National Library of Canada
Bibliothèque nationale du Canada

Canadian Theses Service
Service des thèses canadiennes

Ottawa, Canada
K1A 0N4

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

NL-339 (r. 88/04) c

Canada

THE UNIVERSITY OF ALBERTA

SOLVOLYTIC EXTRACTION OF COALWITH HIGHER AROMATIC SOLVENTS

by

GLEN EDWARD KOROPCHUK

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

IN

MINERAL ENGINEERING

DEPARTMENT OF MINING, METALLURGICAL AND PETROLEUM ENGINEERING

EDMONTON, ALBERTA

SPRING 1989

ISBN 0-315-52996-2

THE UNIVERSITY OF ALBERTA

RELEASE FORM

NAME OF AUTHOR GLEN EDWARD KOROPCHUK

TITLE OF THESIS SOLVOLYTIC EXTRACTION OF COALWITH HIGHER AROMATIC SOLVENTS

DEGREE FOR WHICH THESIS WAS PRESENTED MASTER OF SCIENCE

YEAR THIS DEGREE GRANTED SPRING 1989

Permission is hereby granted to THE UNIVERSITY OF ALBERTA LIBRARY to reproduce single copies of this thesis and to lend or sell such copies for private, scholarly or scientific research purposes only.

The author reserves other publication rights, and neither the thesis nor extensive extracts from it may be printed or otherwise reproduced without the author's written permission.

(SIGNED) Glen Koropchuk

PERMANENT ADDRESS:

11404 - Malmo Rd.
Edmonton, Alberta, Canada
T6H 4M2

DATED April 14 1989

THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled SOLVOLYTIC EXTRACTION OF COALWITH HIGHER AROMATIC SOLVENTS submitted by GLEN EDWARD KOROPCHUK in partial fulfilment of the requirements for the degree of MASTER OF SCIENCE in MINERAL ENGINEERING.

....
Supervisor

....

....

....

Date.....April 14, 1989..........

Dedication

For my Parents

Your faith in me and the direction and encouragement that you have given to me in all my endeavours has made all the difference.

Abstract

The effects of solvents on coal and coal derivatives have been studied since the mid-eighteenth century when coal tars began to be valuable chemical intermediates and upgradable feedstocks. Contemporary coal solvent extraction research has focused on two aspects, (i) generation of acceptable hydrogenable feedstock, and (ii) production of soluble matter more amenable to chemical investigation. These two objectives put different constraints on the solvent action desired. In chemical studies a solvent must have a minimum or predictable interaction with the coal while extracting material representative of the whole coal or a particular moiety. In contrast, conversion of coal to a hydrogenation feedstock requires conversion of the coal into soluble or low-melting solid material which can be processed further. This demands extensive chemical alteration of the coal substance and, usually, the ability of the solvent to donate hydrogen to the coal.

Besides problems incurred by the disparate demands on potential coal solvents, difficulties in reporting solubilization findings have clouded much of the extant literature. Extraction yields obtained through the use of so-called 'specific' solvents such as pyridine or ethylenediamine may be misleading because of failure to distinguish between 'true' solutions and colloidal dispersions. Another aspect of solvent extraction not properly discussed in the literature (which underscores some deficiencies in present understanding of coal structure) is why such compounds as α-naphthol, anthracene or phenanthrene, none of which donate H_2, can seemingly 'dissolve' 70-90% of bituminous coals at temperatures as low as 300°C.

This study was designed to address some of the above concerns and, in particular, to assess whether extraction of coals with α-naphthol, phenanthrene or like solvents in a solvolytic regime could offer a viable first step towards liquefaction. A selection of six Canadian coals, sampling Carboniferous bituminous and Cretaceous bituminous and subbituminous coals, was used to gain a better understanding of reported disparate behaviour exhibited by Eastern and Western Canadian coals. The experimental procedure used micro-bomb solvent extraction, and determination of solubility was based on formation of THF-soluble matter, by definition representing preasphaltenes and lighter hydrocarbons.

Acknowledgement

The preparation of a thesis entails a great deal of time and effort for which one person receives the recognition. In most cases, though, a considerable amount of assistance has been availed by people who become involved with the project voluntarily or through the coercion of the author. In appreciation of such contributions I would like to recognize various individuals whom I am particularily indebted.

My supervisor, Dr. Norbert Berkowitz, is to be commended for encouraging me to develop and pursue an interest in coal science that expanded the horizons of my Mining Engineering training. I especially thank Dr. Berkowitz for his patience and support when my spirits were down and his eminent help when I was charting unfamiliar grounds in organic chemistry. For the most part, Dr. Berkowitz allowed me to 'fly by the seat of my pants', so to speak, which wasn't always the most expedient path, but it ultimately was the most rewarding. The technical assistance and cameraderie provided by Jamie Calderon was greatly appreciated. The practical experience I gained in the lab was invaluable and it was enhanced considerably by a liberal sprinkling of fun. The efforts of my sister, Cara, in helping to prepare and edit the text as well as her tolerance of my somewhat erratic writing style deserve a special thank you. Without her, I would have burned considerably more midnight oil. Lastly, I would like to acknowledge my friends for their support during the course of this undertaking. They accepted and respected the committment I made for this project and yet when I needed a break they were there to give me a rest from the pressure.

Many people have contributed to this thesis but ultimately what is presented here is my responsibility. Any shortcomings or errors are accepted as mine alone.

Table of Contents

Chapter Page

List of Tables

List of Figures

1. An Introduction to Coal Extraction

This research centered on solvolytic extraction of a suite of Canadian subbituminous and bituminous coals, and examined three distinct aspects of such extraction. The first question posed was whether solvent extraction could offer an 'attractive' route to readily upgradable hydrocarbons. The second thrust related to behavioural differences between Western Canadian subbituminous and bituminous coals that could affect extraction and/or subsequent liquefaction. The third aspect was a brief investigation of the differing levels of extractability exhibited by the older Eastern Canadian Carboniferous bituminous coals and the younger Western Canadian Cretaceous coals of similar rank [1].

Extant literature suggests that Western coals behave differently in liquefaction regimes than coals from the Eastern Seaboard or the U.S. Interior [2]. Coal liquefaction studies have demonstrated that, in direct liquefaction, Western Canadian coals require more severe conditions than Eastern coals and that the overall reactions tend to be fraught with more problems. The differences exhibited may be ascribed to the different 'molecular' structures of the coals caused by different diagenetic and/or subsequent metamorphic histories.

In order to facilitate comparative studies, it was decided to operate in a solvolytic regime. Briefly, this involves extraction in the temperature range of 225-350°C under autogenic or artificially induced pressures. It was also decided that the solvents used for extraction and for determining solubility or a 'conversion percentage' would not be 'specific'. These key provisions were incorporated for two interrelated reasons.

The first intention was to operate under low-severity conditions in order to obtain information that would be more practical from an engineering standpoint. The relatively low temperatures and pressures involved in the experimental work enable a simplicity of design

---

[1] During Lower Carboniferous (or Mississippian) times, 360-270 million years ago, coal began to be deposited in Nova Scotia and New Brunswick as well as other areas in Eastern North America and Western Europe. The conditions for coal formation in Western Canada and the United States became suitable during the Cretaceous era, 144-65 million years ago. Berkowitz, N. et al. briefly discussed this disparate behaviour in Fuel, 1974, 53, 141

[2] Whitehurst, D.D., Farcasiu, M., Mitchell, T.O., and Dickert, Jr., J.J.; 1st Rept. EPRI Project # RP-410-1 Feb., 1976

that might offer benefits in any subsequent upscaling of the procedure. High-severity processes, such as Bergius hydrogenation, have been technically proven for over 60 years, but are currently not economically viable under normal circumstances. It was hoped that information obtained from this experimentation would be useful in delineating a low-severity route towards upgrading Western Canadian coals.

The second proviso arose from two aspects of solvent action on coal. So-called specific solvents, such as pyridine, tend to disperse coal as well as bring some of it into true (molecular) solution. This has caused problems in reporting the effects of these solvents on different coals because the distinction between these two phases is often unspecified. Additionally, for practical purposes, hydrocarbon moieties heavier than those defined as asphaltenes are essentially useless as an upgradable petrochemical feedstock. Therefore, from an engineering point of view, it makes little sense to solvate coal with a harsh solvent that yields an extract composed of preasphaltenic and heavier matter.

The experimental work was undertaken under the aforementioned constraints. While this approach may have precluded extensive conversion of Canadian coals to soluble material, it was expected to provide data of 'practical' value for better understanding of the action of solvents on Canadian coals.

The terminology used in fuel science studies can be confusing. In fact, due to ambiguities in the reporting of experimental procedures, and the lack of standards in the definition of key indicators such as extractability, solubility and percent conversion, even persons knowledgeable in this particular field must exercise great caution in interpreting published findings and recording their own. Therefore, it may be helpful to introduce solvent extraction in some detail, and to put it into perspective with related processes in the field of coal upgrading and/or fuel science. It is also imperative to fully appreciate the vagaries of the definition of 'process efficiency' as it refers to coal extraction.

1.1 Coal Extractability

Coal extractability has been found to depend critically on the coal-solvent complex involved. Low and high rank coals tend to behave quite differently under similar conditions, and the nature of the solvent, as well as the extraction conditions, such as duration, pressure, availability of hydrogen, and in particular temperature, have marked effects on the extract yields. Because of the dependence on extraction temperatures, three distinct regimes can be defined: [3]

<u>Extraction Regimes</u>

1. Solvent extraction at or below the atmospheric boiling point of the solvent, normally below 200°C; commonly performed in Soxhlet apparatus. This classification is generally split into two distinct groups, depending on whether non-specific or specific solvents[4] are used. Respectively referred to as <u>Non-Specific</u> and <u>Specific Extraction</u>.

2. Solvolytic extraction at temperatures between approximately 200-350°C, under autogenic or artificially induced pressures. Referred to as <u>Solvolytic Extraction</u> or <u>Extractive Disintegration</u> [5].

3. Extraction near 400°C, when incipient active thermal decomposition of the coal drastically enhances the changes begun in the solvolytic regime. Depending on the degree of coal hydrogenation by the solvent or the reaction atmosphere, either of which may be a hydrogen donor, <u>complete</u> or <u>partial</u> liquefaction will occur. Other opportunities offered by this temperature domain are supercritical gas extraction, and solvent refining of coal (SRC). Referred to as <u>Complete Solubilization</u> or <u>Extractive Chemical Disintegration</u>

---

[3] Oele and Van Krevelen have delineated four groups, the first two being subgroups of the first solvent extraction group here specified.

[4] Dryden, I.G.C.; Nature (London), 1948, <u>162</u>, 959

[5] Oele, A.P., Waterman, H.I., Goedkoop, M.L., and Van Krevelen, D.W.; Fuel, 1951, <u>30</u>, 169

Before discussing coal extraction further, it may be helpful to define some of the terms used to describe coal/solvent interactions. (Some terms are subjective, and open to interpretation, but the following may serve as guidelines.)

As a statistic, extractability is much easier to define than solubility, and may be expressed [6] as an absolute amount of extract obtained under specified conditions. It does not matter what form the extract is in unless one wishes to report specifically the preasphaltene, asphaltene and oil fractions of the extract. By definition, preasphaltenes are soluble in tetrahydrofuran (THF), and insoluble in benzene or toluene. Asphaltenes are benzene- and toluene-soluble, but insoluble in pentane. Low molecular weight oils are pentane-soluble [7]. Solubility, on the other hand, is described by Berkowitz as being "the concentration of a solute in a solution in equilibrium with excess soluble matter". [8] This equilibrium is exceedingly difficult to achieve because coal extracts are inherently unstable. A coal extract exhibiting most of the characteristics of a true solution, including apparent optical clarity, may, even in the absence of oxygen or light, reaggregate into colloidally dispersed matter.

A colloidal dispersion differs from a true molecular solution in that it consists of dispersed particles rather than molecules. These particles may be too small to be resolved at low magnification. They may diffract a beam of light, but this test of optical clarity depends on the resolution of the optical equipment at hand. The use of a low power microscope could mislead a researcher into thinking that he saw a genuine solution.

The misinterpretation of colloidal suspensions as solutions has been a continuing problem when recording the extractability of coals with certain solvents. So-called specific solvents, such as pyridine, other heterocyclic bases and primary aliphatic amines, tend to disperse coal as well as bring it into true solution. This phenomena has been documented by

---

[6] Dryden, I.G.C.; Fuel, 1951, 30, 39-40. "Extractability is measured by the percentage yield obtained on exhaustive extraction and is affected by the association of insoluble residue with the soluble material; solubility is defined as the concentration of solution in equilibrium with excess of the soluble extract, or more loosely as the property of forming an equilibrium solution of considerable concentration (a deep brown colour). Irreversible aggregation on the colloidal scale can prevent attainment of the natural equilibrium."

[7] Berkowitz, N. The Chemistry of Coal. Elsevier, Amsterdam, 1985, p. 303

[8] Ibid., p. 275

Kann [9] in his work with ethylenediamine extracts of coal. He examined coal extracts (in solution in ethylenediamine) microscopically under high magnification, and found that much of the 'dissolved' matter consisted of discrete particles with diameters of several hundred Angstroms. A researcher thus may document 80% extractability of a bituminous coal with pyridine when, in fact, it is 30% solvated and 50% dispersed. Reported results are consequently difficult to compare. In many instances the efficiency of a particular extraction regime is measured by so-called percent conversion, which may be defined by:

$$\frac{org_i - org_r}{org_i} X\ 100$$

where org_i is the initial mass of solid organic material and org_r the solid organic mass residual after extraction.

This expression is ambiguous because there is more than one basis on which to calculate org_i and org_r. For example, one may perform mass balance calculations on either an ash- or a mineral matter free basis [10] which can lead to varying values for percent conversion. However, this problem is compounded by the fact that solvents such as pyridine, which are heavily sorbed and tend to disperse rather than solvate coal, are often used because of their potency. Therefore one must carefully define the solvent and extraction regime utilized to extract the organic fractions. Special attention must be paid to defining the solvent process which yields the ultimate extract, and hence, the residue for which percent conversion is calculated. All conversion determinations raise technical problems which must be minimized, and all procedures must be fully documented.

---

[9] Kann, L; Fuel, 1951, 30, 47

[10] Gluskoter, H.; Fuel, 1965, 44, 285. Mineral matter determinations are carried out in a low-temperature asher which oxidizes the organics without decomposing minerals such as carbonates. This is in contrast to conventional ashing carried out at 900°C.

2. Action of Solvents

2.1 Introduction

The history of solvent extraction of coal, and studies of the action of solvents on coal, can be traced back to the antecedent use of coal for metallurgical purposes. Early iron and steel makers relied on wood for production of charcoal, which they utilized as an efficient fuel, as well as a source of carbon essential for hardening steel. In the late sixteenth century, English ironmasters were faced with a governmental decree prohibiting the use of wood for iron-making, and they turned, first to coal, and later to coal-derived coke, as a readily-available carbon source. The high-temperature carbonization (≥ 900°C) of coal proved to be viable, but in addition to yielding a high-heat content, carbon-rich coke, a seemingly valueless tar residue was also produced.

Low-temperature (≤ 700°C) carbonization was originally designed to manufacture town gas for residential and commercial lighting, and to produce smokeless char for domestic heating and cooking. Dating from the late eighteenth century, commercial low-temperature carbonization developed and thrived in industrialized Europe where the energy economies were founded on coal. The tars produced by these high- and low-temperature carbonization processes were originally considered annoying waste materials, but this viewpoint changed dramatically in the mid-nineteenth century, when development of a modern chemical industry in Western Europe brought about the realization that coal tars represented important feedstocks and chemical intermediates.

A great deal of interest centered on distillation and fractionation of the tars, because isolation and extraction of a myriad of chemical compounds suddenly attained economic importance. Solvents began to be used in these operations because of their ability to selectively extract certain fractions of the tarry material. The focus shifted from analysis of coal tars after Bedson's 1902 discovery that bituminous coals could be substantially solvated in hot pyridine [11]. This prompted redoubled efforts to find more powerful solvents in order to

---

[11] Bedson, P.P.; J. Soc. Chem. Ind. London, 1902, 21, 241

gain more information about coal structure and analyze the product liquids and semi-solids.

Additionally, some early solvent research in the 1920's and 1930's focused on isolation of a hypothesized coking principle which was considered to be responsible for the caking abilities of certain coals. As production of high quality steels was of great national interest, as well as very profitable, this research was encouraged. Many scientists engaged in this work and actively pursued the matter of a coking principle. Although no definitive coking principle was ever found, solvent research has served to emphasize the intricacies of coal structure.

Work in the 1930's shifted towards exploring coal liquefaction either directly or via hydrogenation of industrially produced tars [12]. Solvents have played a significant role in this research through their abilities to solvate the coal and, in some cases, to act as a convenient hydrogen donor. These efforts continue in the present as the quest for a low-severity coal liquefaction route continues to be pursued.

The first coal-extraction regime considered below, formally designated as solvent extraction, is associated with low-boiling solvents, and is generally carried out in a standard Soxhlet apparatus. Following Dryden [13], most researchers have described two distinct solvent groupings whose behavioural differences, under these relatively mild conditions, are quite marked. These categories have been labelled specific and non-specific, with the former capable of extracting as much as 25-40 wt. % of a coal, and the latter generally producing no more than 2-4 wt. % extracts at their normal boiling points [14].

2.2 Non-specific Extraction

Non-specific solvents are now mainly of academic interest. The group includes hydrocarbons (n-hexane, benzene, toluene, etc.), chlorinated hydrocarbons (chloroform, ethylene dichloride, etc.), alcohols (methyl, ethyl, n-butyl, etc.), ethers (diethyl ether,

---

[12] One can also produce liquid hydrocarbons from coal via gasification and subsequent Fischer-Tropsch synthesis. This is sometimes referred to as 'indirect' coal liquefaction.

[13] Dryden, I.G.C.; Fuel, 1951, 30, 39-44.

[14] Berkowitz, N. The Chemistry of Coal , Elsevier Science Publishers B.V., Amsterdam, 1985, p. 276

various glycol ethers, etc.) and ketones (acetone, methyl ethyl ketone, etc.).

Such solvents typically have low boiling points, and cause no thermal degradation of the coal during extraction. The extracts are usually fossil waxes and resins derived from the original organic detritus, but not integral components of the coal substance. They are usually occluded in the interstices of the coal matrix. Such so-called Montan waxes and resins have been extracted for industrial uses, but now command no commercial interest, because similar materials can be produced synthetically from petroleum. In most cases, non-specific extracts are unsuitable for structural analysis of coal because they are not representative of the coal entity. Accordingly, low-severity solvent extraction as a means for coal processing has been primarily focused on so-called specific solvents.

2.3 Specific Extraction

Ever since Bedson's work with hot pyridine, researchers have been pursuing coal solvents with good extractive properties at temperatures below 200°C. Such temperatures are well below the onset of thermal decomposition of coal (≃400°C for most coals); and the attainable extract yields of 25-40 wt.% [15] suggest a potential for economically viable, low-severity solubilization. The resultant extracts could be used as a feedstock for second stage hydrogenation which would produce a stable syncrude.

Relatively strong specific solvents may be classified into two major groups- *nucleophilic solvents,* which include aliphatic amines (ethylamine, ethylenediamine, etc.) and heterocyclic tertiary bases (pyridines, picolines, etc.); and *ampholytic solvents,* such as phenolic compounds (phenol, cresol, etc.) or specific carbonyl compounds (acetophenone, furfural, etc.).

In addition to the obvious structural differences between these two solvent groupings, there is also an apparent mechanistic difference. Oele, et al. [16] recorded in their 1951 work that whereas nucleophilic solvents operated quite effectively at room temperature, ampholytic

---

[15] Berkowitz, N. The Chemistry of Coal. Elsevier Science Publishers B.V., Amsterdam, 1985, p. 276

[16] Oele A.P., Waterman, H.I., and Van Krevelen, D.W.; Fuel, 1951, 30, 169

solvents only proved to be useful at temperatures above 100°C.

2.3.1 Factors Governing Extract Yields

In their definitive 1951 work with bituminous coals, Oele et al. (1951) pointed out that the extraction process, and in particular, extraction with specific solvents, is governed by the nature of the solvent, the particle size of the coal to be extracted, the duration of extraction, the temperature of extraction, as well as some other less important factors.

2.3.1.1 Nature of the Solvent

As mentioned previously, specific solvents are either nucleophilic or ampholytic, and it has been postulated that solvent power is associated with a nitrogen or an oxygen atom containing an unshared pair of electrons [17]. The degree of solvent power is, however, strongly influenced by the availability and accessibility of this electron pair. Where it is partly shielded by steric hindrance and cannot freely interact with functional groups in the coal matrix, solvent capability is diminished. This is why alkyl groups tend to reduce solvent power: thus, diethylamine will precipitate some coal extract from solutions in specific solvents while primary amines generally are good basic solvents. Secondary and tertiary amines are poor coal solvents, being unable to even swell coal. Other interfering influences include excessive hydrogen bonding, (for example, in amines when diluted with water), and the participation of the lone electron pair in resonance of the molecular nucleus (for example, in aniline and pyrrole as contrasted with benzylamine and pyridine) [18].

