaction to manufacture chemical feedstocks. The SGE extract then would be only very mildly hydrocracked.

The economics of SGE I (SGE without product hydrogenation), SGE II (SGE with hydrogenation), other coal liquefaction processes, and SGE III (SGE followed by M-Gasoline process) are compared in Table 29. This comparison is based on approximately 23000 ton per day self sufficient synfuel plants.

The cost and weighed energy output,  $\sum f_i B_i$ , of liquefaction processes are summarized in Table 28. The capital costs of all but SGE processes were updated from an ESCOE analysis [96]. The capital requirements of SGE processes were estimated with the aid of a 10000 t/d plant design by Catalytic Inc. [92]. Other important assumptions are in Ap-

TABLE 27

Variation of Energy Prices of Selected Hydrocarbons and  
Fuels with Hydrogen/Carbon Ratio

| PRODUCT          | H/C MOLE RATIO | PRODUCT PRICE<br>\$/10 <sup>6</sup> kJ |
|------------------|----------------|----------------------------------------|
| Coal             | 0.7            | 1.35                                   |
| Fuel Oil         | 1.3            | 4.76                                   |
| Naphtha          | 1.7            | 7.71                                   |
| Gasoline         | 1.95           | 8.43                                   |
| Premium Gasoline | 2.0            | 8.77                                   |
| SNG              | 4              | 5.75                                   |
| Butane           | 2.5            | 7.07                                   |
| Benzene          | 1.0            | 12.9                                   |
| Ethylene         | 2.0            | 12.0                                   |

pendix F and the summary of liquefaction process product streams are in Appendix G. A sample calculation is shown in Appendix H. As shown in Table 28, most direct liquefaction processes have low weighted energy outputs. This is due to the low value products. On the other hand, SGE II and M-Gasoline have high value products. SGE III, basically SGE II and M-Gasoline in series in carbon processing and parallel in utilization of the auxiliary facilities, has the highest weighted energy output. However, the energy and material balances for the SGE III process are only a rough estimate and detailed analysis may show different product yields. The estimation of capital requirements; material and energy balance assumptions for this process is in Appendix H.

The economic comparison was based on the reference product value. The reference product was premium gasoline and its price in November 1981 was \$8.77/Million kJ. Processes with reference product value lower than \$8.77/Million kJ were assumed profitable. The analysis was made with three different capital recovery factors which reflect optimistic, most likely, and pessimistic financing rates. All but SRC I and SGE I are economically feasible at a very low capital recovery rate,  $k=0.08$ . At the most likely recovery rate,  $k=0.16$ , SGE II, SGE III, and M-Gasoline are feasible; at a pessimistic recovery rate,  $k=0.24$ , none of the processes are

TABLE 28

## Comparative Cost of Selected Coal Liquefaction Processes

|                    | Capital<br>(Million \$) | Coal<br>(Million \$) | Catalyst &<br>Chemicals<br>(Million \$) | Labor<br>(Million \$) | Maintenance<br>(Million \$) | Local Tax &<br>Insurance<br>(Million \$) | $\sum f_i B_i$<br>( $10^{13}$ KJ/year) |
|--------------------|-------------------------|----------------------|-----------------------------------------|-----------------------|-----------------------------|------------------------------------------|----------------------------------------|
| SRC                | 1570                    | 287                  | 4.5                                     | 16                    | 47                          | 79                                       | 5.73                                   |
| SRC II             | 1815                    | 287                  | 9                                       | 14.3                  | 54                          | 90                                       | 8.40                                   |
| EDS                | 1830                    | 287                  | 9                                       | 14.3                  | 55                          | 91                                       | 8.18                                   |
| F-T                | 1610                    | 287                  | 10.5                                    | 14.3                  | 48                          | 81                                       | 7.61                                   |
| M-Gasoline         | 1740                    | 287                  | 13.0                                    | 14.3                  | 52                          | 87                                       | 9.92                                   |
| SGE I <sup>1</sup> | 1450                    | 287                  | 4.5                                     | 14.3                  | 44                          | 72                                       | 5.84                                   |
| SGE II             | 1710                    | 287                  | 9                                       | 14.3                  | 51                          | 86                                       | 9.71                                   |
| SGE III            | 2060                    | 287                  | 11.5                                    | 16                    | 62                          | 103.0                                    | 10.60                                  |

(Basis = 23.000t/day dry coal)

<sup>1</sup>Extract value factor = 0.6; % extraction = 40

TABLE 29  
Economics of Coal Liquefaction Processes

| PROCESS    | REFERENCE PRODUCT PRICE \$/10 <sup>6</sup> kJ |          |          |
|------------|-----------------------------------------------|----------|----------|
|            | k = 0.08                                      | k = 0.16 | k = 0.24 |
| SRC I      | 9.75                                          | 11.95    | 14.15    |
| SRC II     | 7.14                                          | 8.87     | 10.60    |
| EDS        | 7.37                                          | 9.16     | 10.95    |
| F - T      | 7.50                                          | 9.18     | 10.37    |
| M-Gasoline | 5.98                                          | 7.38     | 8.78     |
| SGE I      | 9.21                                          | 11.20    | 13.18    |
| SGE II     | 6.02                                          | 7.42     | 8.84     |
| SGE III    | 6.10                                          | 7.63     | 9.17     |

economically feasible. For SGE processes the two most important economic parameters are the value and amount of extract. As seen in Table 30 which shows the economics of SGE I at varying extract amounts and extract value factors, grass roots SGE processes should upgrade and maximize their extract yields, as in SGE II.

At present, one of major obstacles to commercialization of synfuel plants is the high capital requirements, about 2 Billion dollars for a 25000 t/day coal plant. All the processes have inherent inefficiencies and require substantial facilities for pretreatment of the coal, for purification of the gases, for waste treatment, and for solids handling. As shown in the case of SGE III, one way of improving efficiency is to build complexes which combine the strengths of conversion processes, eliminate unnecessary recycles and share the auxiliary facilities. However, such complexes although more economic, require higher capital than the individual processes.

An alternative to grass-roots synfuel plants is the satellite plant which is a "battery limit" addition of SGE units to existing utility plants. Since utility plants have existing facilities for coal preparation, waste disposal, pollution equipment, water supply, steam, gas, and electricity, the additional cost will be only in SGE units and their

TABLE 30

Sensitivity of SGE I Economics to Percent Extraction  
and Extract Value Factor

| EXTRACT<br>(% of feed) | EXTRACT VALUE FACTOR<br>$f_i$ |      |      |      |
|------------------------|-------------------------------|------|------|------|
|                        | 0.4                           | 0.5  | 0.6  | 0.7  |
| 20                     | 22.2 <sup>1</sup>             | 19.5 | 17.3 | 15.5 |
| 30                     | 18.5                          | 15.6 | 13.6 | 12.0 |
| 40                     | 15.8                          | 13.1 | 11.2 | 9.8  |

<sup>1</sup>In \$/10<sup>6</sup> kJ

Sensitivity of product reference price (\$/10<sup>6</sup> kJ) of SGE I to extract value factor ( $f_i$ ) and percent extraction for capital recovery factor (k) of 0.16.

operating expenses. Although reliability of the SGE unit is very important, it will be of less concern since utility plants can operate with raw coal. Such a plant is shown in Figure 27 [98] and as seen in Table 31 economics of satellite SGE plants are more favorable than grass roots SGE plants. Furthermore, smaller capital expenditure of satellite plants offer a less risky testing grounds for synfuel processes. In this thesis, only SGE I was studied as a satellite plant. The extract was assumed to be relatively stable and marketable as feedstock for further processing.

### 7.3 OPTIMIZATION CONSIDERATIONS FOR SGE

The economic analysis presented in the previous section was a preliminary analysis outlining the potential advantages of SCE of coal over alternative liquefaction processes. In this section, optimization considerations as related to SGE processes will be discussed. Then, the process design implications of the experimental findings of this research will be reviewed.