The most favourable conditions occur in organic compounds containing at least one primary amino group attached to a methylene group (e.g., ethylenediamine) and in certain heterocyclic bases (e.g., pyridine). Other things being equal, nitrogen compounds are better solvents than compounds containing oxygen. This is illustrated by the fact that

---

[17] Dryden, I.G.C.; Fuel, 1951, 30, 39
[18] Pauling, L.: The Nature of the Chemical Bond, London, 1947

primary amines are better solvents than alcohols of similar molecular size[19].

Also characteristic of specific solvents is an ability to swell the coal upon imbibition. In bituminous coals solvent imbibition and subsequent swelling can be directly correlated with extract yields, but in low rank coals this relationship does not hold true. Malanowitz (1932) found that lignites combine high imbibition with negligible swelling and extractability [20].

Massive swelling of the coal matrix enhances extractability in two ways. First, the pores and interstitial voids are expanded, allowing greater access and surface contact for the solvent. There is less obstruction to the passage of heavy molecular entities and colloidal material from the insoluble coal skeleton and hence, quicker, more complete solubilization. Secondly, and perhaps of greater importance when dealing with specific solvents, volume changes tend to be exothermic and add energy to the system, thereby enhancing the kinetics of solvation. This may lead to extensive exfoliation which results in partial or substantial disintegration of the sample.

Although swelling ability tends to be a very good indicator of a solvent's effectiveness in extracting coal, there are some exceptions. The most notable is methanol, which causes extensive swelling when imbibed by coal and yet is a non-specific solvent. Other factors obviously are at work, bolstering a specific solvent's extracting power in relation to ineffective or non-specific solvents.

One characteristic, noted by Dryden (1951) in his work on solvent extraction at lower temperatures [21] [22], is that specific solvents tend to extract and <u>disperse</u> considerable quantities of low rank coals. They also tend to 'stabilize' extracts, so that when extract solution was diluted with water and then precipitated with hydrochloric acid, the precipitate, after washing and drying under vacuum at 105°C, is soluble in specific as well as in some non-specific solvents.

---

[19] Dryden, I.G.C.; Fuel, 1951, <u>30</u>, 39

[20] Malanowitz, L.; Chim. Ind. (Paris), 1932, <u>28</u>, 36

[21] Dryden, I.G.C.; Fuel, 1951, <u>30</u>, 39

[22] This particular work was done on low rank, bright coals. Bright coals are described as vitrain-rich, containing 80-82% Carbon d.m.m.f.

Specific solvents are, however, often strongly sorbed by the coal, and there are even indications that some may interact chemically with it [23]. Work with THF shows that it, like pyridine, may become tenaciously bound to the insoluble coal residue. Although not well documented, this apparent chemical reaction of solvents at low temperatures is a potential source of error in reporting extract yields.

In summary, specific solvents exhibit the ability to extract relatively large amounts of the coal due primarily to the fact that the solvent (i) generally has an unhindered oxygen- or nitrogen-containing functional group with two unshared electrons, and (ii) can swell the coal substance and colloidally disperse much of the coal material. A third attribute which defines a good solvent is its ability to stabilize the resulting extract solution.

2.3.1.2 Coal Particle Size

Another factor which profoundly influences the ultimate extract yield from a given solvent-coal complex is the mean particle size of the coal. The effect tends to be enhanced when non-specific solvents rather than specific solvents are used under the same conditions. Fischer et al. [24] observed that a coal crushed to $\leq 1\ \mu$ size yields up to thirty times as much extract as coarser coal when extracted with benzene or 1,2-dichloroethane. With specific solvents, which solvate ten to twenty times more than non-specific solvents, the size effect is much smaller.

This phenomenon is explained by noting that an increase in surface area due to the smaller % mean particle size allows more extensive solvent-coal interaction, and increases solvation. But since specific solvents swell the coal material considerably, the particle size effect is in such cases much less significant. Further penetration of the coal, no matter how finely comminuted, by the solvent tends to be retarded by outwardly diffusing extract. This is true of both specific and non-specific solvents until conditions for extractive disintegration (solvolytic extraction) or (more severe) extractive chemical

---

[23] Berkowitz, N. <u>The Chemistry of Coal</u> Elsevier Science Publishers B.V., Amsterdam, 1985, p. 276

[24] Fischer, F., Peters, K., and Cremer, W.; Brennst. Chem., 1933, <u>14</u>, 181

disintegration are reached and the dynamics of the coal-solvent interaction change markedly.

2.3.1.3 Duration of Extraction

Although most extraction work has been carried out with bituminous coals, the effect of extraction duration is generally similar in all coals. With Soxhlet equipment, when solvent boiling points remain below 200°C, the following behaviour is observed [25].

Initially, extraction is quite rapid and most of the extract forms in the first few hours. But after approximately eight hours, the rate of extraction drops off markedly, and after three days or so, the incremental yield per unit time is usually negligible. Landau & Asbury who extracted a coal with benzene under pressure [26], found that after 32 hours, the relation between time and the yield:time ratio became linear. This indicates that the slope of that relationship is not changing as it has reached an asymptote. Therefore the ultimate yield can be reasonably determined by using a constant rate and extrapolating.

Vahrman et al. [27] [28], who examined low temperature extraction with non-specific solvents, found that extraction could take up to 250 hours and that the extract could be divided into two distinct groups, viz.

1. 'H-compounds', comprised predominantly of straight- and branched-chain hydrocarbons with lesser amounts of (mostly heterocyclic) oxygen-bearing species, all possessing molecular weights below ≃500.
2. 'O-compounds', made up of mostly petroleum ether-insoluble alkylated OH-substituted aromatics with molecular weights up to ≃1000.

---

[25] Oele, A.P., Waterman, H.I., Goedkoop, M.L., and Van Krevelen, D.W.; Fuel, 1951, 30, 170

[26] Landau, H.G., and Asbury, R.S.; Ind. Eng. Chem., 1938, 30, 117

[27] Vahrman, M.; Fuel, 1970, 49, 5

[28] Vahrman, M.; Fuel, 1972, 51, 130, 235

Cyclic and branched-chain compounds tended to appear first, with the straight-chain hydrocarbons following. These smaller species were very slowly extracted and in some cases, up to 50% of the initial coal mass could be extracted in this fashion. This led Vahrman and co-workers to speculate that non-specific solvents principally extract occluded 'guest molecules' trapped interstitially in the coal matrix.

As noted later, the fact that 50% of the coal matter can be extracted by prolonged extraction tends to discredit current molecular models of coal. It would be hard to envision a rigid 3-dimensionally cross-linked coal structure losing half of its constituent mass without concurrent thermal or chemical decomposition.

It is very time-consuming to exhaustively extract a given coal to its ultimate yield as this could conceivably take weeks, with most of the time contributing but infinitesimally to the yield. One may perform a series of experiments over varying durations and use the resulting data to plot extract yield versus time. The derived equation that fits this data may then be extrapolated to $t=\infty$. It is also acceptable, especially in a comparative study, to follow Dryden's [29] advice and choose an arbitrary standard time for the extraction. This time should suffice to ensure that the bulk of the soluble and/or dispersible material is extracted. With most coals extracted with specific solvents, such as pyridine, one or two days should be adequate. With non-specific solvents the time period should be lengthened to three to four days in order to ensure that the plateau is reached where extraction becomes only slightly dependent upon time.

The shape of the extraction yield versus time curve depends on factors that include solvent character, coal type, and temperature. For any given set of conditions, specific solvents tend to have very similar profiles, with their potency in relation to non-specific solvents reflected in steep initial slopes and higher plateaus evident in their yield vs. time plots.

---

[29] Dryden, I.G.C.; Fuel, 1950, <u>24</u>, 198

2.3.1.4 Temperature of Extraction

The most critical factor for all forms of coal conversion is temperature. The most striking changes occur when the decomposition temperature of the particular coal is reached. This usually occurs in the neighbourhood of 350-400°C, increasing with the rank of the coal, but there is also evidence, outlined by Berkowitz [30], that some molecular rearrangements begin in low rank coals at temperatures as low as 175-200°C.

As a reference point, the decomposition temperature T_d is conveniently defined as the point at which a massive weight loss of the sample begins. Overall decomposition may then be categorically separated into three distinct temperature dependent phases:

1. *Limited thermal alteration of the original molecular structure,* This is usually first encountered in low rank coals at temperatures as much as 200°C below T_d.
2. *Active thermal decomposition,* between T_d and ≈550°C, during which most of the coal's volatile matter is generated and expelled in the form of gases, light oils and tars.
3. *Secondary degasification,* above ≈550°C, which involves formation and elimination of a variety of hydrocarbon gases, elemental hydrogen and oxides of carbon.

The term 'secondary degasification' appears to have been coined by Van Krevelen [31] in 1961. For all intents and purposes, degasification ends at ≈900-1000°C. Some gases may still evolve at higher temperatures, but the rates and ultimate volumes are negligible [32].

One would only encounter very limited thermal alteration of the coal when operating with specific solvents at temperatures below ≈200°C. Any increase in yield as temperatures rise can almost certainly be attributed to physical factors; only when one reaches into the more severe solvolytic regime (200-350°C) and, subsequently, past T_d

---

[30] Berkowitz, N.; The Chemistry of Coal. Elsevier Science Publishers B.V.,Amsterdam, 1985, p. 213

[31] Van Krevelen, D.W. Coal. Elsevier, Amsterdam, 1961, p.

[32] Berkowitz, N.; The Chemistry of Coal. Elsevier Science Publishing B.V., Amsterdam, 1985, p. 214

($\approx$400°C $^+$), do chemical effects influence the extractive process. Physical phenomena such as swelling, dissolution and dispersal still contribute by enhancing chemical reactions occurring in the coal/solvent matrix, but chemical reactions will clearly outstrip physical interactions as T_d of the particular coal is reached.

In their work on solvation of finely ground coal with tetralin, Keppeler and Borchers [33] found that extract yield increased from 1.4% to 13.5% as temperatures were raised from 150° to 350°C. Asbury [34] found further evidence of pronounced temperature effects when benzene type solvents were used. When extracting Edenborn coal ($\approx$85% C) with benzene at 80°C, 160°C, and 220°C, he recorded yields of 0.1%, 0.93%, and 8.9% respectively. This dramatic, nearly 100-fold increase over a range of only 140°C in the solvent extraction regime suggests that chemical changes may be supplanting physical alterations. How coal type influenced this temperature dependence was explored by Tawada et al. [35] who found, in experimentation with benzene-alcohol mixtures and bituminous coals, that although extract yields tended to increase with temperature, the effectiveness of the solvent at temperatures between 68°C and 250°C varied greatly according to the coal type.

Extensive work on the variation of extract yield with temperature was performed by Kiebler [36]. From experiments with various solvents at 150°, 200°, 250°, and 300°C he reported a correlation of the form $Y = a + bP_i$ where Y is the yield of extract, P_i the internal pressure of the solvent, and **a** & **b** are functions of temperature; **b** increases approximately as a linear function of temperature, and **a** does so up to $\approx$250°C where its rate of increase is accelerated.

Kiebler's relationship was developed using specific, non-specific and intermediate type solvents [37]. This relationship is very general in nature as it is the accumulated

---

[33] Keppeler, G. and Borchers, H.; Brennst. Chem., 1934, 15, 241, 404

[34] Asbury, R.S.; Industr. Engng. Chem., 1934, 26, 1301

[35] Tawada, K., Kisida, T., and Ohyama, S.J.; Soc. Chem. Ind. Japan, 1939, S 42, 58b

[36] Kiebler, M.W.; Industr. Engng. Chem. 1940, 32, 1389

[37] Pyridine, benzene, and aniline respectively and those closely related to them.

average of results from all solvent types; there was a large difference between the temperature effect observed for specific solvents in comparison to those less effective. Subsequent work essentially discounted Kiebler's correlation, and this model should therefore be treated as a very limited guideline.

In summary, it may be said that solvents with higher normal boiling points tend to furnish higher extract yields. Due to physical factors, this effect progresses up to ≈200°C, and holds true for specific as well as non-specific solvents. At ≥200°C, yields are still correlated with extraction temperature, but the extraction mechanism comes increasingly to incur chemical alteration of the coal.

2.3.1.5 Other Factors

In addition to the four determinants of extraction yields discussed above, several other factors appear to exhibit some influence on yield. These include; the moisture content of coal and/or the solvent, the degree of oxidation of the coal, and the rank of the coal.

Many researchers have noted an influence of moisture and atmospheric oxygen on extract yields. Better material balances were achieved by Dryden [38] when air in the extraction apparatus was replaced by nitrogen or carbon dioxide, and Berkowitz [39] as well as Dryden [40] [41] have observed that the presence of moisture in the extraction system may be deleterious to the overall extraction efficiency of such solvents as alcoholic potash and ethylenediamine. These effects are observed regardless of whether the moisture is entrained in the solvent or exists in the coal. With other solvents it appears that moisture is not critically important, presumably because such solvents are not miscible with water. But in view of some behavioural inconsistencies respecting the effects of oxygen and moisture, it is prudent to exercise careful control in all cases in order to eliminate spurious observations.

---

[38] Dryden, I.G.C.; Fuel, 1950, 29, 197-221

[39] Berkowitz, N.; Nature (London), 1948, 162, 960

[40] Dryden, I.G.C.; Nature (London), 1948, 162, 959

[41] Dryden, I.G.C.; Nature (London), 1949, 163, 141

Coal rank and degree of oxidation of the coal tend to influence extract yields obtained with a given solvent. Published data are not conclusive, but are worth noting as they again indicate the value of strict parameter control in coal extraction.

Dryden [42] points out that, although there are exceptions, oxidation normally decreases the ultimate yield obtainable with solvents such as benzene and pyridine. Notable exceptions occurred when a benzene-alcohol mixture [43], known to dissolve humic acids, was used to extract coal in a Soxhlet apparatus. Another exception was observed when oxidized and unoxidized Barnsley hard steam coals [44] were compared.

As far as establishing a definite rank dependent extraction trend is concerned, results suggest that experimental differences and the large variations in the petrographic compositions of the coals studied so far preclude establishing a definitive correlation. The only verifiable indication is that coals with carbon contents greater than ≈85-87% tend to generate progressively smaller extract yields with increasing rank, and coals with more than 92-93% carbon are virtually 'insoluble'.

Researchers have attempted to find solvation correlations for both specific and non-specific solvents. The work of Kiebler [45], inferring that solvent potency can be directly related to the internal pressure of the solvent, has been refuted by Dryden (1950) on the grounds of a faulty data base. Others, inter alios Ostwald and Ortlov [46], have sought to define solvent potency in terms of a μ^2/ϵ vs σ diagram [47]. Although their findings appeared to be consistent within their own data set, work by Agde and Hubertus [48] failed to corroborate such a correlation.

Others, such as Van Krevelen (1965) [49], have attempted to define solvent parameters that might be incontrovertible indicators of solvent power, but such efforts

---

[42] Dryden, I.G.C.; Fuel, 1950, <u>29</u>, 197-221

[43] Voitova, E.V.; Brennst. Chem., 1935, <u>16</u>, 21

[44] Bone, W.A., & Sarjant, R.J.; Proc. Roy. Soc., 1920, <u>A 96</u>, 119

[45] Kiebler, M.W.; Industr. Eng. Chem. 1940, <u>32</u>, 1389

[46] Ostwald, W., and Ortlov, H.; Kolloid Z., 1932, <u>59</u>, 25

[47] μ = dipole moment, ϵ = dielectric constant, σ = surface tension.

[48] Agde, G., and Hubertus, R.; Braunkohlenarchiv, 1936, <u>46</u>, 3

[49] Van Krevelen evaluated solvent power in terms of a solubility parameter ratio δ-coal/δ-solvent. cf. Van Krevelen, D.W.; Fuel, 1965, <u>44</u>, 229-241

have proved to be of limited validity because adequate definition of the particular solubility parameters requires several dubious assumptions. The complexity and variance of the hydrocarbon substance that we call 'coal' appears to frustrate current hypotheses respecting solvent potency. Therefore, it is not inappropriate to regard non-specific and specific solvent regimes as two distinct phenomena. In time, they may be reconciled in a single unified solvent theory, but at this juncture they should be considered as separate entities.

In conclusion, it should be noted that the overall effect upon extraction yields and rates for both specific and non-specific solvents is a combination of many, if not all, of the aforementioned conditions and factors. It is because of this complexity of reaction mechanism that the observance of strict experimental control is necessary in order to facilitate the recovery of unambiguous data.

2.4 Extractive Disintegration

The term extractive disintegration, coined by Oele, et al. [50], describes a reaction mechanism associated with solvolysis and solvolytic extraction. Solvolysis literally means to cut or break with a solvent, and therefore could describe any solvent interaction regardless of severity. This broad application of the terminology has resulted in solvolysis or solvolytic extraction being employed to describe conditions ranging from comparatively mild Soxhlet extraction up to total solubilization in a liquefaction environment.

Indeed, the separation of solvent action regimes depends on physical/chemical properties of the solvent as well as on the temperature at which extraction is carried out. To put this in perspective, one may compare a conventional low-boiling solvent such as THF (b.p. = 66°C) and a more potent coal solvent, α-naphthol (b.p. = 288°C). Some form of reflux-boil apparatus could be utilized for extractions with both solvents at their normal boiling points (atmospheric Soxhlet extraction may not work with α-naphthol due to its tendency to sublime), and though the operational temperature for α-naphthol extraction lies

---

[50] Oele, A.P., Waterman, H.I., Goedkoop, M.L., and Van Krevelen, D.W.; Fuel, 1951, <u>30</u>, 169

nominally in the solvolytic range, it may not be mechanistically different from conventional Soxhlet applications. The increased temperature of operation may just enhance the solvent action.

With these subtleties in mind, Berkowitz and others have designated solvolysis as coal-solvent interaction proceeding under conditions substantially more severe than standard Soxhlet extractions, but not harsh enough to incur active thermal decomposition of the coal. Therefore, for the purposes of this dissertation, extractive disintegration is synonymous with solvolysis in the temperature range 200-350°C. The pressure regime will be such as to maintain a liquid solvent phase. It is of no consequence whether the required pressures are artificially induced or autogenic.

Since the Second World War, interest in coal solvolysis has shifted from low-boiling solvents to more exotic high-boiling solvents that promise complete coal solubilization. The resulting dearth of experimental work with low-boiling solvents allows only a few generalizations founded on work during the early 20th century.

Extract yields tend to increase exponentially with temperature, and such temperature effects are more marked in non-specific than in specific solvents. Thus, Asbury [51] reported that a bituminous coal (≃85% C) yielded 0.1, 0.93, and 8.3% when extracted with benzene (b.p. = 80.1°C) at 80, 160, and 220°C respectively. This contrasts with work by Bone and Sarjant [52] who extracted a similar coal with a specific solvent, pyridine (b.p. = 115°C) at 160°C. This increase in temperature of extraction only doubled the amount extracted from 32 to 67.3% in comparison to the nine fold increase exhibited by the benzene extract under similar conditions. Again, due to the lack of interest in low-boiling solvents, it has not been established whether the extraction-temperature relationship extends exponentially into the mid-solvolytic range (250-300 °C). If it does, one could expect non-specific solvents, such as benzene, to approach the extraction capabilities of specific solvents such as pyridine and ethylenediamine at their respective atmospheric boiling points.

---

[51] Asbury, R.S.; Ind. Eng. Chem., 1934, 26, 1301

[52] Bone, W.A., and Sarjant, R.J.; Proc. R. Soc. London, 1920, A 96, 119

Interest in the solvolytic or extractive disintegration regime was rekindled by observations that certain high-boiling solvents could provide exceedingly high extract yields even at atmospheric or slightly above atmospheric pressures. Such solvents are not to be confused with specific solvents that may extract very large amounts at sub-solvolytic temperatures. They are non-specific solvents which operate exceptionally well at the temperatures of their normal boiling points which happen to lie in the upper reaches of the solvolytic temperature range (≈275-300°C).

Early work by Gillet and Pirlot [53] and Nesterenko [54] identified olein and anthracene oil as capable of extracting 90-95% of high volatile bituminous coal at temperatures near 300°C, and comprehensive work by Golumbic, Orchin, Storch et al. [55] [56] [57] has shown various polynuclear compounds to be effective coal solvents. The best of these include naphthalene, phenanthrene, α- and β-naphthol and phenyl phenols, such as o-cyclohexyl phenol. These solvents tend to be as effective as anthracene in extracting bituminous coals. It has been found that 'solubility' of coal before massive disintegration depends mainly on the structure and boiling point of the solvent, the rank of the coal and the solvent:coal ratio.

2.4.1 Factors Affecting Extractive Disintegration

Studies by Golumbic et al. (1950) using (Pittsburgh-Seam) bituminous coal, show extract yields of 95% for phenanthrene (b.p. = 340°C), but such yields are more aptly termed dispersion percentages as the overall benzene-soluble (asphaltenic) fractions amounted to only 19%. A lower-boiling solvent of similar aromatic structure, fluorene (b.p. = 295°C), only managed 26% extraction and a benzene-soluble fraction of 11% under similar conditions.

---

[53] Gillet, A., and Pirlot, A.; Bull. Soc. Chim. Belg., 1935, 44, 504
Ibid. 1938, 47, 518.
Ibid. 1942, 51, 23, 525

[54] Nesterenko, L.L.; Trudy Kharkov Khim. Tekh. Inst. im S.M. Kirova, 1939, 2, 70 - cf. also Chem. Abstr., (1940), 34, 3473

[55] Orchin, M., and Storch, H.H.; Ind. and Eng. Chem., 1948, 40(8), 1385

[56] Orchin, M., Golumbic, C., Anderson, J.E., and Storch, H.H.; USBM Bulletin #505, 1951

[57] Golumbic, C., Anderson, J.E., Orchin, M., and Storch, H.H.; USBM Rep. Invest. #4662, 1950

Rank appears to play a role in the extent of extractability of some solvents. Whereas phenanthrene and other aromatic solvents with angular ring structures tended to be especially potent for high volatile bituminous coals, they were relatively inefficient for lower ranked coals. [58] These same bituminous coals responded quite well to α- and β-naphthol, extracting 80 and 78% respectively at their atmospheric boiling points [59]. α-naphthol was found to be the best overall solvent for both bituminous and subbituminous coals, achieving extractions of 83% for subbituminous coal; phenanthrene only extracted 27% and β-naphthol only 17% [60].

Another factor governing extraction yields is the ratio of solvent to coal. Golumbic et al. (1950) indicated that this ratio could be reduced from 15:1 to 6:1 without significantly affecting extract yields, but further reductions in the ratio decreased extraction yields by 10 to 15 percent in addition to dramatically diminishing the amount of benzene-soluble material. For the most part, though, large-scale extractions were done at a ratio of 3:1 in order to economize on solvent. Other solvolysis experiments have been done at ratios of 4:1 [61], and 1.6:1 [62]. The information derived from these experiments is not directly comparable in light of procedural differences. It merely illustrates that the solvent:coal ratio is another parameter that may be varied depending on the goals of the experiment.

It is important to note that the aromatic nature of the solvent structure contributes to the effectiveness of the solvent. Golumbic et al. (1950) observed that a high-boiling cut (340°C) of a coal-hydrogenation middle oil with a high aromatic content was as effective an extractant as phenanthrene. In contrast, a similar fraction of middle oil with low aromatic content furnished an extract yield of barely 10%.

There is some basis for investigating the chemical structure of the solvents as well. In particular, the exceptionally high extract yields generated from bituminous coal by α- and β-naphthol and the equally high yields obtained from subbituminous coal with α-naphthol [63]

---

[58] cf. Golumbic, C., et al.; 1950

[59] α-naphthol has a b.p. of 288°C while β-naphthol boils at 295°C

[60] cf. Golumbic, C., et al. 1950

[61] cf. Orchin, M., et al., 1948

[62] Maa, P.S., Neavel, R.C., Vernon, L.W.; Ind. Eng. Chem. Process Des. Dev. 1984, 23, 242

[63] The most effective solvolytic solvent found for both subbituminous and bituminous

support a theory espoused by Kiebler [64]. He states that α-naphthol undergoes condensation reactions at about 300°C whereby it is transmuted into α-naphthalene oxide. The resultant hydrogen liberated by this condensation reaction may hydrogenate the coal, thereby enhancing the apparent solvent action of α-naphthol. In a similar vein, Orchin et al. [65] believed that phenols owed their superior solvent qualities to hydrogen-bonding between the phenolic hydroxyl and similar functional groups in the primary reaction products formed under extractive disintegration conditions.

2.4.2 Coal Models and Extractive Disintegration

For less severe solvent extraction, mechanisms of extractive disintegration are still open to conjecture, and as such are intimately related to perceptions of coal structure as defined in 'average structure' models. Whereas extract yields from low-boiling solvents at their normal boiling points are consistent with a view of the coal matrix as a rigid three-dimensionally cross-linked network (see inter alios, Larson, 1978 ; Dryden, 1951b) [66] [67], extracts generated by higher boiling solvents in the solvolytic regime confuse the issue because of the high yields produced at temperatures below T_d. It is the possibility of better insight into coal structure and disintegration mechanisms that contributes greatly to the interest in studying solvolytic coal extraction.

Low-boiling solvents extract predominantly Montan waxes and resins which are viewed as being occluded in the interstitial voids in the coal matrix. Higher-boiling solvents, such as phenanthrene or α-naphthol, may extract up to 95% (cf. Golumbic et al., 1950) of the coal material which would seem to be prohibitive in a rigid cross-linked structure unless there was some associated decomposition of the coal, which appears to be ruled out as suggested by Berkowitz [68]. In order for decomposition during extractive disintegration to be

---

[63](cont'd) coals is α-naphthol. c.f. Golumbic, C., et al., 1950

[64] cf. Kiebler, M.W., 1940

[65] cf. Orchin, M., et al., 1948

[66] Larsen, J.W., and Kovac, J.; ACS Symp. Ser., 1978, 71, 36

[67] Dryden, I.G.C.; Discuss. Faraday Soc., 1951b, 11, 28

[68] Berkowitz, N. The Chemistry of Coal. Elsevier Science Publishing B.V., Amsterdam, 1985, p.300

accepted it would have to be evidenced by active thermal decomposition, hydrogen disproportionation, and internal hydrogen rearrangements supported by H-shuffling between the solvent and the coal.

Berkowitz disputes such mechanics which could support a three-dimensional cross-linked model. Active thermal decomposition may be discounted because massive dissolution of coal has been observed at temperatures 100-150°C below T_d (≃400°C for bituminous coals) [69]. During conventional pyrolysis at temperatures above T_d hydrogen-deficient radicals are capped by concurrently generated hydrogen, and this disproportionation yields a hydrogen-depleted char as well as a hydrogen-enriched fraction (tar and gases). Such processes are enhanced under liquefaction conditions when hydrogen is supplied from either a pressurized H_2 atmosphere or a suitable solvent with H-donor capabilities (eg. anthracene oil, bitumen, tetralin).

In the solvolytic regime, disproportionation is not consistent in all instances. For example, in the case of extraction with anthracene (b.p. = 354°C), which is not an H-donor, there can be no net transfer of hydrogen from the solvent even though the coal becomes highly solubilized. H-shuffling, especially if the coal has a high vitrinite content, has been demonstrated by Collins et al., [70] but so far only been observed at temperatures exceeding 400°C.

Models, such as those proposed by, inter alios Dryden (1951 b) [71], Hill and Lyon [72] and Wiser [73] for bituminous coals show rigid three-dimensionally cross-linked structures. These models are substantially planar in orientation and attempt to describe all the chemical characteristics of the coal as a whole. These models are really only an interpretation of the

---

[69] cf. Golumbic, et al. 1950; Orchin & Storch, 1948; Orchin et al., 1951

[70] Collins, C.J., Raaen, V.F., Benjamin, B.M., and Kabalka, G.W.; Fuel, 1977, 56, 107

[71] Dryden described his coal model as an insoluble matrix consisting of large and strongly linked vitrinitic micelles in intimate association with smaller, less strongly linked molecular aggregates. He theorizes that the smaller moieties can only be extracted if the coal matrix is first swollen by an appropriate solvent. Consequently, the apparent extraction process involves the diffusion of the individual micelles through the swollen pores of the matrix.

[72] Hill, G.R., Lyon, L.B.; Ind. Eng. Chem., 1962, 54(6), 36

[73] Wiser, W.H.; Prep. Pap. - Am. Chem Soc., Div. Fuel Chem., 1975, 20(2), 122

profusion of data from many diverse sources and have several limitations and flaws.

In all cases the models were formulated under the constraints of three important provisoes. They are based on observations of vitrain rich coal as vitrinite is generally the most abundant maceral. The models refer to bituminous coals since there is little available information pertaining to low rank coals. They are not really intended to represent the 'real' coal molecule but are, rather, an average structural configuration which although unlikely to exist as such, demonstrates the chemical interactions ascribed to the coal by the modellers.

Problems are encountered in reconciling a three-dimensionally crossed-linked average coal structure model with high extract yields under solvolytic conditions. It has been shown that non-donor solvents such as phenanthrene, α- and β-naphthol may bring into solution more than 70% of a bituminous coal [74]. Oele et al. [75] confirmed these observations with his work on the solubility of bituminous coal in anthracene oil. At temperatures ranging from 250-350°C he was able to extract 65-78% within 2 hours.

It is inconceivable that the high extraction yields can be solely comprised of adventitious waxes, resins, and other guest species trapped in a predominantly vitrinitic coal matrix [76], although such substances are readily soluble due to their low molecular weight and their relatively weak bonding to the main coal structure they should not constitute such a large component of the aggregate coal entity. Berkowitz [77] has stated that even in lignites, from which Montan waxes and resins have been commercially extracted, such inclusions generally compose only 5-6% of the total, with extraordinary samples [78] containing 10-12% waxy material.

If some relatively small trapped molecules, other than occluded waxes and resins, comprised the bulk of the coal structure, it would follow that they would contribute more to the physical characteristics of the coal entity. Studies of the elastic properties of coal by

---

[74] Golumbic et al.; USBM Repts. Invest. #4662, 1950

[75] Oele, A.P., Waterman, H.I., Goedkoop, M.L., and van Krevelen, D.W.; Fuel, 1951. 30, 169

[76] Vahrman, M.; Fuel, 1970 49, 5

[77] Berkowitz, N. The Chemistry of Coal, Elsevier Science Publishing B.V., Amsterdam, 1985 p. 291

[78] eg. Enugu lignite (Nigeria)

Pomeroy (1956) [79] and Morgans (1958) [80] tend to disallow this as their observations of very low (< 1%) non-recoverable strain indicates a viscoelasticity much like that of bakelite, where most of the deformation is recovered when the stress is removed. These findings tend to be consistent with either an extensively cross-linked or a physically-entangled macromolecular system, rather than with a conglomerate mixture of large molecules and loosely bonded smaller molecules. The reasoning is that molecules which are not held together by covalent bonds tend to flow when subjected to prolonged stress. After such plastic deformation loosely bound structures will not recover their former dimensions.

The coal elasticity research by Pomeroy (1956) and Morgans (1958) may be supportive of an alternative model if one views nodal points at which molecules are entangled as analogous to intersections of a rigid cross-linked matrix. This evidence may further accommodate an entangled model since smaller molecules may be occluded in the matrix without altering elastic response to a great degree. This thereby mitigates the question of the presence of both small and large molecules in solvolytic regime coal extracts where there has been no apparent decomposition (and possible recombination) of the theoretical rigid covalently bonded matrix. Without covalent bonding, entanglment and the resulting H-bonding and/or van der Waals interactions would seem to be inevitable if solvolytic phenomena is to be accounted for.

One particular study by Nelson [81] tends to discount rigid, predominantly aromatized (& therefore planar), structures such as in the aforementioned Hill & Lyon model. Radial distribution curves calculated from X-ray diffraction data indicate a lack of planarity beyond 0.6 nm from any one C atom. Nelson concluded that the maceral structure was consistent with condensed aromatic rings having an average size not greater than that corresponding to three fused rings. The average C - C distances for polynuclear aromatic compounds (.139-.142 nm) [82] preclude the existence of aromatic structures comprised of more than 3-rings. These facts cast serious doubts on some complex 3-dimensionally cross-linked coal

---

[79] Pomeroy, C.D.; Nature (London), 1956, 178, 279

[80] Morgans, W.T.A., and Terry, N.B.; Fuel, 1958, 37, 201

[81] Nelson, J.B.; Fuel, 1954, 32, 153, 381

[82] Van Krevelen, D.W.; Coal, Elsevier, Amsterdam, 1961, p. 158

models.

An alternate model due to Given [83] is more sinuous in orientation, thereby limiting planarity and hence agreeing more closely with Nelson's findings. Coal models such as Given's tend to suggest an alternative to the conventional 3-dimensional cross-linked coal structure. This alternative could be in the form of a physically entangled macromolecule as envisioned by Berkowitz and Hombach.

Berkowitz [84] [85] and Hombach [86] [87] have suggested such a model which, if proven, would make extraction in the solvolytic regime mechanistically unchanged from conventional low temperature soxhlet extraction. This coal model is envisioned as being comprised of highly asymmetric physically entangled molecules which become progressively disentangled and aligned with increased compression during metamorphic development. This regularization is further aided by gradual expulsion of peripheral constituents which enhance 'bonding' by their molecular configuration or their propensity to establish H-bonding.

In order to speculate additionally as to the relative merits of these two model hypotheses and, indeed, to see the importance of solvent extraction in this context, one must look at other related observations. Evidence in the extant literature pertaining to composition and molecular weight distribution of coal extracts supports the notion that relatively large molecules do become soluble under solvolytic conditions. Dormans & Van Krevelen [88], and Larsen et al. [89], inter alios, have done extensive work, and although there are some questions raised as to the significance [90] of this data, they may serve as qualitative indications of the

---

[83] Given, P.H.; Fuel, 1960, 39, 147

[84] Berkowitz, N., Proc. 11th Bienn. Lignite Symp., San Antonio, Texas, U.S. D.O.E., GFETC/IC-82/1, 1981, 1, 414

[85] Berkowitz, N.; Advances in Chemistry Series, 1988, 217, 217-233

[86] Hombach, H.P.; Erdoel Kohle, 1975, 28, 90

[87] Hombach, H.P.; Erdoel Kohle, 1979, 32, 85

[88] Dormans, H.N.M., Van Krevelen, D.W.; Fuel, 1960, 39, 273-292,

[89] Larsen, J.W., Given, P.H.; Proc. 1978 Coal Chem. Workshop, Menlo Park, CL; Conf-790372 SRI Internat., 1978, 69

[90] Number average molecular weights can be seriously misleading (c.f. Larsen & Given, 1978) as they often over-emphasize low molecular weight moieties and researchers do not place enough emphasis on the more important aspect of the molecular weight distribution. There is also some uncertainty as to the validity of measurement procedures. In particular, the ever present question of the definition of solution vs colloidal suspension clouds the issue and hampers accurate comparison.

molecular sizes represented in coal extracts. As an example, Dormans et al. (1960) found extracts from coals containing between 80 and 91% C to have number average molecular weights of ≈500 with a high value of ≈1200 for a coal with a carbon content of 87%. Assuming a predominantly condensed aromatic structure this would translate to average molecules being composed of ≈6 aromatic rings at the lower bound and ≈15 at the 'extreme' upper limit. Larsen et al. [91] identified molecular weights greater than 3000 which would estimate aromatic chains numbering over 37 ring units. As these values probably represent a low and skewed average, the molecular weights of the precursors may well exceed 6000 (Larsen & Given, 1978). It should be noted that aromatic rings are but one component of coal structure that illustrate the molecular size of the structures. Saturated systems as well as many substituted groups are also present.

In light of this information and the apparent ability of solvents such as α-naphthol and phenanthrene to extract up to 95% of bituminous coals under solvolytic conditions, one must doubt the validity of a covalently cross-linked framework for a coal structure.

The matters discussed in the proceeding paragraphs are evidence of apparent discrepancies between certain observed coal phenomena and 3-dimensionally cross-linked coal structure models. The fact that high boiling aromatic solvents such as phenanthrene (b.p. = 340°C), α- and β-naphthol (b.p. = 288° and 295°C respectively) can extract between 78 and 95% [92] of a bituminous coal while lower boiling solvents, such as benzene (b.p. = 80.1°C), extract miniscule amounts of tar at their normal boiling points indicates further flaws in the conventional coal model or else a mechanistic difference between solvent extraction in the different temperature regimes. Asbury [93] found that while benzene only extracted 0.1% of a bituminous coal at its normal boiling point, it could, under pressure, take into solution 8.3% at 220°C. Similarily Bone and Sarjant [94] investigated a specific solvent, pyridine (b.p. = 115°C), and found that increasing the extraction temperature to 160°C doubled the yield from

---

[91] Larsen, J.W., Given, P.H.; Proc. 1978 Coal Chem Workshop, Menlo Park, CL; Conf-780372 SRI Internat., 1978, 69

[92] cf. Golumbic et al., 1950)

[93] Asbury, R.S.; Ind. Eng. Chem., 1934, 26, 1301

[94] Bone, W.A., and Sarjant, R.S.; Proc. R. Soc. London, 1920, A96, 119

32% to 67.3%. These apparent temperature dependencies indicate a mechanistic continuance which may indeed link high and low temperature solvent/coal interactions.

Although there is no conclusive evidence in support of a physically-entangled molecular model, the above points of discussion can be interpreted as pointing to this alternative. The issue of a definitive coal model may not be resolved for many years, but it is important to keep an open mind on this matter as there is a host of information which tends to support an alternate entangled structure. Interpretation of results is sometimes misleading if one attempts to always view findings in light of 'established' constructs. Recognizing an alternate coal form which allows some reconciliation of otherwise disparate features of coal behaviour without increasing the number of incongruities is a step towards more effective research in coal science. The investigation of coal/solvent interactions in the solvolytic regime is not only important to engineers who hope to find more economic paths to liquid petrochemical feedstocks through less severe liquefaction reactions, but also to coal scientists who endeavour to delineate coal structure and behaviour.

2.5 Extractive Chemical Disintegration

The next step in the progression of coal extraction severity is into the realm of extractive chemical disintegration. This domain is typically associated with coal liquefaction and involves extraction at or near 400°C, where the onset of thermal decomposition of the coal accelerates the chemical and physical changes which begin at solvolytic temperatures.

As in the other extractive domains, temperature, pressure, duration of reaction, coal rank, and the composition of contacting solvents or atmospheres are important factors in the progression of the process. The major difference, though, is that these factors are focused on the chemical interactions of the coal, as, by definition, physical breakdown will inevitably ensue once T_d is passed. Although temperature, pressure, and time are important driving forces in any subsequent chemical reaction, the composition of the contacting solvent or atmosphere and, in particular, its ability to donate hydrogen to the coal, are of paramount importance to the composition of the reaction products.

To put this in the proper perspective, a digression into the effects of thermal decomposition on coal properties is necessary. One must understand the effects of heat on coal after the onset of T_d in order to relate liquefaction with other related phenomenon.

2.5.1 Thermal Decomposition

Massive decomposition of coal is generally associated with the temperature range of ≈350-500°C which is when devolatilization is particularly evident. The chemical reactions that take place may be represented, in a rudimentary fashion, as the following two processes occurring sequentially [95].

1. The release of gases and primary tars from thermal decomposition of the coal structure.
2. Thermal cracking and concurrent polymerization of the primary tars to produce gases, lighter secondary tars and a carbonaceous residue.

In some cases these processes may begin at lower temperatures, but the rate and extent of reaction is relatively insignificant. It can be shown in a typical cumulative weight loss curve that the total decomposition effect can be divided into three distinct stages.

The first signs of devolatilization may appear below 200°C with chemically generated water, and loosely bound occluded gases such as methane and carbon dioxide coming off between 100 and 180°C. It should be noted that such gases, if only sorbed, do not constitute 'true' decomposition when liberated. This low level decomposition is continued with the release of various oxides of carbon and hydrogen sulphide as 200°C is approached. Above ≈200°C loosely bound or occluded solids and resins may volatilize. Benzylic carbon begins to isomerize to form methyl phenyl derivatives and small amounts of alkyl benzenes are produced. Little is known of these low temperature changes, but they do alter the original coal structure such that succeeding thermal behaviour is modified. A graphic example of this is the fact that preheating at ≈200°C tends to destroy or greatly diminish any agglutinating

---

[95] Merrick, D. <u>Coal Combustion and Conversion Technology</u>, Macmillan Publishers Ltd., Hong Kong. 1984, p. 199

abilities the coal may possess as well as enhance its solubility in organic solvents [96].

The next zone of activity begins at ≈350-400°C and terminates at ≈550°C. It is usually referred to as active thermal decomposition. A rank dependent, characteristic temperature of decomposition (T_d) is established from recording cumulative weight loss curves and noting where they abruptly turn upward. It is in this temperature regime that ≈75% of all volatile matter such as tars and vapourous hydrocarbons are released.

As the coal is heated above T_d, linkages between aromatic clusters begin to break. In coals with intact caking propensities this activity results in a softening of the coal particles such that in the temperature range of ≈350-450°C a coherent plastic mass is formed.

Aliphatic and oxygen-containing pendants (eg. methyl and hydroxyl groups) and bridges (eg. methylene structures) detach themselves from the aromatic clusters bringing with them low molecular weight fragments of the coal structure. It is these transformations which facilitate the rapid evolution of primary tars, hydrocarbon gases and water in this stage.

The resulting product slate is highly variable depending on, in particular, the ambient pressure and the heating rate. This response occurs because of the vast array of recombination reactions, which may occur in conjunction with heat induced fragmentation.

Free radicals are generated during decomposition and, unless 'capped' by either co-generated hydrogen or hydrogen from a donor source, will encourage polymerization of the aromatic and hydroaromatic clusters leading to the formation of char or coke. As temperatures increase, thermal cracking of the primary tars will intensify unless it is controlled through adequate hydrogenation or by removing the volatiles and quenching them before they have the opportunity to participate in free radical catalyzed cracking reactions.

After one progresses above ≈550°C, the weight loss tapers off dramatically. In this area secondary degasification ensues and the limited activity involves chiefly the elimination of heteroatoms, notably hydrogen and oxygen. The major constituents of this tertiary devolatilization are water, oxides of carbon, hydrogen, methane, and miniscule amounts of C_2 hydrocarbons. At temperatures above 800-850°C, evolution of lighter hydrocarbons has

---

[96] Dryden, I.G.C., Pankhurst, K.S.; Fuel, 1955. <u>34</u>, 363

virtually ceased, and the only significant change is the continued aromatization of the char with accompanying evolution of very small amounts of H_2 and a consequent increase in the mechanical strength of the coke.