Depending on the processing conditions and solvent selection the feed can be either slurried into the reactor or moving bed reactors with lock hoppers can be used. Slurry feed system with transport reactors result in better heat and mass transfer rates, are operable at higher pressures and require lower coal residence times. However, as a re-

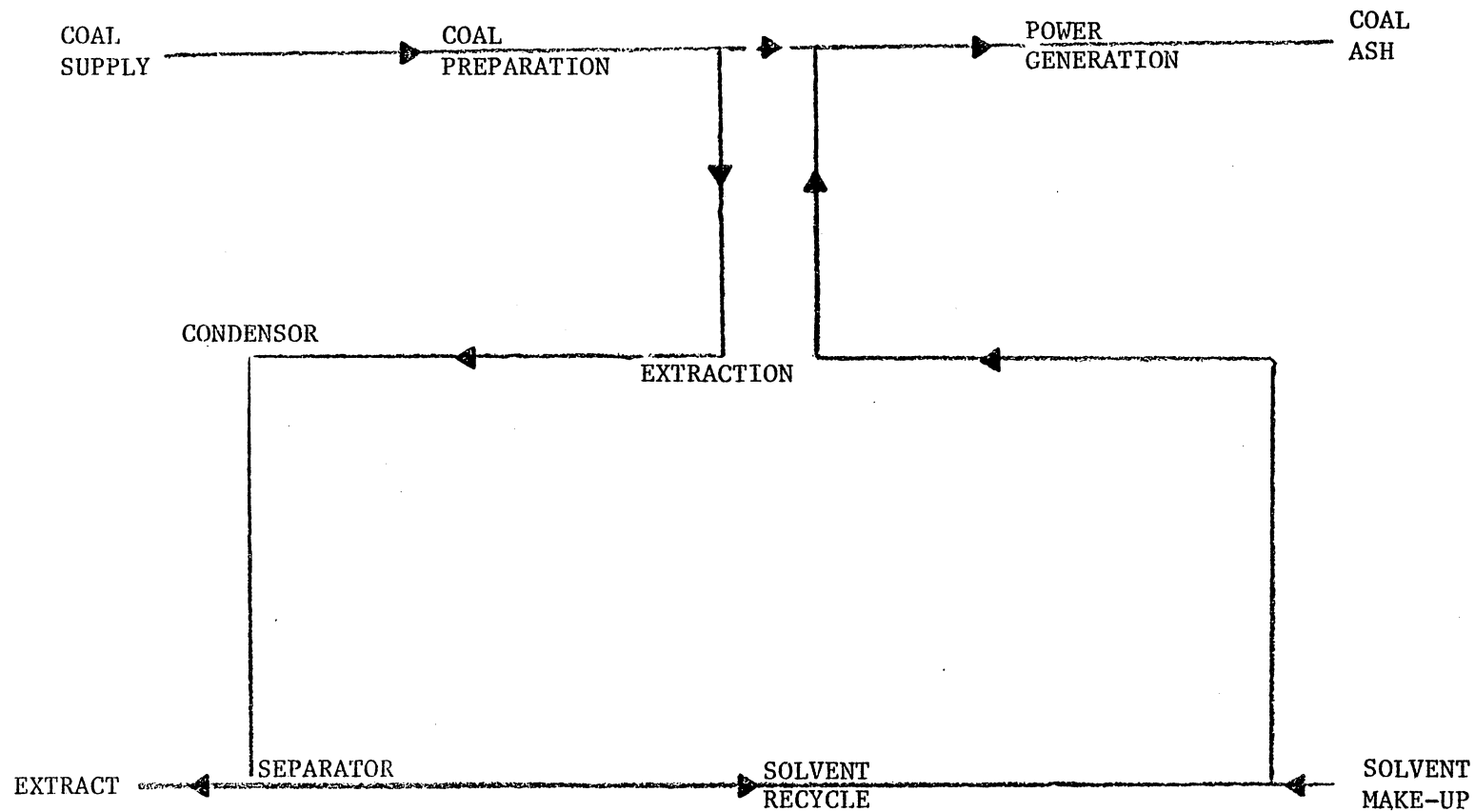


Figure 27: A Satellite SGE Plant

TABLE 31

## Economics of Satellite SGE Plants

Sensitivity analysis based on reference product value (\$/Million kJ)

| Percent Extraction | Value Factor |            |            |
|--------------------|--------------|------------|------------|
|                    | <u>0.5</u>   | <u>0.6</u> | <u>0.7</u> |
| 30.                | 8.86         | 7.68       | 6.78       |
| 40.                | 7.41         | 6.33       | 5.52       |

Basis: 23000 t/d plant  
 Capital Cost : 467 Million dollars  
 Coal Cost : 287 Million dollars  
 Maintenance : 14.1 Million dollars  
 Labor : 5 Million dollars  
 Insurance and local taxes : 23.4 Million dollars  
 Capital recovery factor : 0.08

sult, three-phase fired heaters are necessary and solid-solvent separation is more difficult. The selection of an extractor should be based on the above considerations.

In solvent selection, solvent recoverability and solvent preconditioning energy requirements should be considered as well as extract yield. The solvent may have some donor components. However, hydrogenation at the extraction stage should be very mild and should not destroy the pore structure. Early extract fractionation for better hydrogen utilization, is a option worth considering.

#### 7.3.1 Process Design Implications of Experimental Findings

Two of the major experimental findings of this research were

1. Extractability of raw coal and preheated coal with the aid of entrainers at low temperatures.
2. Extractability of coal with supercritical water.

SCE at low temperatures with entrainers offer energy efficient designs where there are no fired heaters involved and where the extract is precipitated isobarically by a small temperature increase (Figure 28). Since 18% of coal was used for process heat requirements, especially in the fired heaters, the significance of this finding can be better appreciated. Furthermore, possible reduction of operating temperatures to 150 °C imply savings in capital as well.