The introduction of coal solvents and/or hydrogen into a coal conversion system operating at or above the temperature of thermal decomposition will induce extensive disintegration, dissolution and either partial or total solubilization of the coal. The three most prominent functional aspects of the extractive chemical disintegration regime, as far as current extraction research is concerned, are :

1. Solvent Refining of Coal (SRC)
2. Liquefaction
3. Supercritical Gas Extraction

These extractive processes, defined by their disparate products, are related by their position at the terminus of solvent extraction severity and their dependence on donated or autogenously generated hydrogen for product formation.

2.5.2 Solvent Refining of Coal (SRC)

Solvent refining of coal, abbreviated SRC, is a process which converts coal into a low-melting solid or semi-solid but does not liquefy it. Typically, it may be described as the interaction between coal and a suitable H-donor in the temperature range 350-450° C, and thus operates under conditions in which the coal is thermally decomposing. Mechanistically, it is probably the truest extension of solvent extraction into the realm of extractive chemical disintegration. But the distinction between near-total dissolution and liquefaction is, for the most part, arbitrary because the extent of conversion to liquid hydrocarbons at temperatures above T_d depends wholly on the amount of hydrogen incorporated into the coal material. Solvent refining of coal has thus been described as 'arrested liquefaction' due to its hydrogen-rationed processing.

The rationale for producing a semi-solid coal derivative is two-fold. There has always been a market for solid fuels and coal has traditionally supplied the lion's share of this need. In recent years environmental concerns have come to the forefront in most industrialized nations, prompting stringent legislation governing the burning of high-sulphur and/or high-ash coals. This has led to implementation of expensive scrubbing and filtering of flue gases, and consequently to increased operating costs. Affected utilities and industrial complexes have therefore explored alternatives to, cleaner burning but expensive, petroleum and natural gas. Solubilizing the coal and filtering it has thus become an increasingly viable means of eliminating undesirable particulate matter from the coal in order to meet ever toughening pollution guidelines. Additionally, many coal liquefaction procedures have found it more efficient to operate in two stages. In the first phase, a semi-solid coal extract is produced under relatively mild (SRC) conditions, and this is subsequently hydrogenated more vigorously in a second stage. This path has been found to be less harsh on the equipment, and the overall process efficiencies and operating costs show an improvement. Both of these reasonings have led to continued SRC research, particularly in the United States where secure energy supplies as well as environmental protection are important concerns.

Solvent refining is a highly flexible conversion scheme and, as such, can produce a wide array of products, depending primarily on the amount of hydrogen absorbed by the coal in the reaction. Two well known procedures that serve to illustrate the roots of this technology are the *Pott-Broche* [97] and *Ude-Pfirrmann* [98] [99] processes which are the precursors of all current solvent refining research. The first commercial plant operated at Welheim, Germany, between 1938 and 1944. This operated with finely comminuted coal that was slurried with approximately 2-3 times its own weight of a 4:1 ratio of tetralin:cresol (a potent H-donor) [100]. The resultant slurry was fed to the primary digestor where it was heated for approximately 1 hour at 415-430°C under 10-15 MPa. The extract was then cooled to ≃150°C

---

[97] Pott, A., and Broche, H.; Glückauf, 1933, 69, 903

[98] Ude, F., French Patent No. 800920 (1936)

[99] Pfirrmann, T.W., U.S. Patent No. 2167250 (1939)

[100] In the latter stages of the war middle oil from coal and tar hydrogenation was used as a slurrying agent.

and filtered under ≃.3-.4 MPa in order to remove any solid residue that had not settled out in the reaction vessel. The filtrate was vacuum-distilled to reclaim process solvent that was then rehydrogenated and recycled. The resulting yield of substantially ash-free semi-solid hydrocarbon fuel ranged from 78 to 84 wt.% of the d.a.f. feed coal. Variations in overall yield may be attributed primarily to compositional differences of the feed coals.

The principal difference between the Pott-Broche and Ude-Pfirrmann schemes is that the latter operates under more severe conditions to ensure faster transfer of hydrogen into the coal and produce a substantially more fluid product. A consequence of this procedural change is an extension of the life of the H-donor solvent and a reduction of the total reaction time from approximately 30 to 60 minutes. The heteroatom content of the product is also reduced because of more effective removal of oxygen, nitrogen and sulphur. The extra hydrogen consumed in the process contributes to an H-enriched output stream with a lower melting point and enhanced combustion characteristics.

Current adaptations of the aforementioned techniques have been focused on attaining commercial viability through increased reaction efficiency and concurrently lessened process severity. The product slate may be altered by manipulating specific operating conditions, for example pressure, temperature, solvent:coal ratio, and residence time in the reactor vessel. The composition of the charged coal is also an important parameter, and experimentation tends therefore to be geared to tailoring conditions that optimize the product stream for specific coals. Most intently studied, because of environmental as well as economic concerns, is the reduction of sulphur content to acceptable levels while still maintaining economy of hydrogen consumption.

2.5.3 Liquefaction

With increasing severity in coal/solvent interactions, past the onset of thermal decomposition, one enters the realm of coal liquefaction. It has long been a goal of scientists and engineers to economically convert solid hydrocarbons such as coal, lignite, and peat into more easily processed and transported liquids. The possibility of attaining this goal had been anticipated because the fossil fuel series, extending from low molecular weight natural gas, through conventional crude, heavy oil, tar sands, oil shales and 'coaly' hydrocarbons has long been recognized as fundamentally reflecting a sequence of progressively lower hydrogen:carbon ratios.

There are notable chemical differences between coal and crude oil. Crude oil (which most upgrading processes seek to emulate) is a complex assortment of organic compounds of relatively low molecular weight, including paraffins, olefins, napthenes and aromatics. Coal, on the other hand, is merely a generic term referring to solid hydrocarbons that belong to an apparently continuous coal 'series' characterized by increasingly more organically-bound carbon. This series may be written as:

peat→lignite→subbituminous coal→bituminous coal→anthracite

The most definitive difference between crude oil and coal, as in all the hydrocarbon family, is reflected in their respective hydrogen contents. Coal has a relatively low hydrogen content of usually less than 6% while crude oil is fairly rich in hydrogen, containing more than 10% on average. An additional difference between the two 'hydrocarbons' lies in their respective elemental compositions. The heteroatom content of coal is ordinarily much higher than that of crude oil. Sulphur is the main heteroatom in crude oil, while oxygen predominates in coal.

As it stands, though, coal and crude oil have many similarities , and the basic processes involved in converting coal into synthetic liquid fuels have been under development since the early 1900s. Merrick [101] has outlined four interrelated changes which must be executed in order to convert coal into synthetic petroleum feedstock:

1. The complex, high-molecular-weight macromolecular structure of the coal must be broken down into relatively small entities. This may be achieved via three chemical processes: *(i) pyrolysis* (thermal decomposition in an essentially oxygen-free

---

[101] Merrick, D. Coal Combustion and Conversion Technology. MacMillan Publishers Ltd., Hong Kong. 1984

environment); *(ii) solvation and hydrogenation; (iii) partial or total oxidation* (combustion and subsequent gasification reactions).

2. The hydrogen content of the coaly material must be increased. This may be accomplished in two ways: one may add hydrogen or abstract carbon.
3. The heteroatom content of the coal must be reduced. This may also be achieved through hydrogenation, with oxygen, nitrogen and sulphur being removed as water, ammonia and hydrogen sulphide respectively.
4. The inherent mineral matter must be removed. This requires the conversion of the coal substance into a fluid state: a low-melting solid or solution, a gas or condensible vapour.

Currently there are three conversion routes that effect the aforementioned changes on coal and yield substantially liquid products or readily hydrogenable intermediates, viz. direct liquefaction (Bergius hydrogenation and related processes) indirect liquefaction (via gasification and subsequent Fischer-Tropsch processing of the syngas) and low temperature pyrolysis. The most significant of these above processes as they relate to solvent extraction is direct liquefaction. The other two will be summarily covered as 'Alternative Coal Solubilization Techniques'.

Direct liquefaction technology is based on now-classic Bergius hydrogenation, which began to be commercially used in Germany in the late 1920s [102]. The process involved reaction of pulverized coal or, later, coal-oil slurries over a catalyst with gaseous hydrogen at high temperatures and pressures. Typical reaction conditions for hydrogenation of lignites were temperatures in the range of 475-485°C and pressures of ≃25-30 MPa (3500-4300 psi), with the catalyst consisting of iron oxide. Similar conditions and procedures were used for hydrogenation of bituminous coals, but pressures were generally higher, running to 35-70 MPa (5000-10,000 psi). Process derived recycled heavy bottom oils were used as a slurrying medium, while donor hydrogen was contributed by pressurized gaseous hydrogen. The high temperatures of Bergius operations generally precluded efficient transfer of hydrogen from the

---

[102] Bergius was awarded the 1931 Nobel Prize in Chemistry for this work.

slurrying-oil to the coal, and made hydrogenation dependent on hydrogen in the gas phase.

The original commercial plant at Leuna, Germany came on stream in 1927, and eventually spawned eleven others that hydrogenated coal and coal tars in order to produce gasoline, aviation fuels and other hydrocarbon liquids for war-time Germany. Hydrogenation complexes relying on Bergius technology were also built elsewhere, in particular England, but commercial interest in coal or coal-tar processing waned with the advent of cheap oil after World War II. Some plants were kept in operation to process heavy oils while the rest were dismantled.

After the war, some further experimental work on direct coal hydrogenation was carried out, most notably in the United States where the Bureau of Mines set up pilot plants in an effort to improve process efficiency and economics. These efforts, sometimes referred to as second generation liquefaction processes, led to the variety of liquefaction technologies now at hand. Common to these liquefaction schemes are:

1. Dissolution or dispersion of the coal in a solvent/oil slurry medium (extraction).
2. Reaction of the resultant solution or dispersion with hydrogen at ≃400-425°C / 7-21 Mpa.
3. Separation of mineral matter from the liquid product slate.
4. Recovery of products and recycle of the solvent.

The many variations of direct liquefaction are illustrated by the order in which the above steps take place and the extent to which they are combined. One dominant distinction lies in the delineation of single- and two-stage processes. In single-stage operations, solubilization and hydrogenation of the solubilized material occur in the same reactor but at some cost to control over the process. In two-stage regimes, separate reactors are utilized, with greater attention to the process chemistry but increased operating costs. It is because of a search for more cost-effective and less severe operating conditions that interest in solvolytic extraction is being evinced.

Most of the newer coal liquefaction processes place great importance on the transfer of hydrogen from a slurry-oil or solvent to the coal. If an H-donor solvent can be used to solvate and disperse the coal, hydrogen expenditures can be substantially reduced through more efficient H-transfer to the coal. Additionally, if a coal solvent is able to disperse and solubilize a large proportion of the coal at temperatures substantially below T_d, the need for process heat is lessened. Thus, by using an effective slurry-oil or solvent and operating under less severe conditions, engineering and economic gains might be realized.

In order to use effective solvents efficiently, either as a liquefaction pretreatment or as a slurrying liquid, they must be sufficiently cheap to be used in a once-through fashion or recoverable for downstream regeneration. While heavy bottom oils can be used as slurrying agents (as in so-called co-processing) because of their low cost and availability, there is still much merit in searching for coal solvents that will economically promote or support liquefaction under relatively mild conditions.

2.5.4 Supercritical Gas Extraction

A further extension of solvent extraction into the temperature region where active thermal decomposition begins and the coal suffers chemical as well as physical disintegration falls under the heading of supercritical gas extraction. Such extraction occurs when a highly compressed gas comes in contact with a substantially non-volatile solid or liquid. The reaction must occur at or above the 'critical' temperature (T_c) of the gas or vapour at which, regardless of the system pressure, no liquid phase can develop [103]. Under such conditions, the gas phase will have greatly enhanced solvent ability due to its supercritical density. The condensed phase contacted by a supercritical gas will extensively volatilize, with the ultimate yield far exceeding that obtained under atmospheric pressures.

The enhanced solvent power of compressed gases was discovered by Hannay and Hogarth in 1879 [104], is still not fully understood, and appears to go against conventional concepts of vapour pressure. Conventional gas laws stipulate that the vapour pressure of a

---

[103] The *critical temperature* is that temperature above which a gas cannot be liquefied by pressure alone. The pressure under which a substance may exist as a gas in equilibrium with the liquid at the critical temperature is the *critical pressure.*

[104] Deshpande, G.V., Holder, G.D., Bishop, A.A., Gopal, J., and Wender I.; Fuel, 1984, 63, 956

fluid is reduced as the external pressure increases. This, however, is not the case under conditions of supercritical gas extraction, where the vapour pressure of the contacted solid or liquid tend to increase, evidencing an apparent heightened solvent power of supercritical gases.

Paul and Wise [105] have stated that 'gas extraction' is analogous to both solvent extraction and distillation, and is effected under conditions where these processes are physically almost indistinguishable. Liquid extraction is demonstrated by the leaching of a substrate into a stream of liquid (as in Soxhlet extraction). Distillation is defined as the vaporization of a substrate into a carrier gas (as occurs during steam distillation). The mechanisms involved in these processes are closely related, as evidenced by the fact that both conditions may be realized with the same extracting fluid under different external pressures.

Above critical temperatures, high pressures increase the density of the fluid without altering its state, and the energy retained in the compressed supercritical fluid, as well as the enhanced contact between solvent and solute, can increase the volatility of the substrate up to 10,000 times under favourable conditions. [106] The increased volatility is sufficient to extract materials which normally would not vapourize below temperatures at which they would thermally decompose. The technique has proved valuable in the extraction of food derivatives, which are often very heat labile at low temperatures [107] and more pertinently, has been found to be applicable in distilling oils and tars from coal that are normally non-volatile before they thermally disintegrate.

The extracting fluid is usually chosen so that the critical temperature is very close to the temperature at which extraction is to be carried out. In the case of coal extraction, one wishes to extract matter that does not appear at temperatures below 400°C and, in fact, only forms when thermal decomposition ensues. Such substances quickly polymerize to form larger, non-volatile molecular species concurrently with the evolution of lighter condensible fractions when T_d is exceeded. In current coal distillation techniques only a relatively small

---

[105] Paul, P.F.M., and Wise, W.S.; The Principles of Gas Extraction. M&B Monograph CE/5 Mills and Boon, London, 1971.

[106] Whitehead, J.C., and Williams, D.F.J.; Inst. Fuel (London), 1975, 49, 182

[107] cf. Work done at Canadian Energy Developments in Edmonton using supercritical gas extraction with CO_2.

amount of tar is recovered from the decomposing mass. Thus, supercritical gas extraction offers a procedure for recovering nascent coal liquids prior to any heat-induced decomposition reactions.

There are a number of compounds which have critical temperatures in the vicinity of 400°C and therefore could be useful for extractng coal tars and oils. Some examples are: pyridine ($T_c = 346.8°C$), phenol ($T_c = 421.1°C$), toluene ($T_c = 320.8°C$), water ($T_c = 374.1°C$), or any appropriate coal tar or petroleum naphtha fraction with T_c in the range of ≃375-425°C. Much work has been done with toluene and, more recently, supercritical water has also been employed, either alone or in the presence of CO. These latter two solvent systems can operate under relatively mild conditions and have produced promising results.

Berkowitz and Calderon [108] studied the extraction of two Western Canadian coals with supercritical H_2O. These coals were a Saskatchewan lignite and an Albertan high volatile bituminous (hvb) coal which yielded comparatively little tar in Fischer assays. In one procedure, a 30 g coal sample was slurried with 50 ml of H_2O and transferred to the autoclave. A cold-system pressure of 2 MPa was attained by injecting sufficient CO into the vessel. An ≃2:1 H_20:CO mole ratio was achieved and the CO served the purpose of stabilizing the produced coal radicals by supplying a source of external hydrogen through the shift reaction [109]. The resultant mixture was raised to a reaction temperature of 400 or 425°C at a rate of ≃5°C min^{-1} and held there for periods ranging from 0 to 60 minutes. The temperatures were 25-50°C above the critical temperature of water (374.1°C) and sufficient to initiate the thermal decomposition of the coals. Final system pressures ranged from 3500-4200 psi (24.1-29.0 MPa).

The total conversion to primary coal liquids+water+gas was quantitatively determined for both catalyzed and uncatalyzed reactions. Conversion was found to range as high as 35-50 wt.% d.a.f. for the Alberta hvb coal and Saskatchewan lignite respectively. Additionally, it was ascertained that the extraction proceeds essentially to completion within 10 minutes, and that Fe-based catalysts increased the reactivity of the system such that

---

[108] Berkowitz, N., and Calderon, J.; Fuel Proc. Tech., 1987, 16, 245-256
[109] cf. Gasification reactions section 3.5.1

operation at lower system pressures could be achieved.

Corresponding work by Whitehead and Williams [110] with supercritical toluene and by Deshpande et al. [111] with supercritical H_2O has revealed similar high extract yields with a series of European coals. Many others are active in this field and further research will undoubtedly lead to commercial applications as the process economics improve.

2.6 Alternative Coal Solubilization Techniques

In addition to extractive processes, there are several alternative means for deriving soluble coal products. These methods, although effective in their own right, are not closely related to solvent extraction or solvolysis and will only be briefly discussed here. This section deals with:

1. Pyrolysis (Carbonization)
2. Indirect Liquefaction
3. Laboratory procedures

2.6.1 Pyrolysis

Carbonization is the process by which coal is pyrolyzed in order to effect destructive distillation of the solid hydrocarbon. A host of useful compounds and by-products may be generated. These products vary, depending particularily on the temperature at which the coal is pyrolyzed. They include tars, light oils, coke, char, and various gases.

Coal carbonization processes are separated into two regimes distinguished by the low and high temperatures at which they are pyrolyzed. Low temperature carbonization was originally used to manufacture 'town gas' for residential and commercial lighting, and smokeless char for domestic heating and cooking. Dating from the late-eighteenth century,

---

[110] Whitehead, J.C., and Williams, D.F.J.; Inst. Fuel (London), 1975, 49 182-184

[111] Deshpande, G.V., Holder, G.D., Bishop, A.A., Gopal, J., Wender, I; Fuel, 1984, 63, 956

low temperature carbonization operations have been carried out in a vast array of vertical and horizontal retorts. Temperatures are maintained below ≃700°C, and process heat is supplied directly or indirectly, depending on the particular equipment.

High temperature carbonization is the process by which coke is produced from metallurgical or 'coking' coals when heated at ≃900°C. Coke is a highly reactive, porous, structurally strong, carbon-rich coal derivative used particularly in the iron and steel industry as fuel and carbon donor. Coal tars produced in H.T. processing are not directly relevant to this study.

Coal tars produced by low temperature (and H.T. processing) carbonization processes were originally thought of as annoying waste materials. This viewpoint was changed dramatically in the mid-nineteenth century. The development of a chemical industry in Western Europe brought about the realization that coal tars could be used as important feedstocks. A myriad of uses have since been found for tar and refined tar products. Some of the earlier products developed from coal tars include textile dyestuffs, pharmaceuticals, motor fuels, solvents, lubricants, waxes, plastics, and synthetic fibres. Coal tar processing is very closely related to petroleum refining techniques and by the early 1930's most of the liquid fuels and products derived from crude oil could be fashioned from coal tars. These techniques are not economically feasible in times of plentiful oil, but very effective in times of national crisis. The Germans demonstrated this during World War II, in particular, when they fueled their war machine almost entirely with gasolines and diesel fuels obtained from coal and coal tars.

The composition of low temperature tar can best be described as a melange of hydrocarbon compounds. In this respect it closely resembles crude petroleum and shale oil but differs from the relatively homogenous high temperature tars. Compositional analysis of low temperature tars has received very little attention until recently due to the fact that the thousands of compounds present occur in only miniscule amounts. The composition of low temperature tars depends on the actual nature of the coal as well as on the specifics of the carbonizing equipment and carbonization parameters such as temperature, residence time and, most important, the maximum temperature to which the tars are exposed. Tars produced from different coals or from different retorts can be as different as two snowflakes.

Typically, low temperature tars from subbituminous and bituminous coals appear as dark brown fluid oils. They contain relatively high proportions of mono- and dihydric-phenols, methyl-substituted pyridines, n-paraffins and olefins. L.T. tars from lignites are similar but may contain up to 10% paraffin waxes. In general, as the rank of the coal increases, the yields of tars and light oils rises. A plateau is reached at approximately 87% carbon content and, thereafter yields fall rapidly so that anthracites produce very little or no tar. These facts are consistent with a mechanism in which carbon and oxygen compete for hydrogen during the carbonization process.

The determination of liquid and gaseous decomposition products likely to accrue from coal in an inert atmosphere have been standardized in most industrial nations. The two most widely utilized methods are the *(i) Fischer assay* , developed in Germany by Fischer and Schräder [112] and later modified for usage in the United States and other European countries, and the *(ii) Gray-King assay*, which was first defined in Britain [113]. Both of these quantitative destructive distillation procedures are generally conducted at 500° or 600°C. They tend to overestimate light tars and oils, while reporting diminished gas yields.

2.6.2 Indirect Liquefaction

An alternate route for coal liquefaction involves gasification and subsequent Fischer-Tropsch synthesis of the resulting syngas. Where gasification is effected by incompletely combusting coarse coal in fixed-beds (eg. Lurgi, Wellman), or pulverized coal in fluidized-bed (eg. Winkler), or dilute phase coal injection (eg. Koppers-Totzek), reactors. This is a comparatively harsh process since the reactions completely break down the complex molecular structure of the coal. The product slate depends on factors such as reaction pressure, temperature, oxygen content, and operating catalyst.