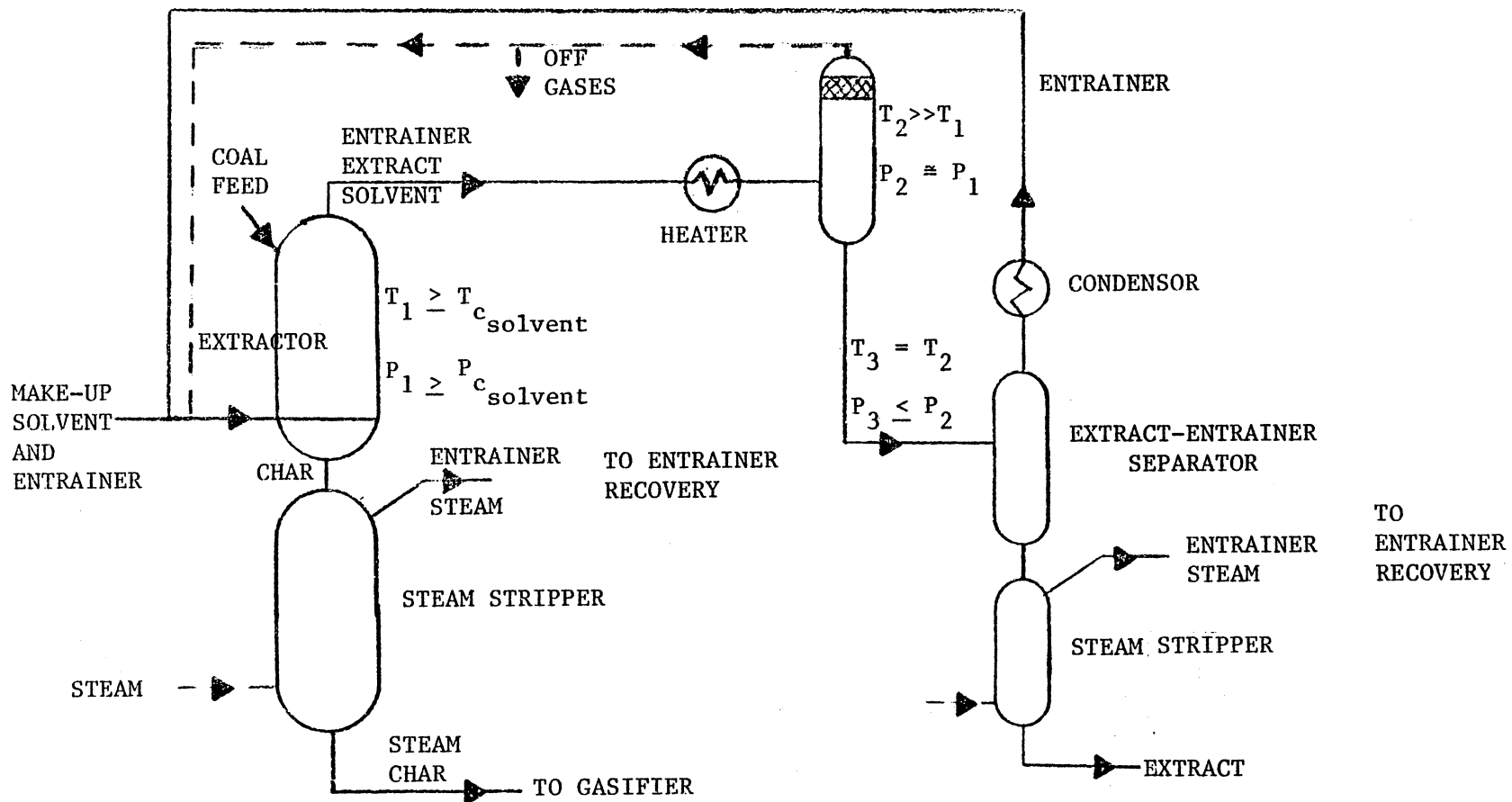


Figure 28: A Design for SCE of Coal with the Aid of Entrainers

Solvent losses due to difficult solvent-extract separations is a major problem in all direct liquefaction processes. Although the solvent losses are as small as 0.4 % for SGE, the solvent (toluene) make-up cost for a 10000 t/day plant amount to approximately ten million dollars. The extractibility of coal, with a readily available disposable solvent which is immiscible with the extract at low pressures, offers ease of solvent regeneration. Furthermore, it tolerates a rather crude solvent-char separation. Part of the solvent (water) may be used to slurry the char to the gasifiers. It is true that relatively high capital, due to pressures around 25 MPa are required. However, the more significant constraint on use of water as the solvent is its high heat of vaporization. If heat requirements are kept low by an ingenious solvent regeneration and recycle scheme, the advantages of using water as the solvent will outweigh the disadvantages.

## Chapter VIII

### CONCLUSIONS

Different avenues were investigated during the course of this study. Before making any conclusion based on the experimental, theoretical, and economic findings of this research, it would not be an overstatement to conclude SCE of coal to be an attractive challenge to researchers, process designers, and the equipment manufacturers. The conclusions and findings of this dissertation can be grouped under three general topic areas.

1. Supercritical extraction mechanism at high temperatures where coal reactions occur simultaneously with solubilization.
2. Supercritical extraction of dried and heat-pretreated coals with or without the aid of entrainers near ambient conditions.
3. New conceptual alternatives to present practices of SCE of coal.

### 8.1 MECHANISM OF SUPERCRITICAL EXTRACTION OF COAL AT TEMPERATURES CLOSE TO COAL PYROLYSIS REACTION TEMPERATURES

SCE at temperatures close to pyrolysis temperatures involves removal of highly unstable decomposition products from the reaction environment to avoid repolymerization, pore blinding, and product degradation. The supercritically extractable fraction is part of the volatile fraction of the coal. The porous structure of coal is not destroyed during extraction.

A significant fraction of coal, mainly volatiles, is converted to asphaltols, asphaltenes, oils, and gas during the initial period of exposure to high temperatures. The rate of initial decomposition reactions are very fast. The rates of decomposition and repolymerization reactions are fastest at higher temperatures and pressures. The initial products are either solubilized or react at slower rate than that of initial decomposition reactions. The products from these slower reactions are smaller molecular weight compounds and repolymerization products, e.g. semi-coke. The smaller compounds can get extracted later as the solvent becomes abundant and/or as they become small enough to solubilize. The repolymerization products can contribute to extract amount by re-decomposing in a later time. Repolymerization products can blind some of the smaller pores trapping the otherwise extractable material.

The importance of solvent strength is not accurately reflected in percent extraction. Percent extraction does not measure degree of product degradation and rate of extraction. The rate of extraction, the relative amounts of extract components (i.e. asphaltols, asphaltenes, and oils) and the amount of gas formed are strongly dependent on the solvent strength. Stronger solvents have critical temperatures close to the extraction temperature and are aromatic. The molecular configuration of the solvent should be such that even the smallest coal pores should be accessible. Stronger solvents remove the decomposition products as they are formed. They result in higher extraction rates, higher asphaltols contents, and less gas formation as well as higher percent extractions. However, the initial decomposition rates are very fast and product degradation even with the strongest solvents is inevitable during the initial few minutes.

In summary, severe reaction conditions and stronger solvents result in faster and higher extraction rates increasing the overall conversion (percent extraction). Because of the strong response to reaction conditions, if maximization of the percent extraction is objective, provided that other parameters are same (e.g. solvent cost, recoverability), the extraction conditions dictate the solvent selection.

Although, it is hard to reach to concrete conclusions based on one experiment, it is apparent that under supercritical conditions water is an effective solvent for coal. The amount of pyrolysis to gaseous products during extraction with water was higher than those with other solvents. The economics of SCE with water depends on recoverability of the high latent heat required to heat water to supercritical temperatures.

## 8.2 SUPERCritical EXTRACTION OF COAL NEAR AMBIENT TEMPERATURES WITH CARBON DIOXIDE

The amounts of extract from dried coal and heat-pretreated coal with carbon dioxide near ambient conditions was negligible. However, SCE of coal and heat-pretreated coals are possible with the aid of liquid entrainers. Heat-pretreated coals give higher yields than dried coals during extractions with carbon dioxide in presence of liquid entrainers due to entrapped pyrolysis products which were formed during heat pretreatment. The yields from supercritical extractions in the presence of depleting entrainers were comparable but not more than the Soxhlet extractions with pure entrainers. However, unlike Soxhlet extraction solvents, the entrainers are almost completely recoverable.

### 8.3 PROCESS DESIGN ALTERNATIVES

Coal liquefaction processes must maximize the product quality in order to maximize revenue in energy markets. Maximization of thermal efficiency and minimization of hydrogen use are key constraints in maximizing amount of quality products. Three new design concepts are suggested as alternatives to present commercialization efforts.

1. SCE of coal followed by gasification of the extraction residua. The gasification products can be used to synthesize premium fuels or petrochemicals. Hydrogen requirements are to be met, in part, through steam reforming. This attractive synfuel complex conceptually makes best use of the hydrogen, the auxiliary facilities, and maximizes the amount of high quality products. The capital requirements of such complexes will be 10-20 % higher than other liquefaction processes.
2. Satellite SCE plants at utility sites. This alternative to high capital synfuel plants may be very attractive if the supercritical extraction products are stable enough to be transported from such satellite plants to coal liquids refineries to be further processed. Water, which is abundant at utility sites, can be an attractive solvent for a satellite plant, provided that an energy efficient recirculation

scheme, which compensates its high latent heat of vaporization, can be found.

3. The SCE of coal at near ambient conditions with the aid of entrainers. This is an energy efficient SCE route and its economics will depend on the extraction depth. Near complete recovery of entrainers by cheaper supercritical gases, make expensive but effective solvents attractive for coal processing. This alternative should best be considered as a battery limit addition to an existing plant due to low extraction yields. The low extraction yields can be improved by heat-pretreatment of the extractor feed.

## Chapter IX

### RECOMMENDATIONS FOR FURTHER RESEARCH

Supercritical extraction is a relatively unexplored area. Although coal conversion studies are abundant, SCE of coal is not fully understood. Further research efforts may concentrate in any or both of these areas:

1. SCE of Coal with mixtures of different classes of solvents may be studied.
2. An equation of state which predicts solubility of hydrocarbons in super critical fluids (SCF) should be either identified or developed.
3. SCE of different coals should be studied.
4. A computer program which correlates and predicts the solubility and graphically displays phase behaviour should be developed.
5. Extraction with water at near critical conditions should be further studied.
6. More elaborate and precise analysis procedure should be developed.
7. The products from SCE of coal may be studied using SCF chromatography.
8. A extract fractionation step should be included in the present apparatus to study the extract-solvent separation step.