---

[112] Fischer, F., and Schräder, H.; Z. Angew. Chem., 1920, <u>33</u>, 172
[113] Gray, T., and King, J.G.; GB. DSIR Fuel Res. Tech., 1921, Paper <u>1</u>

When coal is reacted at high temperatures in controlled oxidizing atmospheres so as to effect incomplete combustion a completely different slate of products is generated than in destructive distillation of coal. If the reaction is propagated with air, the resulting off-gas, termed 'producer gas', will have a heat content of ≈150 Btu/scf and will contain ≈33% CO, the rest being CO_2 and N_2. If steam is admitted to the reactor, a carbon-steam reaction will occur, yielding more CO and H_2. This so-called 'water gas' has a greater heat content than the producer gas. The aforementioned reactions may be undertaken with steam and oxygen rather than air and steam. The resultant gas will then be a nitrogen-free synthesis gas consisting primarily of CO_2, CO and H_2 which, after removal of CO_2, constitutes an important chemical feedstock. At elevated pressures and temperatures above 1150°C, hydrogen will also interact directly with carbon to form methane.

This is in sharp contrast to 'town gas' derived from low temperature carbonization which only represents the lighter volatiles (not the tar component) and therefore only constitutes ≤ 10% of the original coal material. The gasification reactions are :[114]

1.	$C + O_2 \rightleftarrows CO_2$	(+395.4 MJ)	combustion
2.	$C + CO_2 \rightleftarrows 2CO$	(-167.9 MJ)	Boudouard reaction
3.	$C + H_2O \rightleftarrows CO + H_2$	(-135.7 MJ)	carbon-steam reaction
4.	$CO + H_2O \rightleftarrows CO_2 + H_2$	(+32.18 MJ)	shift reaction
5.	$C + 2H_2 \rightleftarrows CH_4$	(+91.6 MJ)	carbon hydrogenation

Whereas carbonization yields and composition always depend on coal rank and the temperature at which the coal is carbonized, these factors only affect the rate of gasification. The amount of oxygen available makes the largest impact on the product gases due to the extensive and controllable secondary interactions of volatile matter and residual char (or coke) with oxygen. The resultant syngas[115] or product gas may be used for heating purposes or as

---

[114] cf. Berkowitz, N. An Introduction to Coal Technology. p. 251

[115] This is nitrogen-free synthesis gas derived from gasification reactions conducted with pure O_2. Producer gas has a lower heat content and is not as amenable to petrochemical upgrading due to its dilution with atmospheric nitrogen.

an upgradable petrochemical feedstock for subsequent liquefaction via Fischer-Tropsch CO hydrogenation: [116]

$$2n\ H_2 + nCO \rightleftarrows (CH_2)_n + n\ H_2O$$

2.6.3 Laboratory Procedures

One of the more noteworthy discoveries in coal science of the last 15-25 years has been the finding that several relatively mild chemical reactions tend to 'depolymerize' the coal material. A more soluble, lower molecular weight substance is generated at temperatures far below the onset of thermal decomposition. These methods include ***transalkylation*** (aromatic interchange), ***reductive alkylation, and Friedel-Crafts alkylation.*** Although these techniques offer little potential for large-scale liquefaction, they do contribute to a better understanding of the structure and chemical properties of coal. This is achieved through their ability to solubilize the coal macromolecules without, it is presumed, markedly altering their basic structures.

Depolymerization reactions were first reported by Heredy and Neuworth et al. [117] [118] and are based on the ability of boron trifluoride (BF_3) -catalyzed phenol to cleave aryl-alkyl-aryl systems. When applied to coal, this ***transalkylation*** reaction proceeds at temperatures as low as 100°C and may reach completion within 4-5 hours. It yields a 'depolymerized' product that is up to 75% soluble in phenol [119] Phenol solubilities tend to decrease with increasing carbon content of the coal falling from 75% in the case of lignites

---

[116] The Republic of South Africa produces motor fuels and chemicals from coal based on the Fischer-Tropsch reaction by passing H_2 and CO in specific ratios over iron catalysts at elevated temperatures and pressures. Their first Sasol plant has been operating commercially since 1955 and consists of Lurgi coal gasification followed by Lurgi-Rectisol gas purification with the resultant high purity synthesis gas being hydrogenated to produce liquid hydrocarbons. Additional complexes, Sasol I & II, have since been commissioned in 1980 and 1984 respectively. (cf. Berkowitz, N. The Chemistry of Coal. p. 393)

[117] Heredy, L.A., and Neuworth, M.B.; Fuel, 1962, 41, 221

[118] Heredy, L.A., Kostyo, A.E., and Neuworth, M.B.; Fuel, 1963, 42, 182

[119] McCaulay, D.A., in "Friedel-Crafts and Related Reactions", (Olah, G.A., ed.), Vol 2, Part 2, 1062. Wiley (Interscience), New York, 1964.

(70% C) to 9% for low-volatile bituminous coals (91% C).

It has also been found that an extensive increase in coal solubility in organic solvents may be effected by ***Friedel-Crafts alkylation***. This reaction is brought about by reacting coal with an alkyl halide (such as n-propyl chloride or benzyl chloride) and $AlCl_3$ in carbon disulphide at 45°C [120]. In this fashion up to 10 or 11 alkyl groups per 100 carbon atoms could be introduced, and up to ≃70% of the alkylated material could be taken into solution with pyridine. The reaction products were found to be more aromatic than the precursor coals despite their increased solubility. This may be due to simultaneous $AlCl_3$-induced condensation reactions.

Sternberg et al. [121] investigated a ***reductive alkylation*** method which also increased the solubility of coal in organic solvents. In this procedure the coal is reacted with metallic potassium and tetrahydrofuran (THF) in the presence of naphthalene. Via electron transfer by naphthalene, a coal anion is produced which can then be alkylated by treatment with alkyl halides. This reductive alkylation generates a product that is for the most part soluble in benzene. Although alkylation is generally supposed to split ether linkages and some C-C bonds, [122] such rupture is limited and alkylated materials consequently have number-average molecular weights ranging as high as 3300 [123]. But the mechanics of reductive alkylation are still a subject of debate.

---

[120] Kröger, C. and de Vries, H.; Liebig's Ann., 1962, 652, 35

[121] Sternberg, H.W., Delle Donne, C.L., Pantages, P., Moroni, E.C., and Markby, R.E.; Fuel, 1971, 50, 432

[122] Berkowitz, N. An Introduction to Coal Technology. Academic Press Inc., New York, 1979.

[123] Sternberg, H.W., Delle Donne, C.L., Pantages, P., Moroni, E.C., and Markby, R.E.; Fuel, 1971, 50, 432

3. Experimental

3.1 Introduction

The objective of this research was to study solvolytic extraction of a suite of Canadian subbituminous and bituminous coals in order to evaluate three features of such extraction. The first query was whether relatively mild solvent extraction could offer a viable route to easily upgradable hydrocarbons. The second sought to compare behavioural differences between Western Canadian subbituminous and bituminous coals that could affect extraction and/or subsequent processing. The third aspect was to briefly examine possible differences in extractability between Eastern Canadian Carboniferous and Western Canadian Cretaceous coals.

The initial experimental work focused on comparing the relative abilities of four organic solvents, α-naphthol, β-naphthol, phenanthrene and naphthalene, to generate THF-soluble products when extracting Alberta coals under mild conditions (low temperature and autogenic pressure). Further investigation examined differences in extractability between Western Canadian Cretaceous subbituminous and bituminous coals, and Eastern Canadian Carboniferous bituminous coals. Additionally, the feed coals were exhaustively Soxhlet-extracted with THF in order to observe any solubility and/or THF-retention trends.

It is important to understand the basis of comparison in these experiments, that being the conversion to THF-soluble material. THF was chosen as the classifying agent over such commonly used solvents as pyridine, benzene, toluene or chloroform for a number of reasons. THF, for the most part, will bring soluble hydrocarbons into a true molecular solution. Other solvents, such as pyridine, tend to disperse varying amounts of coal material in addition to solvating them. The inadvertant, but obviously incorrect representation of colloidal dispersions as solutions has long muddied the waters of coal-solvent research. A THF-soluble extract, by definition, contains preasphaltenes and lighter matter. It is really of no practical significance to isolate precursors to preasphaltenes, as such material is generally deemed unsuitable as an hydrogenation feedstock. Most potent coal solvents, such as pyridine and ethylenediamine tend to become intimately bound to the coal matrix making their recovery from the coal and extract prior to analysis prohibitively difficult. Retention of THF is virtually negligible as it has been found to be limited to ≈5% for the coals under study [124]. Lastly, THF is able to completely dissolve the four extracting agents used in this study [125]. This fact is important from a material balance point of view when calculating the proportion of organic matter extracted from the coal, and also allows THF to be used as a cleaning and material transfer solvent.

The extracting agents were chosen from a selection of notable coal solvents mentioned in extant literature. α-Naphthol was focused upon after an initial comparative study because it is reportedly equally effective for subbituminous and bituminous coals [126]. Although it has been noted in the literature that the proportion of benzene-soluble material increases with the solvent:coal ratio, this ratio has been kept low in these experiments. This was done in order to economize on chemicals which would be prudent if one were to consider the practical viability of any scaled-up extraction process for yielding readily upgradable hydrocarbons. It should also be noted that the main thrust was a comparison of the different coals under set solvolytic conditions rather than maximizing extract yields and subsequent proportions of THF-solubles.

The difference between extract yield and the fraction of THF-soluble material should be reiterated. The extracting agent (e.g. α-naphthol) may produce an amount of extractable material through interaction with the coal, but the determination of the mass of such extract was not the objective in this study. The aim of this work was to quantify and compare THF-soluble material in the gross extract.

As previously stated, this study was centered on solvolytic extraction and avoided subjecting the coals to severe conditions. Temperatures were limited to 350°C, which is well below the onset of massive decomposition of most coals, and pressures were either autogenic or induced with pressurized nitrogen gas. The nominal pressures achieved at the operating

---

[124] See Table 4 for THF-imbibition tests.

[125] See Table 5 for results of solubility tests.

[126] Golumbic, C., et al.; USBM Repts. Invest. #4662, 1950

temperature were sufficient to maintain the organic solvents in the liquid phase, therefore sustaining good solvent/coal contact. Agitation of the solvent/coal mixture was deemed necessary to further guarantee satisfactory solvent/coal contact. The final consideration was of scale.

In order to achieve the aforementioned goals while keeping technical problems to a minimum, the experiments were performed in stainless steel micro-bombs. Such small pressure vessels have been used effectively in conjunction with electrically heated sand baths by, inter alios, Maa et al., [127] Neavel [128] and Gillet et al. [129] [130] [131]. Other apparatus used in conjunction with the micro-bombs in this work included a fluidized sand bath, a temperature controller, a bomb agitation device, a gas charging system, a gas collection system, a top load balance and conventional equipment for coal preparation (such as crusher, pulverizer, sample splitter, vacuum oven, etc.) Additionally, an ultrasonic cleaner was required for sample retrieval and adequate cleaning of the bombs. Extraction was performed in standard Soxhlet apparatus and gas analysis was conducted in a Fischer gas chromatograph. A schematic of the experimental apparatus is shown in Figure 1.

3.2 Coal Preparation

Six Canadian coals were used for the experimentation. They included three Carboniferous high volatile A bituminous (hv Ab) coals from Nova Scotia and three coals from Alberta. The latter are of Cretaceous age and consisted of one high volatile A bituminous coal (hv Ab) from the Foothills and two subbituminous coals from the Plains areas. Descriptions of these coals, as well as their proximate and ultimate analyses [132] are contained in Tables 1.1 and 1.2. Ash analyses required for calculations are shown in Table 2.

---

[127] Maa, P.S., Neavel, R.C., Vernon, L.W. W. Ind. Eng. Chem. Process Des. Dev. 23, 1984. 242-250

[128] Neavel, R.C.; Fuel, 1976, 55,

[129] Gillet, A. and Pirlot, A.; Bull. Soc. Chem. Belg., 1935, 44, 504

[130] Gillet, A. and Pirlot, A.; Bull. Soc. Chem. Belg., 1938, 47, 158

[131] Gillet, A. and Pirlot, A.; Bull. Soc. Chem. Belg., 1942, 51, 23, 525

[132] Analyses performed at the ARC laboratory in Devon, Alberta.

Table 1.1 Elemental and Proximate Analysis of Feed Coal:
Alberta Cretaceous Coals
Units of Wt %

Coal No.	Type	Location		Ash	Vol Mat	Fixed C[d]	C	H[b]	N	S	O[c]
9	Subbituminous	S. Tofield	dry	24.6	31.9	43.4	52.5	2.7	1.22	0.92	42.7
			d.m.m.f.		42.3	57.5	69.6	3.6	1.61	1.23	24.0
10	H.V. A-Bituminous	Obed-Marsh	dry	13.5	35.4	50.9	64.7	3.6	1.54	0.25	29.9
			d.m.m.f.		41.0	58.9	74.8	4.2	1.78	0.29	18.9
11	Subbituminous	Vesta	dry	16.0	35.7	47.9	59.8	3.1	1.40	0.52	35.2
			d.m.m.f.		42.5	57.1	71.2	3.7	1.67	0.62	22.8

a. As received moisture values aren't recorded as they are ambiguous in the present context.
b. H values do not include % H of moisture.
c. O values are by difference and rounded to one decimal.
d. Fixed C = (100 - Volatile Matter - Ash)

Table 1.2 Elemental and Proximate Analysis of Feed Coal:
Nova Scotia Carboniferous Coals
Units of Wt %

Coal No.	Type	Location		Ash	Vol Mat	Fixed C[d]	C	H[b]	N	S	O
14	H.V. A-Bituminous	Lingan (N.S.)	dry	4.6	38.4	56.9	81.5	5.1	1.53	2.51	9.4
			d.m.m.f.		40.2	59.7	85.5	5.4	1.60	2.63	4.9
15	H.V. A-Bituminous	Prince (N.S.)	dry	2.4	38.0	59.5	79.0	5.0	1.56	1.77	12.7
			d.m.m.f.		38.9	60.9	80.9	5.1	1.60	1.81	10.6
16	H.V. A-Bituminous	Phalen (N.S.)	dry	3.0	34.3	62.7	82.3	5.1	1.45	0.85	10.3
			d.m.m.f.		35.3	64.6	84.8	5.2	1.49	0.88	7.6

a. As received moisture values aren't recorded as they are ambiguous in the present context.
b. H values do not include % H of moisture.
c. O values are by difference and rounded to one decimal.
d. Fixed C = (100 - Volatile Matter - Ash)

Table 2 Proximate Analysis of Feed Coal [a] :
Alberta Cretaceous & Nova Scotia Carboniferous Coals
Units of Wt %

Coal	Type	Location	H.T. Ash initial	H.T. Ash final	H.T. Ash ave.	Moisture	Vol Mat
9	Subbituminous	S. Tofield	26.5	23.8	25.2	6.3	29.9
10	H.V. A-Bituminous	Obed-Marsh	13.7	12.9	13.3	4.9	34.5
11	Subbituminous	Vesta	14.0	11.6	12.8	12.4	39.3
14	H.V. A-Bituminous	Lingan (N.S.)	4.2	4.4	4.3	0.8	34.5
15	H.V. A-Bituminous	Prince (N.S.)	2.3	2.1	2.2	3.5	35.1
16	H.V. A-Bituminous	Phalen (N.S.)	2.8	2.6	2.7	2.3	31.2

a. Analyses performed at the U of A.

Prior to preparation, all coals were stored under water and frozen. As needed, they were thawed and dried at low heat in a nitrogen-purged vacuum oven. The dried coal was then crushed, mixed, and split to obtain a representative sample. The required portion was then ground to -100 mesh particle size and stored in an air-tight, CO_2-purged bottle prior to usage.

3.3 Apparatus

1. **Micro-Bombs and Steel Tubing** Small cylindrical stainless steel micro-bombs (see Fig. 1.5) were chosen over a standard autoclave for their ease of handling small samples, and an ebullated bed sand bath was employed to rapidly heat them. The micro-bombs were of two sizes: 75cc and 150cc volume. Most experiments were performed with the 75cc bombs, using a 2:1 solvent to coal ratio; the larger volume bombs were used for ratios of 4:1. The micro-bombs were made of a special low carbon grade stainless steel 304L, and have a service pressure of 1800 psi (≃1240 MPa).

   All hardware in the pressurized system was comprised of Swagelok high-pressure fittings. The complete bomb assembly included the micro-bomb (see Fig. 1.5) and a 10 1/2" length of 1/4" O.D. tubing (see Fig. 1.9) that acted as both linkage to the agitator and the connection to the gas charging and withdrawal system. This tubing was connected by a length of coiled 1/8" tubing (see Fig. 1.10) to the valve tree. The coiled tubing functioned as a vibration damper between the oscillating micro-bomb and the gas system and also served to isolate the valve assembly from the hot sand bath. The tubing used was standard 1/8" and 1/4" O.D. 316 stainless steel.

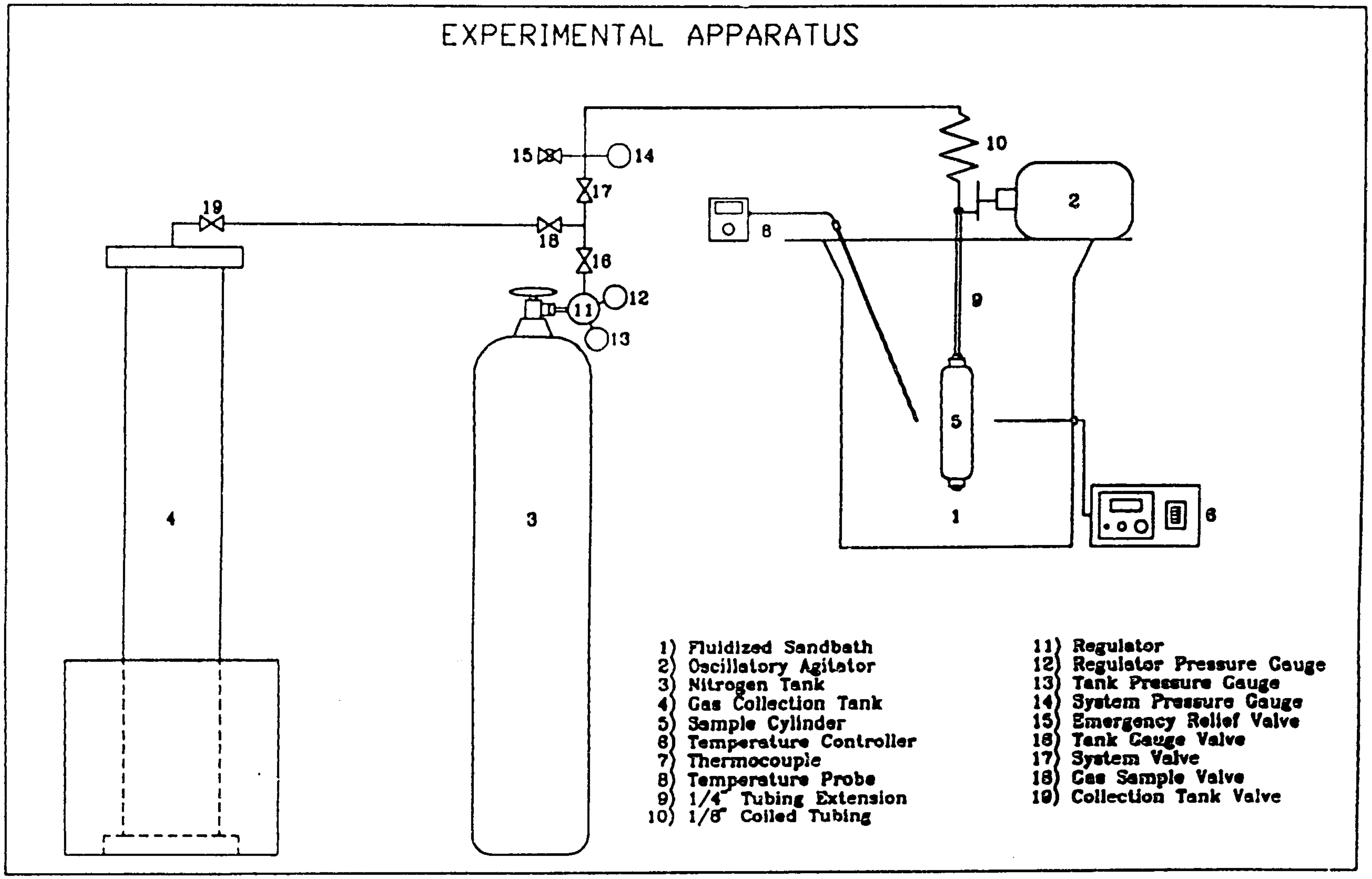


Fig. 1 Schematic of Experimental Apparatus

2. **Gas Charging and Collection System** Coupled to the bomb assembly and coiled 1/8" tubing was a valve tree used for charging the micro-bombs with pressurized nitrogen and evacuating them after they had cooled. As seen in Figure 1, the valve assembly consisted of a double 'T'-shaped, 4-valve system. That comprised three manually activated control valves and one pressure relief valve set to release at 1700 psi.