9. Stability of the SCE products may be studied.
10. Hydrocracking of the SCE extracts may be studied.

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## Appendix A

### OPERATING PROCEDURES FOR EXPERIMENTAL SYSTEMS

#### A.1 PROCEDURE FOR OPERATING THE HIGH TEMPERATURE SYSTEM

The high temperature system is shown in Figure 19 and the operating procedure is as follows:

1. Vent the system by opening T1 towards Autoclave A<sub>2</sub>
2. Close R<sub>1</sub>
3. Charge about 2 liters of solvent to Autoclave A<sub>2</sub> and fill Autoclave A<sub>1</sub>.
4. Heat the lower Autoclave, A<sub>2</sub>, starting at a lower variac setting of 80 and going up as seems necessary.
5. Turn the fluidized bath heater at the state where the extractor is not immersed in it.
6. When the temperature of solvent in Autoclave A<sub>2</sub> is above T , pressure reaches extraction pressure, and bath temperature is  $T_c(\text{Extraction}) + \Delta T$  where  $\Delta T$  is the temperature drop the bath experiences when the bed is raised to contact with the extractor ( $\Delta T$  depends on the A<sub>2</sub> outlet temperature and is usually less than 5°C. Then, raise the bath and open valve R<sub>1</sub> slowly to fully open position.
7. Charge approximately 30 cubic cm. to compensate for the solvent in extractor section from Autoclave A<sub>1</sub> to Autoclave A<sub>2</sub> using metering valves M<sub>1</sub> and M<sub>2</sub>

8. If the extractor temperature and pressure is the desired values then open  $R_2$  carefully and very slowly.  $R_2$ 's primary purpose is to measure out a specific amount of solvent loaded with extract to the solvent reclaiming section.
9. At a desired time or when the desired amount of solvent is passed, close valves  $R_2$  and replace extract collector, C.
10. Repeat steps 8 and 9 with new collectors until either coal is exhausted, i.e. solvent comes out clear, or after a specified extraction time.
11. Close  $R_1$
12. Bring the solvent pre-conditioning section to a new temperature and pressure.
13. Lower the bath and drain the extraction section inventory, by opening  $R_2$  slowly into a drain collector, a flask same as the sample collector.
14. Vent the extractor section with nitrogen
15. Replace the extractor with a new one.
16. Vent the new extractor with nitrogen and now, the extractor section is ready for a new run.
17. REPEAT OR SHUT DOWN  
For shut down:

Turn all the heaters off. Then Autoclave A<sub>2</sub> temperature is below 150°F, the system is ready to unload the remaining solvent through valve D.

#### A.2 PROCEDURE FOR OPERATING THE LOW TEMPERATURE SYSTEM

The low temperature system is shown in Figure 20 and the operating procedure is as follows:

1. Set the BPR(s). BPR<sub>2</sub> is set to extraction pressure plus 50 psia while BPR<sub>1</sub> is set at extraction pressure plus 200+ psia.
2. Open the solvent feed valve. When the system pressure (PI<sub>1</sub>) reaches the solvent tank outlet pressure, turn the compressor on. The initial feed setting should be low gradually increasing to maximum and as the system pressure approaches desirable extraction pressure (about BPR<sub>1</sub> setting) lower the feed rate. The solvent feed rate should rate as low as possible to ensure saturation and safe and smooth operation. Pressure surges are least desirable due to inaccuracies created as well as for safety of the glassware downstream.
3. There are two criteria for scheduled termination of an experimental run.

- a) If the experiment is thermodynamic solubility limited as opposed to mass transfer or reaction rate limited operations, an experimental run is terminated when a desired amount of solvent is passed through the wet test meter.
  - b) If mass transfer and/or reaction rate limitations are important, then the run should be best terminated after a specific run time.
4. The run termination is best achieved by increasing the BPR<sub>2</sub> setting so that no through flow is permitted, turning the compressor off, and closing the solvent feed valves. Then the wet test meter reading is recorded, glass beaker and U tube are replaced with a waste beaker and BPR<sub>1</sub> and BPR<sub>2</sub> dome loading gas is vented slowly. Venting BPR<sub>2</sub> dome gas load fast will result in broken glassware.

## Appendix B

### SAMPLE CALCULATIONS FOR HIGH TEMPERATURE SYSTEMS

#### B.1 HIGH TEMPERATURE SYSTEM RUN DATA LOG

Run number = 9

Sample number= 1,2,3

Date= April 14, 82

Initial Coal Weight= 14.7857 g.

Temperature= 375 °C

Pressure= 1500 psia

Solvent = Toluene

0.012 cu. ft. gas at 17°C

Time bed up= 3.22

Time R2 opened= 3.24

Time R2 closed= 3.37

Time R2 opened= 3.39

Time R2 closed= 4.07

Time R2 opened= 4.08

Time R2 closed= 4.37

## B.2 SAMPLE CALCULATION: PERCENT EXTRACTION

Coal feed  $[m_1] = 14.7857 \text{ g.}$

Moisture content  $[\%H_2O] = 3\%$

$$\begin{aligned} \text{Dry Coal feed } [m_2] &= m_1 * (100 - \%H_2O) / 100 && \text{Eq. B.1} \\ &= 14.7857 * (100 - 3) / 100 = 14.34 \text{ g.} \end{aligned}$$

Extraction Residue  $[m_3] = 12.0772 \text{ g}$

Moisture content of residua  $(\%H_2O) = 2\%$

$$\begin{aligned} \text{Dry Residue weight } [m_4] &= m_3 * (100 - \%H_2O) / 100 && \text{Eq. B.2} \\ &= 12.0772 * (100 - 2) / 100 = 11.83 \text{ g.} \end{aligned}$$

$$\begin{aligned} \text{Percent extraction} &= (m_2 - m_4) / m_2 * 100 && \text{Eq. B.3} \\ &= (14.34 - 11.83) / 14.34 * 100 = 17.5 \% \end{aligned}$$