   Immediately before the first control valve (see Fig. 1.17), which effectively isolated the pressurized bomb and relief valve (see Fig. 1.15) from the rest of the system, was a gauge (see Fig. 1.14) which measured micro-bomb system pressure. Another valve (see Fig 1.18) was used to control the flow of product gases into a gas reservoir and to isolate this from the nitrogen charging tank. It was also used to apply vacuum to the micro-bomb as well as to bleed off any excess pressure in the system. The fourth valve (see Fig 1.16) isolated the regulator and nitrogen tank from the system.

   The product gases were vented through Tygon tubing into a clear acrylic water displacement cylinder (see Fig. 1.4). This cylinder was calibrated for volume determination and allowed gas samples to be drawn off for analysis through a septum. The water in the cylinder was saturated with salt in order to minimize product gases going into solution in the water.

3. **Fluidized Sand bath, and Temperature Controller** The micro-bombs were heated in an air actuated fluidized sand bath (see Fig. 1.1). An expanded metal skirt around the top of the unit minimized sand loss. The temperature of the bath was regulated by a temperature controller (see Fig. 1.6) which responded to signals from a thermocouple (see Fig. 1.7) inserted into a port in the sand bath. Temperature readings were recorded from a digital read-out on the controller and verified by a temperature probe (see Fig. 1.8) inserted directly into the sand beside the micro-bomb.

4. **Micro-Bomb Agitator** An improvised system was built for agitating the pressure vessels and ensuring proper mixing. It consisted of an eccentric wheel and clamp driven by a 3/8" power drill (see Fig. 1.2). This provided an oscillatory motion that raised and lowered the bomb at the end of 1/4" O.D. extension tube (see Fig. 1.9). The throw of

this motion from top dead center to bottom was ≈1.5" and the operating frequency was maintained at ≈120 cycles per minute. The micro-bomb was connected to the gas charging system via a length of coiled 1/8" O.D. tubing attached at the top of the micro-bomb extension.

5. Ultrasonic Cleaner A 3/4 gallon capacity ultrasonic cleaner was employed for cleaning the micro-bombs. A glass liner and cover were designed to protect the cleaner from the THF used as cleaning fluid and extract solvent. The liner and cover also served to limit solvent evaporation from the unit due to heating during prolonged sonic action.
6. Soxhlet Extraction Apparatus Extraction of the unreacted coal/solvent residue, and of THF-soluble products was performed in standard Soxhlet apparatus at atmospheric pressure. The complete mixture of THF-solubles and insolubles was quantitatively transferred from the ultrasonic cleaner to cellulose extraction thimbles and further extracted with THF to determine the total amount of THF-solubles.
7. Gas Analyses All gas analyses were done in a Fisher Gas Partitioner model #1200. It incorporated two columns and two detectors. The first column was a gas/liquid chromatography (GLC) partition column which separated carbon-dioxide and most of the hydrocarbons, and consisted of 27.3% DC-200/500 on 80/100 mesh Chromasorb P-AW. The second was a molecular sieve adsorption column which separated methane and most of the fixed gases such as CO, N_2, O_2, H_2S and H_2. It consisted of 2 sections, the first packed with 80/100 mesh Chromasorb P-AW and the second packed with 60/80 mesh Molecular Sieve 13X. The gas partitioner was connected to an on-line Spectra-Physics model SP4290 integrator.

3.4 Experimental Procedures

3.4.1 Preparation of Micro-bombs

The micro-bomb assembly was comprised of the micro-bomb (either 75 or 150 cc capacity) and the Swagelok fittings required to seal the micro-bomb and connect the tubing extension. New micro-bombs were burnished prior to first usage to oxidize any coatings which might alter the tare mass. It was important to ensure proper seals at all pipe and tubing connections [133], and considerable care was taken in assembling and pressure testing the bombs.

The micro-bomb and extension were pressure-tested after initial fitting and prior to each usage. The system was charged with nitrogen to the anticipated final pressure of ≈1500 psi. All connections were swabbed with soap solution to detect leaks and the pressure was held for approximately one hour. Any bubbling at the joints or an appreciable drop in pressure indicated a leak and the faulty connections were tightened or replaced.

3.4.2 Charging Micro-Bombs

In preparing the micro-bombs for each experiment, the first step was to take the required coal mass out of the sealed containers and dry it, in vacuo, in a tared sample dish for approximately one hour. Similarly, the extracting solvent was dried in a desiccator over anhydrous $CaSO_4$ to remove any sorbed moisture. The dry weights of both coal and solvent were recorded, and both were then quantitatively transferred to the tared micro-bomb. The empty weight of the micro-bomb was recorded for later reference as a gauge of cleaning efficiency.

The filled micro-bomb was then fully assembled, care being taken in teflon-taping and sealing each fitting, and the complete unit connected to the coiled tubing linking it to the gas charging system. Thereafter the micro-bomb was once more pressure tested, and all residual air purged from the system. If the run was to be done under autogenic pressure, the bomb was evacuated by connecting a vacuum line to the valve tree. If a pressurized run was desired, the bomb was recharged with N_2.

---

[133] It should be noted that pipe sizes are gauged on an I.D. basis while tubing values are for O.D.

3.4.3 Experimental Procedure

The sand bath was preheated to the desired operating temperature. This usually required approximately three hours to reach stability. The airflow was adjusted so that it just fluidized the sand, and a constant temperature could be maintained throughout the sand mass. The temperature was read from the controller as well as from a remote sensor placed directly in the sand bath.

The sealed bomb was tightly wrapped in foil to the top of the tubing extension in order to keep abrasive sand out of the threads and fittings. The whole assembly was then lowered into the sand bath, clamped into position on the oscillatory agitator, and the agitator was turned on to operate at ≈120 cycles/min. Experiments ran for 30 minutes with temperature and pressure readings being monitored continually and recorded at five minute intervals. Any sharp pressure drop indicated a faulty seal and the run was discontinued.

The heat-up period for the stainless steel micro-bombs was ≈2 minutes as determined by observation of initial pressure changes. To compensate for this, the bombs were not quenched until 2 minutes after being lifted from the sand bath. Thus, residence time was defined as the time from initial placement in the sand bath to the time the bombs were lifted from the bath.

At the completion of the extraction, the micro-bomb was lifted from the sand bath and allowed to air cool for two minutes. Thereafter it was quenched in cold water and the final cold pressure was recorded. (A value below the initial cold pressure indicated a leak)

After cooling to room temperature, the product gases were vented into the evacuated gas reservoir and the volume determined. The gas mixture was then ready for analysis.

3.5 Product Recovery & Analysis

3.5.1 Analysis of Product Gases

The trapped gases were analyzed immediately after collection in order to avoid absorption of water-soluble gases (such as H_2S or CO_2), and gas stratification which would lead to nonrepresentative sampling.

Gas samples were drawn through a septum port at the top of the collection cylinder into a calibrated volumetric syringe and injected into the gas partitioner. Calibration of the gas partitioner with known volumes of pure gases enabled accurate detection and quantification of product gases. Volume determinations and, ultimately, the mass and the mass percent were calculated using gas laws and calibration formulae. These values are summarized in Appendix 2.

3.5.2 Cleaning Bombs and Extraction of Soluble Matter

After collecting product gases from the micro-bomb, the complete micro-bomb assembly was removed from the charging/collecting apparatus. The bomb and extension tubing were disconnected at the juncture of the 1/8" coiled tubing. The extension tube was then separated from the rest of the bomb and fittings, and rinsed with THF into the glass liner of the ultrasonic cleaner which was the catchpot for all residues and generated products.

The bomb assembly was further dismantled and all the fittings, as well as the micro-bomb, placed in the liner, which was subsequently filled with the cleansing solvent (THF). As yield was based on the amount of THF-soluble matter, using THF as the cleanser simplified the procedure. A fitted glass lid placed on the ultrasonic cleaner during cleaning prevented any accidental loss of material.

The ultrasonic cleaner required two to three days to completely clean the fittings and micro-bomb. When the bomb and fittings were almost clean, the contents of the glass liner were quantitatively transferred to a 4 litre pyrex beaker, and the bomb and fittings placed back in the liner with fresh solvent in order to complete cleaning. That point was determined by drying and weighing the parts of the micro-bomb assembly and comparing their weights with those recorded prior to charging. This additional extract was also quantitatively transferred to the beaker where it was allowed to settle while covered.

3.5.3 Separation and Soxhlet Extraction of Solid Residue

The soluble material was decanted from the residual solids and filtered through tared vacuum-dried 33mm x 94mm cellulose extraction thimbles to remove any solid particles. The solid residue was then quantitatively transferred to the extraction thimbles which, when dry, were placed in Soxhlet apparatus and exhaustively extracted with THF. This process took approximately 5 days. The extract solution was combined with the previous extract and saved. The thimbles were then dried under vacuum and further extracted with acetone to remove residual THF absorbed by the solid residue and extraction thimble. This was accomplished in approximately 2 days.

The solid residue and the extraction thimbles were dried again under vacuum, and the final weights were compared with the initial tared weights of the dried thimbles in order to determine the weight of the solid residue. This weight was most important because it served as the basis for determining percentage conversion to THF-soluble material.

3.6 Experimental Results and Discussion

3.6.1 Results

The detailed extraction results are tabulated in Appendix 1. Gas analysis data are summarized in Appendix 2. The elemental and proximate analysis of the suite of coals under study are detailed in Table 1 [134]. Table 2 contains the ash values and other feed coal analyses performed at the University of Alberta (Average ash values were used for all calculations.). Table 3 presents THF-solubility data for the feed coals, and Table 4 shows the results of a study that tested the potential of THF to become entrained in the residual coal and extract. Table 5 lists the solubility of the extracting agents in common laboratory solvents.

---

[134] These values were determined at the Alberta Research Council labs in Devon.

Table 3 Soxhlet Extraction of Feed Coal:
Summary of Experimental Data

Coal		Initial	Values			Final	Values		Extractability [a]
No.	Mass, g	Ash %	Organics, g	Ash, g	Mass, g	Ash %	Organics, g	Ash, g	%
9	9.77	25.2	7.31	2.46	9.64	25.08	7.18	2.42 (2.46)	1.78 [b]
10	10.29	13.3	8.92	1.37	10.05	13.33	8.68	1.34 (1.37)	2.69 [b]
11	9.41	12.8	8.21	1.20	9.13	15.43	7.72	1.41	5.97
14	10.37	4.3	9.92	0.45	8.79	5.45	8.31	0.48	16.23
15	9.95	2.2	9.73	0.22	8.92	2.55	8.69	0.23	10.69
16	9.62	2.7	9.36	0.26	8.34	2.86	8.34	0.25	10.90

a. Exhaustive extraction with THF and then Acetone.

b. Where ash content decreases, initial ash mass is used and value is bracketed ( ).

Table 4 THF Imbibition of Feed Coal :
Alberta Cretaceous & Nova Scotia Carboniferous Coals

Coal	Type	Location	Mass (g)				% Solvent Imbibed
			initial	final	final+extract	difference	
9	Subbituminous	S. Tofield	10.53	10.68	10.93	0.40	3.8
10	H.V. A-Bituminous	Obed-Marsh	10.68	10.66	11.17	0.49	4.6
11	Subbituminous	Vesta	9.45	9.61	9.77	0.32	3.4
14	H.V. A-Bituminous	Lingan (N.S.)	11.19	9.50	11.78	0.59	5.3

Table 5 Solubility of Extracting Agents[a] :

Extracting Agent			Solvents			
	Ether	Methanol	Acetone	Toluene	THF	Benzene
α-naphthol	s	s	s	s-h	s	s
β-naphthol	s	s	s	s-h	s	s
naphthalene	s	in	s	s	s	s
phenanthrene	s	sl	s	s	s	s
anthracene	in	in	in	in	in	s
coal tar	s	sl	s	s	s	s

a. Analyses performed at the U of A.

s = soluble
sl = slightly soluble
s-h = soluble when heated
in = insoluble

The initial series of experiments (No. 1-28) were performed under autogenically induced pressures, the system being originally purged with nitrogen and then evacuated. Coal #11 (Cretaceous subbituminous) was extracted at 325°C with 4 organic solvents - naphthalene, β-naphthol, α-naphthol, and phenanthrene - at a 1:1 coal to solvent ratio. As shown in Figure 2, α-naphthol produced the greatest amounts of THF-soluble material under these conditions.

Coal #10 (Cretaceous bituminous) was extracted with both α-naphthol and phenanthrene at a 2:1 solvent to coal ratio and at temperatures of 225° and 325°C. Both solvents generated negligible amounts of THF-soluble matter at 225°C, but α-naphthol produced significantly more than phenanthrene at 325°C. This is illustrated in Figure 3.

Extraction with α-naphthol at 225°C, and at a 2:1 solvent:coal ratio, is shown in Figure 4. The Cretaceous coals from Alberta (#9 & #11 are subbituminous while #10 is bituminous) produce negligible yields of THF-soluble matter while the Carboniferous coal from Nova Scotia (#14 - bituminous) produced a substantial conversion to THF-soluble material. Under similar operating conditions, coals #10 and #14 were extracted with phenanthrene. Again the Carboniferous coal yielded some THF-soluble material whereas exhaustive extraction of the Cretaceous coal produced insignificant yields of THF-soluble matter (see Fig. 4).

When the above 4 coals were extracted at 325°C with α-naphthol at a 2:1 solvent coal ratio, all furnished significant yields, with the Carboniferous coal showing the greatest conversion to THF-soluble matter (see Fig. 5).

An experiment was performed to investigate the solubility of the feed coals in THF. Exhaustive Soxhlet extraction of the 4 coals as well as 2 other Carboniferous bituminous coals from Nova Scotia (#15 & #16) was undertaken. It was noted that the Carboniferous coals generally yielded at least twice as much THF-soluble material as the Cretaceous in this treatment. This data is outlined in Table 3 and graphically shown in Figure 8.

Additionally, a brief material balance study of the potential for THF to associate with the coal residue and extract was undertaken. It was found that a mass increase of up to ≃5%

of the original mass of coal can be attributed to retained THF (see Table 4).

After run No. 28, experiments were carried out under pressure generated by charging the micro-bombs with nitrogen prior to heating. All 6 of the aforementioned coals were used.

When extracted with α-naphthol (2:1 solvent:coal) at 325°C, all coals produced significant conversion to THF-soluble matter, but at 275°C all coals showed a marked decrease in yield (see Fig. 6). When the solvent:coal ratio was increased to 4:1 while maintaining a temperature of 325°C, the generation of THF-solubles with α-naphthol was greatly enhanced (see Fig. 7).

The gas analyses, as tabulated in Appendix 2, compare the gas produced on a basis of % mass of original organics, and show some interesting trends. At 325°C and autogenic pressures, the Cretaceous subbituminous coals tended to yield more gas than the Cretaceous bituminous coals, with no apparent extracting agent bias. This trend continues at elevated pressures. However, Carboniferous bituminous coals produced greater gas yields than their Cretaceous counterparts, and Coal #11 produced somewhat more gas than coal #9.

At elevated pressures, gas makes tend to vary directly with temperature. A higher system pressure slightly enhances gas production for both Carboniferous and Cretaceous coals. The gas produced was predominantly CO_2.

3.6.2 Discussion of Results

As stated, the first runs were used to select a suitable extracting agent for the main body of experiments. Coal #11 (subbituminous) was used for these extractions which were conducted under autogenic pressures at 325°C. A low solvent:coal ratio (1:1) was used as it was assumed that any solvent concentration effect would be substantially similar for all solvents. This assumption was deemed permissible as it really did not matter to the rest of the experiments which extracting agent was chosen as long as it was kept constant for the balance of the runs. It was found that α-naphthol was most effective in generating THF-soluble material under these conditions (see Fig. 2).

Another experiment was conducted under similar conditions to check the validity of the aforementioned results for a bituminous coal, #10. In this case only two extracting agents were used, α-naphthol which was by far the most effective agent for generating THF-solubles from the subbituminous coal, and phenanthrene which was a good extracting agent for bituminous coal. The solvent:coal ratio was raised to 2:1, and α-naphthol again emerged as the better producer of THF-solubles (see Fig. 3). These results support the findings of Golumbic et al. in their 1950 work [135]. α-naphthol was thus chosen as the primary extracting agent and the solvent:coal ratio was standardized at 2:1.

A further trial at 225°C was conducted in order to assess the temperature effect on the performance of the two extracting agents. An apparent negative conversion to THF-soluble material was observed in both instances (see Fig. 3). This suggests that the extracting agents tend to be sorbed into, and in some instances become associated with, the coal at lower temperatures. It should be noted that there was evidence of some extraction occurring in that small quantities of of dark brown to black THF-solubles were produced. Therefore, the recorded negative conversion is really an example of an eqilibrium between a slight conversion to THF-solubles and solvent/extract association with the residual coal. It may be that chemical and/or physical interaction between the solvent and the coal at lower temperatures is offset by decomposition of resultant complexes at the higher temperatures.

From the results of the above tests one sees the great difference in the extract yields produced by α- and β-naphthol. These are isomers with very similar physical and chemical properties but yet they behave drastically different under solvolytic conditions. No insight was gained through the course of these experiments but it has been suggested that fundamental differences in gas phase acidity/basicity may contribute to their different behaviour. R.W. Taft, from the Department of Chemistry at the University of California, has been pioneering work with gas phase ion and neutral thermochemistry, but as of yet the naphthols have not been investigated.

---

[135] Golumbic, C., et al.; USBM Repts. Invest. #4662, 1950.

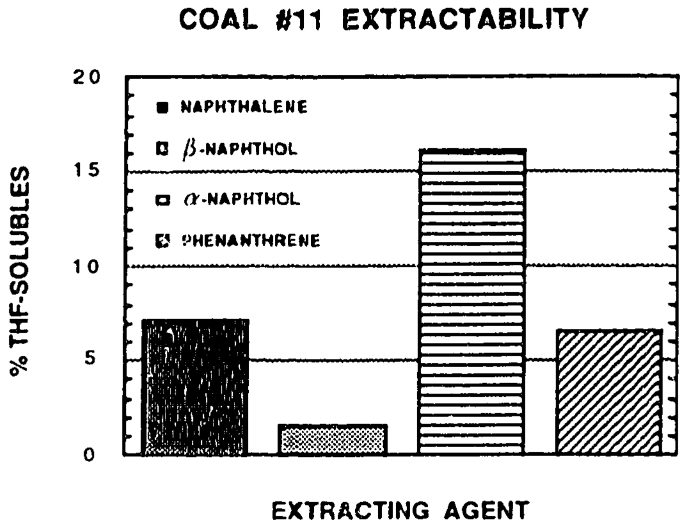


Fig. 2 - Extraction at 325°C under autogenous pressure with a 1:1 Solvent:Coal ratio.

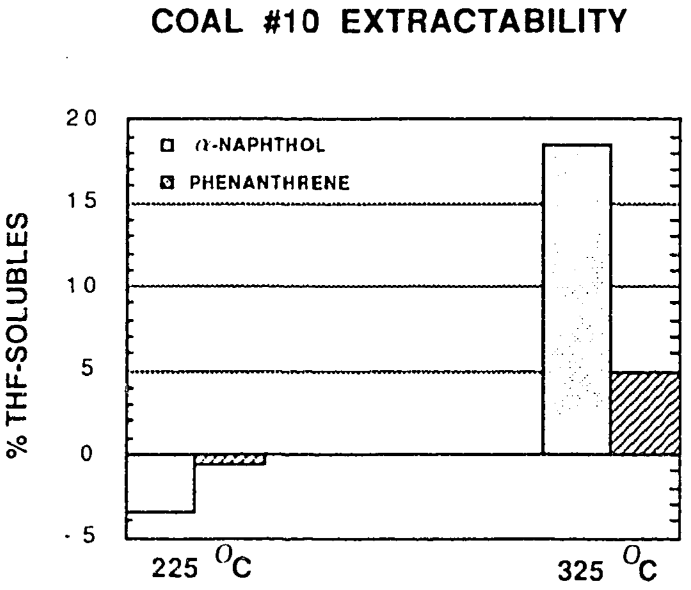


Fig. 3 - Extraction at 225°C and 325°C under autogenous pressure with a 2:1 Solvent:Coal ratio.

A set of experiments was run at 225°C with α-naphthol, in a 2:1 ratio, as the extracting agent, in order to investigate low severity effects on the production of THF-soluble matter. In the case of the Cretaceous coals (#9 & #11 - subbituminous and #10 - bituminous) the results were similar to those outlined in Figure 3, but the Carboniferous coal (#14) yielded a substantial amount of THF-solubles (see Fig. 4). This outcome was mirrored when phenanthrene was used to extract the two bituminous coals (#10 & #14) under similar conditions. The Eastern Carboniferous coal produced THF-soluble material (albeit less than when α-naphthol was the extracting agent), while the Western Cretaceous coal led to a negative result (see Fig. 4).

This marked difference in behaviour between the Carboniferous and higher-oxygen Cretaceous coals when extracted under relatively mild conditions tends to agree with the observations of Berkowitz et al. [136] in their study of chloroform soluble extracts and oxidation products of similar coals. It was speculated that the form and number of oxygen-bearing groups may have induced the disparate behaviour. However, one problem with this supposition is the fact that Alberta subbituminous coals react like other coals of similar rank, and this may point to an alternative hypothesis, namely that the rate of transition from subbituminous to bituminous ranking may have had a profound effect on the coal properties. Western Canadian coals matured relatively quickly, compared to coals laid down elsewhere, because of the rapid (geologically speaking, approximately two million years) uplift of the Rocky mountains.