### B.3 EXTRACT FRACTIONATION DATA LOG

Sample No.= 9/1

Date = 5/18-5/23

Weight of the beaker after solvent transfer= 77.1077

Weight of cleaned beaker= 77.0970

Additional solvent used= 20 ml

#### DISTILLATION OF SCE SOLVENT

Weight of the flask before transfer ( $w_1$ ) = 118.5579

Amount of solvent distilled= 88 ml

Weight of the flask after solvent transfer ( $w_2$ )= 119.9689

#### FILTRATION OF ASPHALTOLS

Weight of filter paper before filtration ( $wf1_1$ ) = 1.5413

Weight of filter paper after filtration ( $wf1_2$ ) = 2.0842

#### Distillation of Benzene

Weight of the flask after distillation ( $w_3$ ) = 119.3675

#### Filtration of Asphaltenes

Weight of filter paper before filtration ( $wf2_1$ ) = 1.4618

Weight of filter paper after filtration ( $wf2_2$ ) = 1.9142

#### Distillation of cyclohexane

Weight of the flask after distillation ( $w_4$ ) = 118.8823

Weight of Clean Flask ( $w_5$ ) = 118.5611

Sample No.= 9/2

Date = 5/18-5/23

Weight of the beaker after solvent transfer= 76.8855

Weight of cleaned beaker= 76.8632

Additional solvent used= 0 ml

#### DISTILLATION OF SCE SOLVENT

Weight of the flask before transfer ( $w_1$ ) = 127.9417

Amount of solvent distilled= 137 ml

Weight of the flask after solvent transfer ( $w_2$ )= 128.1995

#### FILTRATION OF ASPHALTOLS

Weight of filter paper before filtration ( $wf1_1$ ) = 1.4207

Weight of filter paper after filtration ( $wf1_2$ ) = 1.5341

#### Distillation of Benzene

Weight of the flask after distillation ( $w_3$ ) = 128.4787

#### Filtration of Asphaltenes

Weight of filter paper before filtration ( $wf2_1$ ) = 1.4843

Weight of filter paper after filtration ( $wf2_2$ ) = 1.5315

#### Distillation of cyclohexane

Weight of the flask after distillation ( $w_4$ ) = 127.9776

Weight of Clean Flask ( $w_5$ ) = 127.9398

Sample No.= 9/3

Date = 5/18-5/23

Weight of the beaker after solvent transfer= 78.5580

Weight of cleaned beaker= 78.4811

Additional solvent used= 0 ml

DISTILLATION OF SCE SOLVENT

Weight of the flask before transfer ( $w_1$ ) = 112.8535

Amount of solvent distilled= 119 ml

Weight of the flask after solvent transfer ( $w_2$ )= 113.1352

FILTRATION OF ASPHALTOLS

Weight of filter paper before filtration ( $wf1_1$ ) = 1.5746

Weight of filter paper after filtration ( $wf1_2$ ) = 1.7227

Distillation of Benzene

Weight of the flask after distillation ( $w_3$ ) = 113.0015

Filtration of Asphaltenes

Weight of filter paper before filtration ( $wf2_1$ ) = 1.5702

Weight of filter paper after filtration ( $wf2_2$ ) = 1.6478

Distillation of cyclohexane

Weight of the flask after distillation ( $w_4$ ) = 112.9239

Weight of Clean Flask ( $w_5$ ) = 112.8611

B.4 SAMPLE CALCULATIONS: EXTRACT FRACTIONATION AND EXTRACT AMOUNTS FOR EACH RUN

$$\text{Asphaltols amount} = wf1_2 - wf1_1 \quad \text{Eq. B.4}$$

$$= 2.0842 - 1.5341 = 0.5429 \text{ g (sample 1)}$$

$$= 1.5341 - 1.4207 = 0.1134 \text{ g (sample 2)}$$

$$= 1.7227 - 1.5746 = 0.1481 \text{ g (sample 3)}$$

$$\text{Asphaltenes amount} = wf2_2 - wf2_1 \quad \text{Eq. B.5}$$

$$= 1.9142 - 1.4618 = 0.4522 \text{ g (sample 1)}$$

$$= 1.5315 - 1.4843 = 0.0472 \text{ g (sample 2)}$$

$$= 1.6478 - 1.5702 = 0.0776 \text{ g (sample 3)}$$

$$\text{Oils amount} = w_4 - w_5 \quad \text{Eq. B.6}$$

$$= 118.8823 - 118.5611 = 0.3212 \text{ g (sample 1)}$$

$$= 127.9776 - 127.9398 = 0.0378 \text{ g (sample 2)}$$

$$= 112.9239 - 112.8611 = 0.0628 \text{ g (sample 3)}$$

$$\text{Total extract amount} = \text{asphaltols} + \text{asphaltenes} + \text{oils}$$

$$= 0.5429 + 0.4524 + 0.3212 = 1.3165 \text{ g (sample 1)}$$

$$= 0.1134 + 0.0472 + 0.0378 = 0.1984 \text{ g (sample 2)}$$

$$= 0.1481 + 0.0776 + 0.0628 = 0.2885 \text{ g (sample 3)}$$

TABLE 32

Extract Components at Different Periods of Each Run

| Run No.         | Solvent   | P E R I O D     |                    |             |                 |                    |             |                 |                    |             |
|-----------------|-----------|-----------------|--------------------|-------------|-----------------|--------------------|-------------|-----------------|--------------------|-------------|
|                 |           | [0-15 minutes]  |                    |             | [15-45 minutes] |                    |             | [45-75 minutes] |                    |             |
|                 |           | Asphalts<br>[g] | Asphaltenes<br>[g] | Oils<br>[g] | Asphalts<br>[g] | Asphaltenes<br>[g] | Oils<br>[g] | Asphalts<br>[g] | Asphaltenes<br>[g] | Oils<br>[g] |
| 1 <sup>1</sup>  | Toluene   | .5026           | .8106              | .6566       | .1441           | .1191              | .1060       | .0523           | .0371              | .0337       |
| 2               | Toluene   | .6967           | 1.0669             | .7991       | .2310           | .1831              | .1668       | .1346           | .0749              | .0638       |
| 3               | Toluene   | .6070           | 1.0100             | .6151       | .1790           | .1378              | .1113       | .1486           | .1238              | .1251       |
| 5               | Toluene   | .4387           | .8602              | .6090       | .1739           | .1234              | .1115       | .1443           | .0956              | .1702       |
| 6               | Toluene   | .3248           | .6752              | .6009       | .2028           | .1340              | .1179       | .1888           | .0862              | .0595       |
| 7               | Toluene   | .5630           | .5072              | .4210       | .1337           | .0693              | .0547       | .1490           | .0727              | .0545       |
| 8               | Toluene   | .4516           | .4301              | .3669       | .2167           | .0735              | .0536       | .0847           | .0637              | .0688       |
| 9               | Toluene   | .5429           | .4524              | .3212       | .1134           | .0472              | .0378       | .1481           | .0776              | .0628       |
| 10              | Toluene   | .5088           | .4584              | .3713       | .2040           | .1115              | .1014       | .1959           | .1146              | .1283       |
| 11              | Toluene   | .2511           | .2486              | .1765       | .0934           | .0662              | .0676       | .0901           | .0501              | .0648       |
| 13              | Xylene    | .9374           | 1.0302             | .6284       | .2866           | .1027              | .0729       | .2947           | .1075              | .0957       |
| 14              | Xylene    | .8850           | .5861              | .3458       | .1801           | .0747              | .0404       | .0991           | .0416              | .0183       |
| 15              | Xylene    | .9167           | .7576              | .3106       | .2020           | .0765              | .0604       | .0609           | .0219              | .0140       |
| 16              | Water     | .2305           | .5623              | .5679       | .4119           | .2452              | .2722       | .3605           | .3277              | .3408       |
| 17              | n-pentane | .1489           | .3354              | .3656       | .1504           | .1699              | .2204       | .1094           | .0986              | .1390       |
| 19              | Methanol  | .2137           | .2638              | .2929       | .1146           | .0600              | .0708       | .1629           | .1790              | .1915       |
| 20 <sup>1</sup> | Methanol  | .0727           | .0928              | .1123       | .0745           | .0528              | .0682       | .0556           | .0424              | .0597       |

<sup>1</sup>Based on Soxhlet extraction

B.5 RESIDUE DATA LOG

Run No.= 9

Date of analysis= 4/23-25

Weights [grams]

Before TGA [w1] = 56.5101

After TGA [w2] = 56.4037

Jar [wj] = 44.4329

Thimble [wT] = 6.9726

Soxhlet feed [ws] = 116.0547

Benzene insolubles [w3] = 116.0297

Pyridine insolubles [w4] = 115.5420

Weighing beaker [wb] = 97.1834

B.6 SAMPLE CALCULATIONS: RESIDUA

Weight loss for TGA sample = WL1

$$WL1 = w1 - w2 = 56.5101 - 56.4037 = 0.1064 \quad \text{Eq. B.7}$$

Weight Loss due to transfer from jar to thimble = WL2

$$\begin{aligned} WL2 &= (w2 - wj) - (ws - wb - wT) \quad \text{Eq. B.8} \\ &= (56.4037 - 44.4329) - (116.0547 - 97.1834 - 6.9726) \\ &= 0.0721 \end{aligned}$$

$$WL = WL1 + WL2 = 0.1785 \quad \text{Eq. B.9}$$

$$\%loss = WL / (w1 - wj) * 100 \quad \text{Eq. B.10}$$

$$= 0.1785 / (56.5101 - 44.4329) * 100 = 1.5 \%$$

$$\%asphaltenes = (w3 - ws) / (w1 - wj) * 100 / (100 - \%loss) \quad \text{Eq. B.11}$$

$$= (116.0547 - 116.0297) / 12.0772 * 100 / 98.5 * 100$$

$$= 0.21 \%$$

$$\% asphaltols = (w4 - w3) / (w1 - wj) * 100 / (100 - \%loss) \quad \text{Eq. B.12}$$

$$= (116.0297 - 115.5420) / 12.0772 * 100 / 98.5 * 100$$

$$= 4.1 \%$$

B.7 SAMPLE CALCULATIONS: GAS

Temperature [T] = 290 °K

Pressure [P] = 1.0 atm.