The effect of temperature was further investigated by raising the extraction temperature to 325°C while maintaining the other conditions. The three Western Canadian coals (#9, #10 & #11) produced significant THF-soluble material (see Fig. 5) but still lagged behind the Eastern Carboniferous coal (#14). This fact again supported the notion that differences in depositional and geological history contribute to different behaviour.

---

[136] Berkowitz, N., et al.; Fuel, 1974, 53, 141

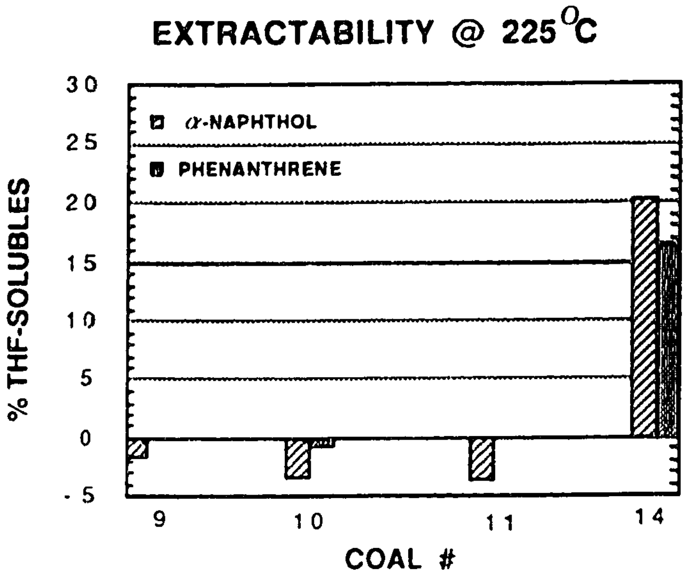


Fig. 4 - Extraction at 225°C under autogenous pressure with a 2:1 Solvent:Coal ratio.

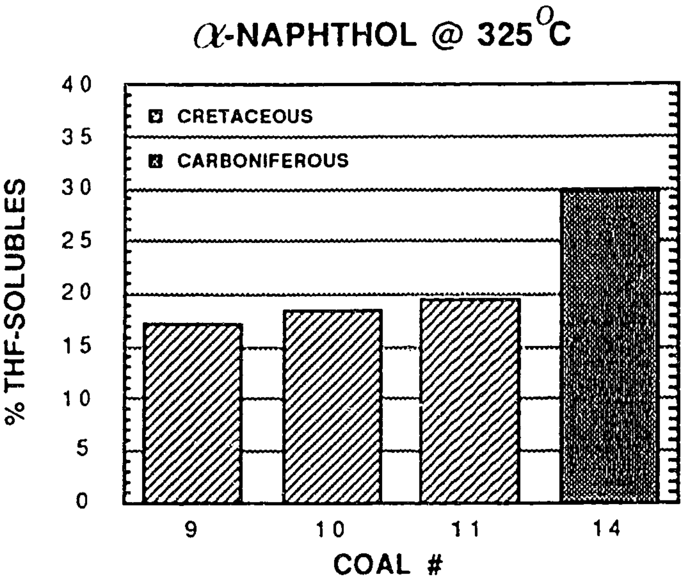


Fig. 5 - Extraction at 325°C under autogenous pressure with a 2:1 Solvent:Coal ratio.

Under mild extraction conditions rank does not appear to be a major factor in governing conversion to THF-soluble matter. The difference in yield between the Cretaceous subbituminous and bituminous coals is not significant (see Fig. 5), because their proximate and ultimate analyses are quite similar. The Cretaceous hv Ab coal is relatively close in composition to the Alberta subbituminous coals, perhaps more so than to the Carboniferous hv Ab coals from Nova Scotia (see Table 1).

Other aspects of composition may play a larger role in determining extractability than previously thought. Davis et al. (1961) [137] explored the effect of oxygen-bearing groups on the behaviour of Alberta subbituminous coals. It was found that Alberta subbituminous coals produced less tar but more water and light gases than U.S. coals of the same rank. This feature of generating significantly less tar than one would expect for a coal of a given rank has been corroborated by, inter alios, Chakrabartty (1981) [138]. Similarly, Newman et al. (1986) [139] found that Australian subbituminous coals produced less tars than New Zealand coals of the same age. Generally tar production decreases with an increase in oxygen content as the oxygen competes with carbon for hydrogen in the coal. This may account for the diminished tar yields attributed to lower ranked coals as noted by Krönig in his work with lignites [140], but does not explain differences between seemingly similar subbituminous coals. It has been postulated that oxygen may be held in different molecular structures or environments. Davis et al. did, in fact, note that the tar yield varied directly with the concentration of carbonyl groups (=CO) in the coal.

Coal solubilities are also influenced by the petrographic composition of the coal. Exinites and vitrinites are much more likely to be solubilized than inertinites, and fusinites are virtually insoluble. Coals rich in vitrinites, so-called 'bright' coals, will produce larger quantities of extract than 'dull' coals of similar rank [141]. These observations hint at a variability of coal properties that is not accounted for by rank or by proximate or ultimate

---

[137] Davis, G., Moreland, C., and Berkowitz, N.; ARC Inf. Ser. 34, 1961

[138] Chakrabartty, S.K., Fryer, J.F., and Campbell, J.D.; ARC, Info. Ser. 34, 1961

[139] Newman, R.H., and Davenport, S.J.; Fuel, 1986, 65, 533

[140] Krönig, W; Katalytische Druckhydrierung, Springer, New York, 1950

[141] Berkowitz, N., Calderon, J., and Liron, A.; Fuel, 1986, 67, 626; 1139

analyses per se. Therefore differences in the composition of the coal, even within a rank classification, can profoundly impact on solubility results.

One factor which may affect the results of the runs initiated under vacuum is the actual equilibrium state of the solvent at elevated extraction temperatures. If one extrapolates the vapour-pressure characteristics of the solvents under study, one finds that at 325°C, naphthalene, α- and β-naphthol may exist in a mixed liquid/gas equilibrium while phenanthrene remains in the liquid state. Consequently, the ultimate concentration of the solvent contacting the coal during extraction may change slightly from run to run inducing variability in the extraction results.

This effect is not very pronounced for α- and β-naphthol as only a small gas-phase may develop. For naphthalene, there is potential for a substantial gas-phase to form. Some gas phase undoubtedly developed, but there was little physical evidence. The system pressure only reached approximately 1 atmosphere (gauge) of which off gases such as CO and CO_2 were major contributors. Therefore, the partial-pressure contribution of the extracting agent was probably very small. Additionally, no significant condensation of the extracting agent was observed in the 1/4" tubing extension above the micro-bomb which suggests that the gas/liquid equilibrium favoured the liquid phase. Although extraction may have been slightly affected by reduced solvent-coal contact, particularily for naphthalene, these preliminary runs served their purpose of helping to isolate α-naphthol as the preferred extacting agent. In comparing the non-pressurized experiments with subsequent pressurized runs one should note that any pressure-dependence or variability observed may be attributed to differences in the gas/liquid equilibria maintained.

Experiments were also run using the entire slate of 6 coals at 275°C and 325°C and at elevated final system pressures. The pressures induced in these subsequent extractions were more than sufficient to guarantee the maintenance of the extracting agent in the liquid phase. Figure 6 shows that greater severity promotes higher yields of THF-soluble material and also tends to homogenize the results. A further experiment was run at 325°C with a 4:1

solvent:coal ratio (see Fig. 7). This validated findings by, inter alios, Golumbic et al.[142] that extract yields depend markedly on solvent concentration. It has been noted by Dryden (1948, 1949) [143] [144] that extract yields increase with severity, but the fact that the Carboniferous and Cretaceous coals generate similar yields of THF-solubles warrants closer attention.

A survey of feed coal solubilities was performed, as outlined in Figure 8. (see also Table 5) This showed that under mild Soxhlet conditions the Carboniferous coals were markedly more amenable to THF-extraction than the 3 Cretaceous coals.

The incremental THF-solubility (ie. the proportion of THF-solubles generated over what existed in the raw coals) was plotted in Figures 9 and 10 for extraction at 275° and 325°C respectively, and clearly shows that the Cretaceous coals, regardless of rank, generate a larger incremental yield of THF-solubles. This observation again demonstrates behavioural differences between Cretaceous and Carboniferous coals. One possible reason for this phenomena may be that the high oxygen contents of the Cretaceous coals generate highly polar extracts which the 'weakly' polar THF has trouble wresting from the polar coal matrix. It is also conceivable that heating alters the structure of the coal and the extract allowing THF to bring more into solution. Low temperature changes in coal structure due to decarboxylation and related reactions are well documented in the extant literature [145].

---

[142] Golumbic, C., et al.; USBM Repts. Invest. #4662, 1950

[143] Dryden, I.G.C.; Nature (London), 1948, 162, 959;

[144] Ibid, 1949, 163, 141

[145] cf. Iyengar, M.S., and Ghosh, R.S.; Proc. Conf. on Science in the Use of Coal, Sheffield, Inst. Fuel, London, 1958, C, 49

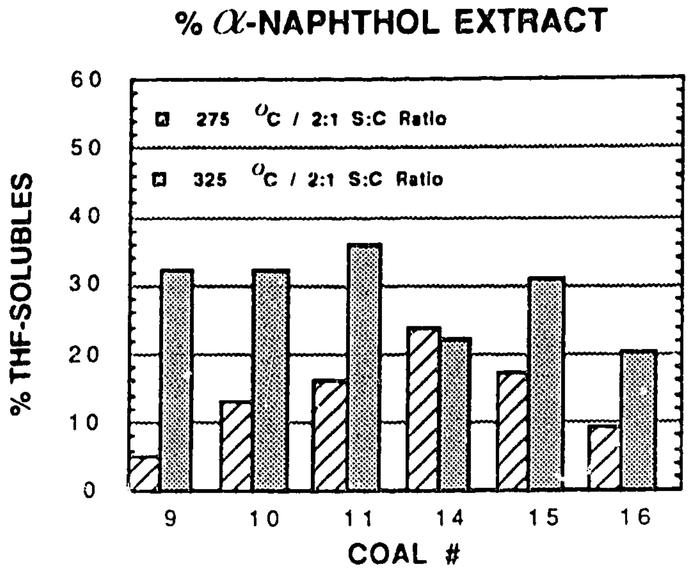


Fig. 6 - Extraction at 275° and 325°C under induced pressure with a 2:1 Solvent:Coal ratio.

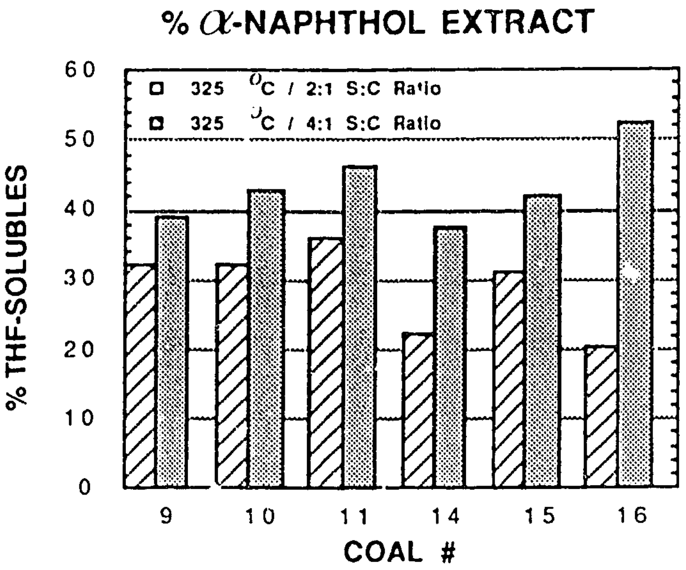


Fig. 7 - Extraction at 325°C under induced pressure with Solvent:Coal ratios of 2:1 and 4:1.

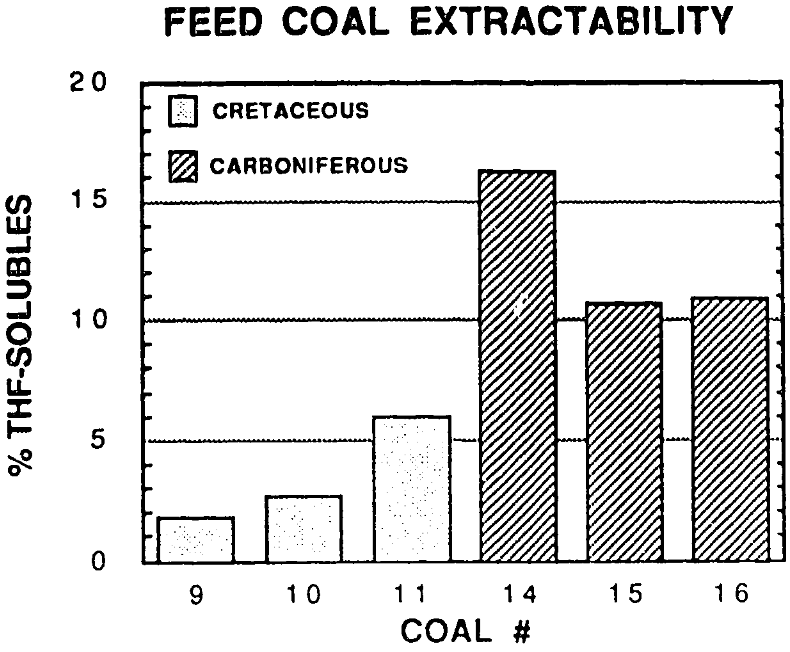


Fig. 8 - Soxhlet THF-extraction of Feed coals.

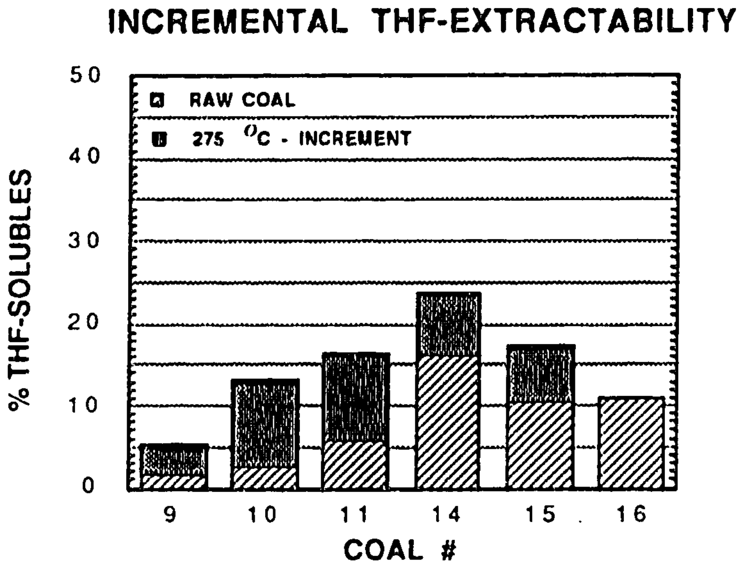


Fig. 9 - Extraction at 275°C under induced pressure with a Solvent:Coal ratio of 2:1.

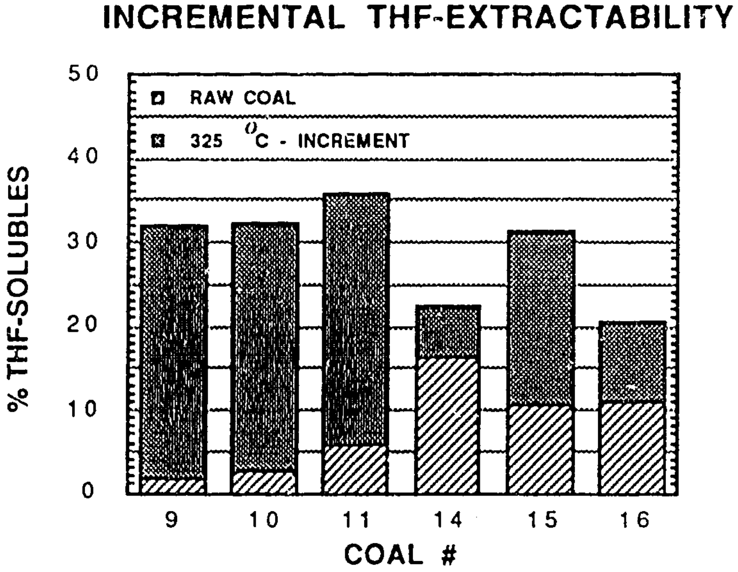


Fig. 10 - Extraction at 325°C under induced pressure with a Solvent:Coal ratio of 2:1.

The gas analyses did not yield any particularly significant data (see Appendix 2). It was found that subbituminous coals generate more gas (expressed as wt.% d.a.f. coal) than the bituminous coals regardless of the extracting agent, pressure or temperature. Cretaceous bituminous coals produce more gas than Carboniferous coals of similar rank, possibly because of their higher oxygen contents.

Gas makes are directly proportional to the extraction temperature. This correlates well with extant literature on gas generation during coal pyrolysis. Oxygen in coal is held predominantly in hydroxyl (-OH), carbonyl (=CO) and carboxyl (-COOH) functional groups, and as the temperature of extraction is increased, the concentrations of these groups tend to fall in the coal mass while volatiles are generated [146]. This phenomena has been observed in Alberta subbituminous coal in unpublished work by Takeuchi [147]. The hydroxyl concentration may increase slightly before it too begins to diminish past 450°C but there is sufficient loss of oxygen groups to produce oxides of carbon below T_d. The carboxyl and carbonyl oxygen are eliminated first, at lower temperatures, and it is through decarboxylation and decarbonylation reactions that the oxygen groups are liberated predominantly as CO_2. Iyengar et al. [148] noted that carboxyl groups were liberated from an Indian lignite in the temperature range 100 to 300°C with almost complete loss at 300°C. This supports the gas-make observations in this study.

3.6.3 Error Treatment

It is noted that there is some variability in the results outlined above. Based on the data collected on the induced pressure runs, replicates generally reproduced the trend of the data but there were a few outliers. The majority of the duplicate runs were performed at 325°C with a 2:1 α-naphthol:coal ratio. For each of coals #9, #10 and #11 the first of three observations was discounted as being spurious. These values were the first ones

---

[146] Mrázíková, J., Sindler, S., Veverka, L., and Macák, J.; Fuel, 1986, 65, 342-345
[147] Takeuchi, M., and Berkowitz, N.; Unpublished data, University of Alberta, 1988
[148] Iyengar, M.S., and Ghosh, R.S.; Proc. Conf. on Science in the Use of Coal, Sheffield, Inst. Fuel, London, 1958, C, 49

obtained under induced pressure and were considerably lower than subsequent numbers. Two acceptable runs were performed with coal #14 under similar conditions, as well as satisfactory triplicate runs with coals #15 and #16. The following averages and error limits were calculated:

Coal # 9 - 32.1 ∓ 0.5%
Coal #10 - 32.4 ∓ 0.3%
Coal #11 - 35.9 ∓ 1.8%
Coal #14 - 22.4 ∓ 1.3%
Coal #15 - 31.2 ∓ 3.6%
Coal #16 - 20.4 ∓ 2.7%

Such variation is quite acceptable in compiling small set statistics for work with coal solubility, particularly at temperatures below T_d. Chemical instability of newly generated soluble coal material is often observed in liquefaction work with subbituminous coals. It has been demonstrated that material may vary between toluene-soluble and -insoluble at temperatures as low as 250-300°C [149] and that small changes in the heating and cooling profiles as well as in the residence time [150] could dramatically affect the preasphaltene/asphaltene ratios in the extract. In the case of these experiments, some variation in the extraction temperatures due to fluctuations in the sand bath air-flow were noted. Although two sand bath temperature readings were continuously monitored, no accurate measure of the 'internal' micro-bomb temperature was performed. Therefore, temperature vacillations may have been the major contributor to reproducibility errors.

If extraction in the solvolytic regime were simple solubilization and generated relatively stable molecular solutions, one could hope to produce replicates in close agreement. In fact, the wide variances suggest that the mechanisms of solubilization include complicated equilibria which almost certainly involve colloidal dispersion.

---

[149] Berkowitz, N., Calderon, J. and Liron, A; Fuel, 1988, 67, 1139
[150] Freel, J., Anderson, R.P., Alexander, B.F., and Wright, C.H.; Fuel, 1986, 65, 86

4. Conclusions

4.1 Introduction

As stated, this study sought to investigate solvolytic extraction of a suite of Canadian subbituminous and bituminous coals with some higher aromatic solvents in order to gain information on three aspects of such extraction. The first thrust was to determine whether mild solvent extraction could offer a viable path to easily upgradable hydrocarbons. The second aspect involved comparing behaviour of Cretaceous subbituminous and bituminous coals that might affect extraction and/or subsequent processing. The final aim was to briefly explore possible differences in extractability between Canadian Carboniferous and Cretaceous coals.

This 'survey', in effect, touched on the two features of coal solvent extraction research of current interest, namely, (i) the effort to generate soluble matter that might prove more conducive to structural and/or chemical analysis than the solid coal, and (ii) the production of an acceptable hydrogenation feedstock.