Volume [V] = 0.012 cubic ft.

Molecular Weight [Mw] = 30. lb/lb-mole

R = 1.314 atm. cu. ft/°K lb-moles

mass = Mw P V/R/T 454 g/lb

Eq. B.13

= 30.\*0.012\*454/290/1.314 = 0.43 g.

## Appendix C

### SAMPLE CALCULATIONS FOR LOW TEMPERATURE SYSTEMS

#### C.1 LOW TEMPERATURE SYSTEM RUN DATA LOG

Run number = L14

Date = Feb. 22, 82

Solvent = Carbon Dioxide

Initial Solute weight= 11.8252 g.

Pretreatment = yes at 400°C for one h.

Entrainer = Toluene 2.37 g

Temperature = 75 °C

Pressure = 1520 psia

Time of Extraction = 78 min

Solvent used = 15.3 cubic ft. at STD

Final Weight = 10.8161 g.

C.2 SAMPLE CALCULATIONS: LOW TEMPERATURE SYSTEM

$w_1$  = initial extractor feed weight = 11.8252 g

$w_2$  = residua weight = 10.8161 g

F%H<sub>2</sub>O = Feed moisture Content [%] = 2 %

R%H<sub>2</sub>O = Residua moisture Content [%] = 1 %

y = conversion = percent extraction

$y = (w_1(100-F\%H_2O) - w_2(100-RH_2O)) / w_1(100-F\%H_2O)$  Eq.C.1

$y = (11.8252 * .98 - 10.8161 * .99) / (11.8252 * .98) * 100$

Conversion= 7.6 %

## Appendix D

### SAMPLE CALCULATION: HILDEBRAND SOLUBILITY PARAMETER

$$\xi_g = 1.25 P_c^{1/2} \rho_g / \rho_c^{2.66} \quad \text{Eq. D.1}$$

For methanol at 425 °C (698 °K) and 13.8 MPa (136.1 atm.)

Molecular Weight (Mw)= 32.05 g/g-mole

P =8.8 MPa= 79.9 atm

=0.272 g/cc

z=0.86 (via Lee-Kessler EOS by Dick Elliot)

R=82.057 atm.\*cc/g-moles/°K

$$\begin{aligned} \xi_g &= 1.25 * (79.9)^{1/2} * 136.1 * 32.05 / 82.057 / .86 / 698 / .272 / 2.66 \\ &= 1.37 \end{aligned}$$

## Appendix E

### STATISTICAL ANALYSIS

#### E.1 SELECTION OF EXPERIMENTAL DESIGN

In this dissertation, two level factorial designs were chosen over one-factor-at-a-time method and other response surface methods which lead to mechanistic models. In one-factor-at-a-time method, experimental parameters are varied one at a time with the remaining factors held constant. This method was formerly regarded as the only correct way to conduct research. This method provides an estimate of the effect of a single variable at fixed conditions of other variables. It assumes the variables to act additively on the response. If the variables do act additively, the factorial does the job with more precision. In general, for  $k$  factors to be analyzed, a  $k$ -fold increase in the number of experiments over factorial design are required by one-factor-at-a-time method. If the variables do not act additively, the factorial design, unlike the one-factor-at-a-time design, can detect and estimate interactions that measure non-additivity. Thus, two level factorial design was chosen over the one-factor-at-a-time design. The reason for not choosing another design which will permit mechanistic modelling was to minimize the number of experiments. With highly non-

linear reaction kinetics, multiple products, and simultaneous phase equilibrium relations the required number of experiments would have been many fold over the present design.

## E.2 CALCULATION OF MAIN EFFECTS: AVERAGING INDIVIDUAL MEASURES OF EFFECTS

What can we find from a factorial design? Analysis of percent extraction of coal will be used as an example. What does factorial analysis tell us about the effect of temperature on percent extraction? Effect is the change in response (e.g. percent extraction,  $y$ ) as we move from the "-" to the "+" version of that factor (e.g. temperature,  $T$ ) Recall Table 19

| <u>Individual measure of the effect of changing T from</u> | <u>Conditions</u> |                   |
|------------------------------------------------------------|-------------------|-------------------|
| <u>375 to 425 °C</u>                                       | <u>P (MPa)</u>    | <u>Q (cc/min)</u> |
| $y_2 - y_1 = 25.7 - 16 = 9.7$                              | - (4.8)           | - (2.2)           |
| $y_4 - y_3 = 29.5 - 18.8 = 10.7$                           | + (13.8)          | - (2.2)           |
| $y_6 - y_5 = 26 - 16.3 = 9.7$                              | - (4.8)           | + (4.1)           |
| $y_8 - y_7 = 31.4 - 19.1 = 12.3$                           | + (13.8)          | + (4.1)           |

The average of the four individual measures which is the main effect of temperature is 10.6. Similarly one can obtain main effects for pressure ( $P$ ), or toluene flow rate ( $Q$ ).

### E.3 CALCULATION OF INTERACTION EFFECTS

In the previous section, the main effect of temperature was 10.6. It is obvious from the data however that the temperature effect is greater at the higher pressure. The variables temperature and pressure interact. A measure of this interaction is supplied by the difference between the average temperature effect at the lower pressure, 4.8 MPa, and the average temperature effect at the higher temperature, 13.8 MPa.

| <u>Pressure</u>             | <u>Average Temperature Effect</u> |
|-----------------------------|-----------------------------------|
| 13.8                        | 11.5                              |
| 4.8                         | 9.7                               |
| Difference                  | 1.8                               |
| TP interaction= $1.8/2=0.9$ |                                   |

Similarly one can calculate other two factor interactions as well as n-factor interactions.

#### E.4 QUICKER METHODS OF CALCULATING EFFECTS: YATES ALGORITHM

It would be very tedious if effects had to be calculated from first principles whenever factorial designs were used. Fortunately, this is not necessary. One can use quicker methods such as Tables of Contrast Coefficients or Yates Algorithm. Yates Algorithm is used in estimation of effects in this research. First, observations are rearranged in the order shown in Table 19. Then, the computations are carried out as shown in Table 33. In general, for a  $2^k$  factorial design  $k$  columns will be generated by adding and subtracting appropriate pairs of numbers. The first divisor will be  $2^k$  (for the average effect) and the remaining divisors will be  $2^{k-1}$ . The arithmetic of computations can be checked by looking into the sum of the squares of each column. In general, for a  $2^n$  factorial design, in column  $n$  the sum of the squares should be  $2^n \Sigma y^2$ . For example, in Table 33

$4433.6 \times 2 = 8865$  or  $4433.6 \times 2 = 17734.4$  or  $4433.6 \times 2 = 35461.2$

TABLE 33

## Calculations for Carrying Out and Checking Yates Algorithm

## Sample Calculation for Effect Analysis for Percent Extraction with Toluene

| Average Results | (1)          | (2)          | (3)          | Division | Estimates     | Effect       |
|-----------------|--------------|--------------|--------------|----------|---------------|--------------|
| 16<br>25.7      | 41.7<br>48.3 | 90<br>92.8   | 82.8<br>42.4 | 8<br>4   | 22.85<br>10.6 | Average<br>T |
| 18.8<br>29.5    | 42.3<br>50.5 | 20.4<br>22.0 | 14.8<br>3.6  | 4<br>4   | 3.7<br>0.9    | P<br>TP      |
| 16.3<br>26.0    | 9.7<br>10.7  | 6.6<br>8.2   | 2.8<br>1.6   | 4<br>4   | 0.7<br>0.4    | Q<br>TQ      |
| 19.1<br>31.4    | 9.7<br>12.3  | 1.0<br>2.6   | 1.6<br>1.6   | 4<br>4   | 0.4<br>0.4    | PQ<br>TPQ    |

Sum of the Squares Check:

4433.6                  8865                  17734.4                  35461.2

Solid line ————— Denotes addition

Dashed line ----- Denotes subtraction of top number from bottom number

### E.5 SAMPLE CALCULATION: STANDARD DEVIATION

When replicates are made, the estimate of the standard deviation of a single observation can be used to obtain standard deviation of the effects through pooled estimate of the run averages. However, in this research only two extreme conditions are replicated. Thus, the standard deviation can not be estimated using the technique outlined above. However, we can estimate a standard deviation if certain assumptions are made. If all the three and four factor interactions are assumed negligible, these higher order interactions would measure differences arising principally from experimental error (noise). In this research, 3 and 4 factor interactions are used to calculate the standard deviations in all  $2^4$  designs.

$$S_d = [\Sigma(\text{effect})^2 / (\text{no. of effects})]^{1/2} \quad \text{Eq. E.1.}$$

For effect analysis on asphaltols fraction

$$S_d = [((-0.04)^2 + (-0.03)^2 + (0.02)^2 + 0^2 + 0^2) / 5]^{1/2} = 0.024$$

## E.6 DIAGNOSTIC CHECKS

There are two problems which arise from assessment of effects from unreplicated factorials:

1. Real and meaning high-order interactions occur
2. A selection of the meaningful effects has to be made.

A selection based on the standard deviations from higher order interactions does not confront the first of these problems. A method by which effects are plotted on normal probability papers often provides an effective way of overcoming both difficulties [99]. First, the effects and their identities are ordered and their probabilities are found (See Table 34 for sample) Then, they are plotted on normal probability paper as shown in Figure 29. The effects which do not fit well on a straight line are the effects whose existence can not be easily explained as chance occurrences. For example, the effects of time and temperature on asphalt fraction can not be explained by noise in Figure 29. The effects of pressure and temperature-pressure interaction are significant too. However, their effects are much less than that of temperature and time.

TABLE 34

The Fifteen Ordered Effects and Probability Points,  $P_i$   
 Effect Analysis of Relative Asphaltols Fraction in Extract

| Order           | 1     | 2     | 3     | 4     | 5             | 6             | 7            | 8     | 9    | 10             | 11            | 12           | 13           | 14   | 15         |
|-----------------|-------|-------|-------|-------|---------------|---------------|--------------|-------|------|----------------|---------------|--------------|--------------|------|------------|
| Effect Identity | -0.11 | -0.04 | -0.04 | -0.03 | -0.03         | -0.02         | -0.02        | -0.01 | 0    | 0              | 0             | 0.01         | 0.02         | 0.04 | 0.16       |
| Effect Estimate | T     | TP    | TPQ   | PQ    | TP $\Delta t$ | PQ $\Delta t$ | Q $\Delta t$ | Q     | TQ   | TPQ $\Delta t$ | TQ $\Delta t$ | P $\Delta t$ | T $\Delta t$ | P    | $\Delta t$ |
| P               | 3.3   | 10.0  | 16.7  | 23.3  | 30.0          | 36.7          | 43.3         | 50.0  | 56.7 | 63.3           | 70            | 76.7         | 83.3         | 90.0 | 96.7       |

$$P = 100(i - \frac{1}{2})/15$$

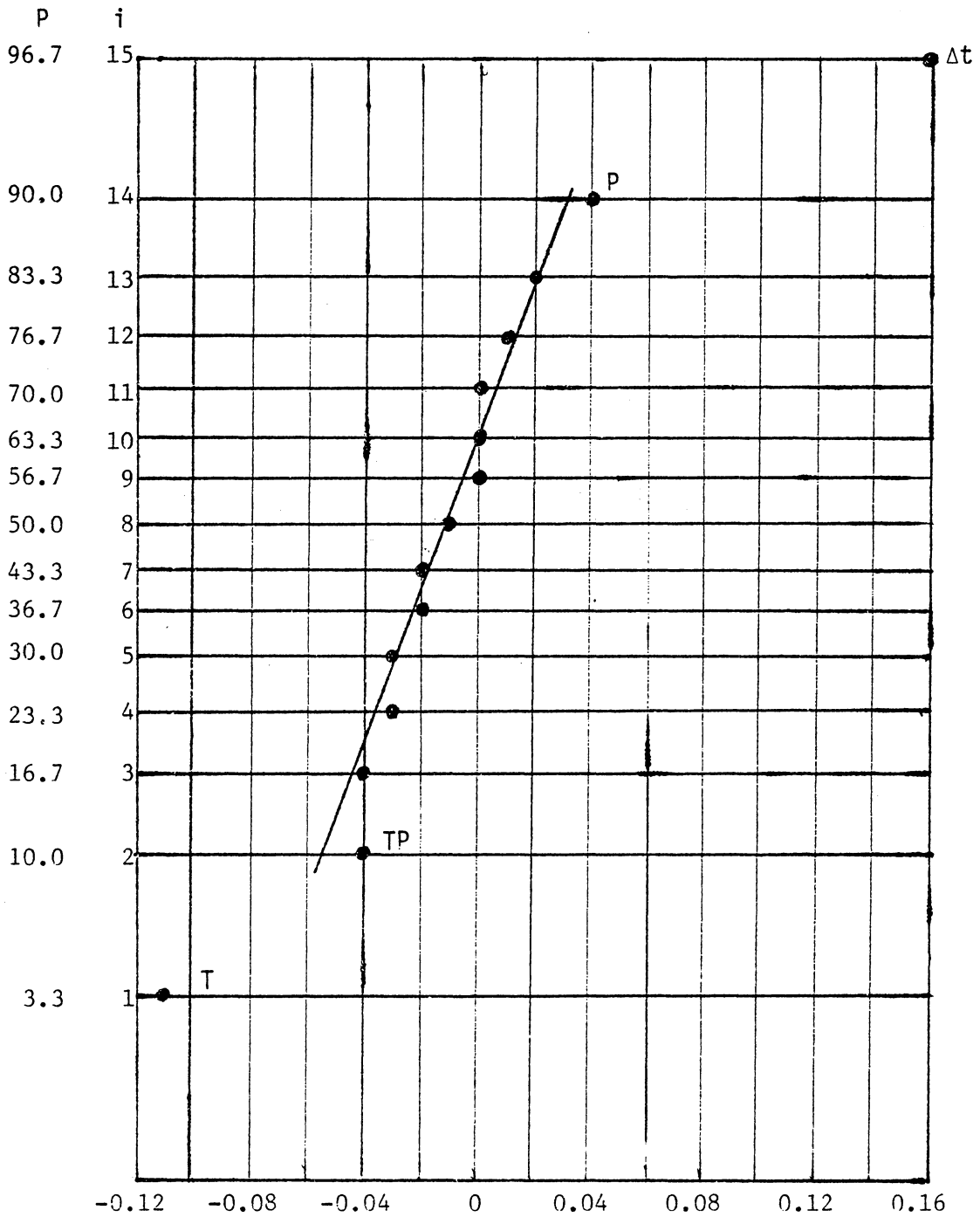


Figure 29: Normal Plot of Effects on Asphaltols Distribution

## Appendix F

### ASSUMPTIONS FOR COST ESTIMATION

#### F.1 COST ASSUMPTIONS

The assumptions used in economic analysis are:

1. Feed coal has a heating value of 23333 kJ/kg dry coal.
2. CE plant cost indices.  
November 1981 : 315  
Mid. 1978 : 219  
Mid. 1977 : 205
3. Capacity scale factors are:  
0.9 if multiple parallel trains are used to achieve the capacity change  
0.6 if single train is used
4. Total capital investment =  $1.63 \times \text{bare plant cost}$
5. Maintenance cost is 3% of the capital cost
6. Local taxes and insurance sum to 5% of the capital cost
7. Fringe benefits total up to 40% of labor
8. On-stream time of processes are assumed 328.5 days
- 9.

Labor Requirements

| <u>Category</u>        | <u>Rate (\$/h)</u> | <u>People</u> |
|------------------------|--------------------|---------------|
| Operator               | 14                 | 120           |
| Operator Supervisor    | 20                 | 25            |
| Maintenance labor      | 16                 | 150           |
| Maintenance Supervisor | 15                 | 30            |
| Administrative         | 15                 | 30            |

# APPENDIX G

## PRODUCT SUMMARY FOR COAL LIQUEFACTION PROCESSES

Basis: Plant feed rate = 23,000 tons/day dry coal

| <u>Process</u> | <u>Product</u>   | <u>Quantity</u><br><u>(amount/day)</u>             |
|----------------|------------------|----------------------------------------------------|
| SRC I          | SRC Solid        | 9890 tons                                          |
|                | No. 6 Fuel Oil   | 1190 m <sup>3</sup>                                |
| SRC II         | LPG              | 875 m <sup>3</sup>                                 |
|                | Naphtha          | 1700 m <sup>3</sup>                                |
|                | Fuel Oil         | 7200 m <sup>3</sup>                                |
|                | Gas              | 65400 Standard m <sup>3</sup>                      |
| EDS            | Propane          | 520 m <sup>3</sup>                                 |
|                | Butane           | 557 m <sup>3</sup>                                 |
|                | Naphtha          | 3165 m <sup>3</sup>                                |
|                | Fuel Oil         | 4565 m <sup>3</sup>                                |
|                | Gas              | 118600 Standard m <sup>3</sup>                     |
| M-Gasoline     | Premium Gasoline | 8380 m <sup>3</sup>                                |
|                | LPG              | 1160 m <sup>3</sup>                                |
| F-T            | Gasoline         | 2894 m <sup>3</sup>                                |
|                | LPG              | 2898 m <sup>3</sup>                                |
|                | No. 2 Oil        | 190 m <sup>3</sup>                                 |
|                | No. 6 Oil        | 318 m <sup>3</sup>                                 |
|                | Gases            | 362100 standard m <sup>3</sup>                     |
| SGE I          | Extract          | 22727 x % dAF extract                              |
|                | Char             | 22727 x .94 x .82 - extract <sup>1</sup><br>amount |
| SGE II         | SNG              | 7.4 J/100J feed                                    |
|                | LPG              | 2.4 J/100J feed                                    |
|                | Naphtha          | 28.9 J/100J feed                                   |
|                | No. 2 Oil        | 8.9 J/100J feed                                    |
|                | No. 3 Oil        | 20.3 J/100J feed                                   |
| SGE III        | Naphtha          | 20J/100J                                           |
|                | No. 2 Oil        | 6J/100J                                            |
|                | No. 3 Oil        | 14J/100J                                           |
|                | Premium Gasoline | 4190 m <sup>3</sup>                                |

<sup>1</sup>18% of char is used for process heating and the process efficiency to products (char and extract) is 94%.

## Appendix H

### SAMPLE CALCULATIONS: ECONOMIC ANALYSIS

The process economics calculations for all alternatives but SGE processes were updates for time and value factors of an ESCOE study [97]. The SGE analysis was an update and scaling of a study made by Catalytic Inc.[92] to the same basis as the ESCOE analysis. For material balance of SGE II, a paper by Whitehead [90] was used. SGE III process is a conceptual complex where SGE residua, char, is fed to M-Gasoline process. The material balance and cost calculations for this alternative are noting more than back-of-an-envelope-type analysis. After coal preparation, 40% (dry weight basis) of coal is extracted. Residua, which is equivalent to 50% of coal feed in energy basis, is fed to a gasifier. Thus, we have 11500 t/day M-Gasoline process. The premium gasoline formed is, then, half of the value reported in ESCOE analysis.

Premium Gasoline amount=  $8380/2 = 4190 \text{ m}^3/\text{d}$

For every 100 MJ coal feed, the SGE process would yield

7.4 MJ SNG

2.4 MJ LPG

28.9 MJ Naphta

8.9 MJ No.2 oil

20.3 MJ No.3 oil

for a self sufficient plant where residua are gasified to meet the hydrogen and heat requirements (This is SGE II). To expect to have sum of both yields, M-Gasoline and SGE II, would be overly optimistic since that would be equivalent to energy efficiency of 93 %. So an overall 66% energy efficiency was assumed for the complex. There was no SNG or LPG produced since they were used to produce hydrogenation requirements. M-Gasoline section product is equivalent to 26 % of the complex and the calculated SGE section output is

20 MJ/100MJ feed Naphta

6 MJ/100MJ feed No. 2 oil

14 MJ/100MJ feed No. 3 oil

Then, the weighted output of the process can be calculated

$$\sum f_i B_i = 1 \times 4190 \text{ m}^3/\text{d} \times 33200 \text{ MJ}/\text{m}^3 \times 328.5 \text{ d} + (0.88 + 0.82) \times .2 \text{ J}/\text{J}$$

$$\text{feed} \times 23000 \text{ t coal}/\text{d} \times 23333 \text{ MJ}/\text{t} \times 328.5 \text{ d} = 1.06 \times 10^{11} \text{ MJ}/\text{year}$$

The capital cost of the process is calculated as follows:

The capacity of gasification, reactor, and conversion sections of M-Gasoline process were half of the capacity for which ESCOE cost data exists and this cost data was updated by a scale factor of 0.9. The auxiliary facilities, such as coal preparation, are shared and the cost of extraction, separation, and hydrogenation sections of SGE are fully added. Then they are updated for time using the scale factors given

in Appendix F. Finally, the capital cost is found as 163% of this bare plant cost. The cost of the complex is 2060 million dollars. The maintenance cost is taken as 3% of capital cost while local tax and insurance is 5% of the capital cost. Thus, maintenance cost is 62 million dollars, and the total of local tax and insurance is 103 million dollars. The labor cost is taken same as SRC and is 16 million dollars. The catalyst and chemical costs are 11.5 million dollars. The coal cost is same as in other processes 287 million dollars. For a capital recover factor (k) of 0.16 the reference product price can be found as

$$P_R = (F + M + kC)/(\sum f_i B_i) \quad \text{Eq. 7.3}$$

$$P_R = (287+11.5+16+62+103+0.16*2060)/1.06*10^{14}$$

$$P_R = 7.61 \text{ \$/Million kJ}$$

Similarly, reference product for other capital recovery factors can be calculated. This reference product price can be compared to the reference product price of other processes or the todays market price 8.77 \$/Million kJ. Prices, for the actual products, which will break-even can be calculated from Eq. 7.2. For example, premium gasoline from SGE III can be sold at 7.61 \$/Million kJ since value factor for premium gasoline is 1.

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# Supercritical Extraction of Coal

By

Aydin Kemal SUNOL

(ABSTRACT)

Supercritical extraction of coal is removal of a select fraction of the coal by a solvent which is slightly above its critical temperature and above its critical pressure. The objective of this dissertation was to understand the mechanism of supercritical extraction, to test some promising solvents, and to explore the design implications of the findings.

Supercritical extraction of Wyodak coal was studied by passing various solvents upwards through a 15-gram sample of 12-20 mesh coal. For the high temperature experiments, the coal was heated to 375°C and 425°C in a hot fluidized sand bath. The main solvent used was toluene, while extractions with n-pentane, xylene, methanol, and water were also done. The extract was fractionated into oils, asphaltenes, and asphaltols. Supercritical extraction of coal near pyrolysis temperatures affords an opportunity to remove unstable

decomposition products from the reaction environment to avoid repolymerization and pore blinding. Stronger aromatic solvents removed the decomposition products as they were formed. However, product degradation even with the strongest solvents was inevitable during the initial few minutes.

For the low temperature experiments (below 95°C), the solvent was carbon dioxide. Effects of liquid entrainers (pre-mixed with the coal), and heat-pretreatment of the coal (at 400°C for 1 hour) were also studied. The major difference between the high and low temperature extractions was that coal reactions occurred at high temperatures simultaneously with solubilization. Extraction of raw coal and heat-pretreated coals with carbon dioxide was negligible. However, extractions as high as 12% were possible when small amounts of liquid entrainers such as pyridine, toluene, and tetralin were pre-mixed with the coal. The entrainers were almost completely recovered with the extract.

The process design implications of the supercritical extractions of coal were studied using the method developed by ESCOE (Engineering Societies Commission On Energy Inc.). Preliminary design estimates showed that the following supercritical extraction processes were possible alternatives to present commercialization efforts and deserve further attention:

1. Gasification of the extraction residua;
2. Satellite plants operating in parallel with coal-burning utilities;
3. Entrainer-aided extraction.