4.2 Inferences

As detailed in extant literature, α-naphthol was found to be a very good extracting agent, under solvolytic conditions, for both subbitumious and bituminous coals. A marked temperature-dependence was observed for all coal/solvent combinations investigated. Additionally, yields of THF-soluble extract varied directly with the relative concentration of extracting solvent.

Under mild solvolytic conditions the Fastern Canadian Carboniferous coals were found to yield greater amounts of THF-soluble extract than their Western Cretaceous counterparts. But there was little difference between the Cretaceous subbituminous and bituminous coals at any temperature, and this suggests that, in this case, solubility depends more on a common geological history than on rank.

Under more severe conditions the differences between Carboniferous and Cretaceous coals all but disappeared. The unreacted (raw) Carboniferous coals were markedly more amenable to Soxhlet extraction with THF; but the Cretaceous coals actually produced larger incremental amounts of THF-soluble material.

Under mild conditions and low solvent:coal ratios, yields of THF-solubles (asphaltenes and lighter matter) were generally fairly low, and the product slate is likely to be of limited practical as well as scientific value because of its possible high molecular weight. Overall, solvent extraction, as investigated in this study, does not appear to be a useful route to an hydrogenation feedstock.

4.3 Some Recommendations for Further Work

It would be of interest to analyze the THF-soluble extract produced in this work in order to further investigate differences between Cretaceous and Carboniferous coals. It is not known whether or not these extracts are essentially similar in composition. One might also look at some Western U.S. coals of Cretaceous age in order to determine whether depositional factors affect low-severity solvolytic extraction. The effect of the solvent:coal ratio is marked in these low temperature extractions. One could further quantify this phenomenon through more careful control and variation of the solvent concentration. Finally, the effect of extraction time and potential solubilization catalysts (such as FeS) could be investigated.

References

1. Agde, G. and Hubertus, R.; Braunkohlenarchiv, 1936, 46, 3
2. Asbury, R.S. Ind. Eng. Chem., 1934, 26, 1301
3. Bedson, P.P.; J. Soc. Chem. Ind. (London), 1902, 21, 241
4. Berkowitz, N. An Introduction to Coal Technology . Academic Press Inc., New York, 1979.
5. Berkowitz, N. The Chemistry of Coal . Elsevier Science Publishers B.V., Amsterdam, 1985.
6. Berkowitz, N.; ACS Adv. Chem. Ser. 217, 1988, 217-233
7. Berkowitz, N.; Proc. 11th. Bienn. Lignite Symp., San Antonio, TX. U.S. Dept. of Energy, GFETC/IC-82, 1981, 1, 414
8. Berkowitz, N., Calderon, J.J.; Fuel Proc. Tech., 1987, 16, 245-256
9. Berkowitz, N., Calderon, J., Liron, A.; Fuel, 1986, 67, 626-631, 1017-1019, 1139-1142
10. Berkowitz, N.; Nature (London), 1948, 162 , 960
11. Berkowitz, N., Fryer, John F., Ignasiak, Boleslaw S., Szladow, Adam J.; Fuel, 1974, 53, 141
12. Bone, W.A., Sarjant, R.J.; Proc. R. Soc. London, 1920, A 96, 119
13. Chakrabartty, S.K., Liquid Fuels Technology, 1985, 3(1), 1-13
14. Chakrabartty, S.K., Freyer, J.F., and Campbell, J.D.; ARC Info. Ser. 99, 1981
15. Collins, C.J., Raaen, V.F., Benjamin, B.M., Kabalka, G.W.; Fuel, 1977, 56, 107
16. Davis, G., Moreland, C., and Berkowitz, N.; Alberta Research Council, Inf. Ser., 34, 1961
17. Deshpande, G.V., Holder, G.D., Bishop, A.A., Gopal, J., Wender, I.; Fuel, 1984, 63, 956
18. Dormans, H.N.M., Van Krevelen, D.W.; Fuel, 1960, 39 , 273-292
19. Dryden, I.G.C.; Nature (London), 1948, 162, 959
20. Dryden, I.G.C.: Nature (London), 1949, 163, 141
21. Dryden, I.G.C.; Discuss. Faraday Soc., 1951, 11, 28
22. Dryden, I.G.C.; Fuel, 1950, 29, 197-221
23. Dryden, I.G.C.; Fuel, 1951, 30, 39-44
24. Dryden, I.G.C.; Fuel, 1951, 30, 145-158

25. Fischer, F., Peters, K., and Cremer, W.; Brennst. Chem., 1933, 14, 181

26. Franklin, R.E.; Acta Crystallogr., 1950, 3, 107

27. Freel, J., Anderson, R.P., Alexander, B.F., and Wright, C.H.; Fuel, 1986, 65, 86

28. Gillet, A. and Pirlot, A.; Bull. Soc. Chem. Belg., 1935, 44, 504

29. Gillet, A. and Pirlot, A.; Bull. Soc. Chem. Belg., 1938, 47, 158

30. Gillet, A. and Pirlot, A.; Bull. Soc. Chem. Belg., 1942, 51, 23, 525

31. Given, P.H.; Fuel, 1960, 39, 147

32. Given, P.H.; Fuel, 1961, 40, 427

33. Gluskoter, H.; Fuel, 1965, 44, 285

34. Golumbic, C., Anderson, J.E., Orchin, M., and Storch, H.H.; USBM Repts. Invest. #4662, 1950.

35. Green, T., Kovac, J., Brenner, D., Larsen, J.W. *In Coal Structure*. (Meyers, R.A., Ed.) Academic Press, New York, 1982

36. Heredy, L.A., and Neuworth, M.B.; Fuel, 1962, 41, 221

37. Heredy, L.A., Kostyo, A.E., and Neuworth, M.B.; Fuel, 1963, 42, 182

38. Hill, G.R., Lyon, L.B.; Ind. Eng. Chem, 1962, 54(6), 36

39. Hombach, H.P.; Erdoel Kohle, 1975, 28, 90

40. Hombach, H.P.; Erdoel Kohle, 1979, 32, 85

41. Hoogendoorn, J.C.; Phil. Trans. R. Soc. (London), 1981, A 300, 99-109

42. Ignasiak, B., Carson, D., Szladow, A.J., and Berkowitz, N. *Studies on Non-catalytic Liquefaction of Western Canadian Coals* - ACS Symp. Ser. 139, 97-110, 1980

43. Iyengar, M.S., and Ghosh, R.S.; Proc. Conf. on Science in the Use of Coal, Sheffield, Inst. Fuel, (London), 1958, C, 59

44. Kann, L.; Fuel, 1951, 30, 47

45. Keppeler, G. and Borchers, H.; Brennst. Chem., 1934, 15, 241, 404

46. Kiebler. M.W. (Ed. H.H. Lowry) *The Chemistry of Coal Utilization* Vol. 1, pg. 677-760, New York, 1945.

47. Kiebler, M.W.; Industr. Eng. Chem. 1940, 32, 1389

48. Kröger, C. and de Vries, H.; Liebig's Ann., 1962, 652, 35

49. Krönig, W; Katalytische Druckhydrierung, Springer, New York, 1950

50. Landau, H.G., and Asbury, R.S.; Ind. Eng. Chem., 1938, 30, 117

51. Larsen, J.W., Given, P.H.; Proc. 1978 Coal Chem. Workshop, Menlo Park, CL; Conf - 790372 SRI Internat., 1978, 69

52. Larsen, J.W., and Kovac, J.; ACS Symp. Ser., 1978, 71, 36

53. Maa, Peter S., Neavel, Richard C., Vernon, Lonnie W.; Ind. Eng. Chem. Process Des. Dev., 1984, 23, 242-250

54. Malanowitz, L.; Chim. Ind. (Paris), 1932, 28, 1277

55. McCaulay, D.A., in "Friedel-Crafts and Related Reactions" , (Olah, G.A., ed.), Vol 2, Part 2, 1062. Wiley (Interscience), New York, 1964.

56. Merrick, D. Coal Combustion and Conversion, MacMillan Publishers Ltd., Hong Kong, 1984

57. Morgans, W.T.A. and Terry, N.B.; Fuel, 1978, 37, 201

58. Mrazkiova, J., Sindler, S., Veverka, L., Macak, J; Fuel, 1986, 65, 342-345

59. Neavel, R.C.; Fuel, 1976, 55, 234

60. Nesterenko, L.L.; Trudy Kharkov Khim. Tekhnol. Inst. im S.M. Kirova, 1939, 2, 70 c.f. also Chem. Abstr., 1940, 34, 3473

61. Nelson, J.B.; Fuel, 1954, 32, 153

62. Newman, R.H., Davenport, S.J.; Fuel, 1986, 65, 533

63. Oele, A.P., Waterman, H.I., Goedkoop, M.L., and Van Krevelen, D.W.; Fuel, 1951, 30, 169

64. Orchin, M., Golumbic, C., Anderson, J.E., Storch, H.H.; USBM Bulletin #505, 1951

65. Orchin, M., and Storch, H.H.; Ind. and Eng. Chem., 1948, 40(8), 1385-1389

66. Ostwald, W. and Ortlov, H.; Kolloid Z., 1932, 59, 25

67. Parr, S.W., and Hadley, H.F.; Fuel, 1925, 4, 31, 49

68. Paul, P.F.M., and Wise, W.S. The Principles of Gas Extraction. M&B Monograph, CE/5, Mills & Boon, London. 1971

69. Pauling, L. The Nature of the Chemical Bond, London, 1947.

70. Pfirrmann, T.W., U.S. Patent 2167250 (1939)

71. Pomeroy, C.D.; Nature (London), 1956, 178, 279

72. Pott, A., and Broche, H.; Glückauf, 1933, 69, 903

73. Rudnick, L.R. and Whitehurst, D.D.; ACS Symp. Ser. 1981, 169 (New Approaches In Coal Chemistry)

74. Speight, J.G., The Chemistry and Technology of Coal , Marcel Dekker, Inc., New York. 1983

75. Sternberg, H.W., Delle Donne, C.L., Pantages, P., Moroni, E.C., and Markby, R.E.; Fuel, 1971, 50, 432

76. Takeuchi, M., and Berkowitz, N., Unpublished Data, University of Alberta, 1988

77. Tawada, K., Kisida, T., and Ohyama, S.J.; Soc. Chem. Ind. Japan, 1939, S 42, 58b

78. Ude, F., French Patent No. 800920 (1936)

79. Vahrman, M.; Fuel, 1970, 49, 5

80. Vahrman, M., and Watts, R.H.; Fuel, 1972, 51, 130, 235

81. Van Krevelen, D.W. Coal. Elsevier Science Publishers, Amsterdam. 1961.

82. Van Krevelen, D.W.; Fuel, 1965, 44, 229-241

83. Voitova, E.V.; Brennst. Chem., 1935, 16, 21

84. Wachowska, H.; Fuel, 1979, 58, 99

85. Whitehead, J.C., and Williams, D.F.J.; Inst. Fuel (London), 1975, 49, 182

86. Whitehurst, D.D. and Derbyshire, F.J.; Chemistry of Coal Liquefaction: Conference Sponsored by National Science Foundation, Salt Lake City, Utah, January 11-13, 1982.

87. Whitehurst, D.D., Farcasiu, M., Fitchell, T.O., and Dickert, Jr., J.J.; 1st. Rep. EPRI Project #RP-410-1. Feb., 1976.

88. Wiser, W.H.; Prep. A.C.S., Div. Fuel Chem., 1975, 20(2), 122

Appendix 1 - Experimental Data

Table 6 Solvent Extraction :
Summary of Experimental Data

Run No.	Coal No.	Solvent	Temp. (°C)	Press. Max. (MPa)	Solvent (g)	Coal, g initial (final)	Ash % initial (final)	$\frac{\text{Solvent}}{\text{Coal}}$ Ratio	Product Extractability[b.] %
1	11	α-Naphthol	325.	a.	9.92	10.20 (8.67)	12.82 (13.99)	0.97	16.1
2	11	Phenanthrene	323.	a.	9.80	9.74 (8.97)	12.82 (12.82)	1.01	7.9
3	11	β-Naphthol	315.	a.	10.18	10.00 (9.84)	12.82 (12.82)	1.02	1.6
4	11	Naphthalene	325.	a.	10.16	10.10 (9.44)	12.82 (13.36)	1.01	7.1
5	11	α-Naphthol	326.	a.	20.13	9.47 (7.98)	12.82 (16.64)	2.13	19.4
6	11	Phenanthrene	331.	a.	9.75	9.61 (9.11)	12.82 (12.82)	1.01	5.2
7	11	β-Naphthol	328.	a.	20.12	9.23 (8.80)	12.82 (15.01)	2.18	7.1
8	11	Phenanthrene	317.	a.	30.33	9.87 (8.10)	12.82 (12.91)	3.07	18.0

a. Cold system under vacuum, hot system pressure ≃1 atmosphere.

b. Percent organics soluble in THF.

Table 6 Continued :

Run No.	Coal No.	Solvent	Temp. (°C)	Press. Max. (MPa)	Solvent (g)	Coal, g initial (final)	Ash % initial (final)	$\frac{\text{Solvent}}{\text{Coal}}$ Ratio	Product Extractability[b.] %
9	9	Phenanthrene	327.	a.	14.37	5.19 (5.18)	25.12 (26.16)	2.77	1.6
10	11	α-Naphthol	326.	a.	15.05	4.70 (3.85)	12.82 (16.56)	3.20	21.6
11	9	Phenanthrene	328.	a.	19.88	10.12 (9.46)	25.12 (27.92)	1.96	10.0
12	9	α-Naphthol	325.	a.	20.34	9.37 (7.83)	25.12 (25.77)	2.17	17.2
13	9	β-Naphthol	325.	a.	19.96	9.47 (8.68)	25.12 (27.92)	2.11	11.8
14	9	Phenanthrene	319.	a.	19.33	9.33 (9.10)	25.12 (25.59)	2.07	5.7
15	10	α-Naphthol	314.	a.	18.94	9.59 (8.09)	13.30 (16.25)	1.97	18.5
16	10	Phenanthrene	326.	a.	20.60	9.73 (9.36)	13.30 (14.28)	2.12	4.9

a. Cold system under vacuum, hot system pressure ≃ atmosphere.

b. Percent organics soluble in THF.

Table 6 Continued :

Run No.	Coal No.	Solvent	Temp. (°C)	Press. Max (MPa)	Solvent (g)	Coal, g initial (final)	Ash % initial (final)	$\frac{\text{Solvent}}{\text{Coal}}$ Ratio	Product Extractability[b] %
17	10	α-Naphthol	226.	a.	19.15	9.97 (10.31)	13.30 (13.30)	1.92	-3.4
18	10	Phenanthrene	224.	a.	19.07	10.14 (10.22)	13.30 (13.76)	1.88	-0.3
19	9	α-Naphthol	223.	a.	20.16	8.97 (9.30)	25.12 (27.80)	2.25	0.0
20	9	α-Naphthol	226.	a.	19.10	9.02 (9.37)	25.12 (25.77)	2.12	-3.0
21	11	α-Naphthol	226.	a.	20.43	9.03 (9.56)	12.82 (14.27)	2.26	-4.1
22	14	α-Naphthol	227	a.	20.42	10.81 (8.72)	4.29 (6.42)	1.89	19.3
23	14	α-Naphthol	318.	a.	19.96	10.82 (8.17)	4.29 (6.02)	1.84	25.9
24	14	α-Naphthol	226.	a.	20.62	11.15 (8.90)	4.29 (5.48)	1.85	21.2

a. Cold system under vacuum, hot system pressure ≃1 atmosphere.

b. Percent organics soluble in THF.

Table 6 Continued :

Run No.	Coal No.	Solvent	Temp. (°C)	Press. Max. (MPa)	Solvent (g)	Coal, g initial (final)	Ash % initial (final)	$\frac{\text{Solvent}}{\text{Coal}}$ Ratio	Product Extractability[b.] %
25	14	α-Naphthol	326.	a.	20.92	11.07 (7.54)	4.29 (6.70)	1.89	33.6
26	11	α-Naphthol	229.	a.	20.48	9.49 (10.03)	12.82 (15.21)	2.16	-2.8
27	10	Phenanthrene	222.	a.	20.97	10.16 (10.26)	13.30 (13.30)	2.06	-1.0
28	14	Phenanthrene	229.	a.	20.64	10.37 (8.82)	4.29 (5.89)	1.99	16.4
29	10	α-Naphthol	323.	6.0	21.04	10.06 (8.12)	13.30 (17.60)	2.09	23.3
30	14	α-Naphthol	321.	6.4	21.05	10.23 (8.18)	4.29 (5.60)	2.06	21.1
31	11	α-Naphthol	322.	9.0	20.44	9.47 (7.90)	12.82 (19.60)	2.16	23.1
32	9	α-Naphthol	325.	9.6	20.27	10.04 (8.48)	25.12 (30.70)	2.02	21.8

a. Cold system under vacuum, hot system pressure ≃1 atmosphere.

b. Percent organics soluble in THF.

Table 6 Continued :

Run No.	Coal No.	Solvent	Temp. (°C)	Press. Max. (MPa)	Solvent (g)	Coal, g initial (final)	Ash % initial (final)	$\frac{\text{Solvent}}{\text{Coal}}$ Ratio	Product Extractability[b.] %
33	10	α-Naphthol	325.2	9.3	20.93	9.72 (7.88)	13.30 (16.80)	2.15	22.2
34	14	α-Naphthol	314.	8.6	21.01	10.63 (8.29)	4.29 (6.30)	1.98	23.7
35	11	α-Naphthol	322.	10.1	21.00	9.63 (6.85)	12.82 (19.26)	2.18	34.1
36	9	α-Naphthol	320.	10.6	21.22	9.60 (7.44)	25.12 (33.92)	2.21	31.6
37	10	α-Naphthol	270.	9.3	21.87	9.69 (8.64)	13.30 (15.48)	2.26	13.1
38	14	α-Naphthol	272.	8.9	20.69	10.17 (7.92)	4.29 (6.37)	2.03	23.8
39	11	α-Naphthol	269.	9.7	20.52	8.59 (7.59)	12.82 (17.46)	2.39	16.3
40	9	α-Naphthol	269.	9.8	20.79	10.03 (9.58)	25.12 (25.73)	2.07	5.3

b. Percent organics soluble in THF.

Table 6 Continued :

Run No.	Coal No.	Solvent	Temp. (°C)	Press. Max. (MPa)	Solvent (g)	Coal, g initial (final)	Ash % initial (final)	$\frac{\text{Solvent}}{\text{Coal}}$ Ratio	Product Extractability[b.] %
41	15	α-Naphthol	325.	10.3	20.71	9.94 (6.65)	2.20 (4.68)	2.08	34.8
42	16	α-Naphthol	324.	10.3	20.43	9.47 (7.62)	2.65 (4.35)	2.16	20.9
43	15	α-Naphthol	321.	9.2	20.86	9.39 (7.88)	2.20 (4.06)	2.22	17.7
44	16	α-Naphthol	326.	9.7	20.59	9.92 (7.15)	2.65 (4.29)	2.08	29.1
45	15	α-Naphthol	272.	8.8	21.15	9.70 (8.13)	2.20 (3.64)	2.18	17.4
46	16	α-Naphthol	274.	9.0	21.47	10.02 (9.15)	2.65 (3.35)	2.14	9.3
47	15	α-Naphthol	318.	10.2	40.68	9.94 (5.91)	2.20 (4.69)	4.09	42.1
48	16	α-Naphthol	321.	10.1	41.09	9.98 (4.85)	2.65 (4.63)	4.12	52.4

b. Percent organics soluble in THF.

Table 6 Continued :

Run No.	Coal No.	Solvent	Temp. (°C)	Press. Max. (MPa)	Solvent (g)	Coal, g initial (final)	Ash % initial (final)	$\frac{\text{Solvent}}{\text{Coal}}$ Ratio	Product Extractability[b.] %
49	10	α-Naphthol	325.	10.0	41.29	9.33 (5.91)	13.30 (21.73)	4.43	42.8
50	14	α-Naphthol	323.	10.1	41.42	10.04 (6.64)	4.29 (9.67)	4.13	37.6
51	9	α-Naphthol	324.	10.1	20.38	9.84 (8.20)	25.12 (39.33)	2.07	32.5
52	9	α-Naphthol	322.	10.2	40.48	9.67 (6.91)	25.12 (36.34)	4.19	39.2
53	11	α-Naphthol	321.	10.8	42.67	8.92 (5.59)	12.82 (25.53)	4.78	46.5
54	11	α-Naphthol	325.	10.1	21.04	8.67 (6.14)	12.82 (23.23)	2.43	37.6
55	15	α-Naphthol	323.	9.5	20.27	9.74 (6.98)	2.20 (4.24)	2.08	29.8
56	16	α-Naphthol	324.	10.2	20.55	9.76 (7.65)	2.65 (3.90)	2.11	22.6
57	10	α-Naphthol	325.	10.1	20.68	10.07 (7.43)	13.30 (20.77)	2.05	32.6

b. Percent organics soluble in THF.

Appendix 2 - Gas Generation Data

Table 7 Gas Generation during Solvent Extraction :
% Initial Organic Mass

Run No.	Coal No.	Solvent	Temp. (°C)	Press., (MPa) initial (final)	CO_2 (%)	C_2H_6 (%)	C_3H_8 (%)	CH_4 (%)	CO (%)	Total (%)
11	9	Phenanthrene	327.	a. (0.1)	2.67	0.07	0.00	0.17	2.33	5.24
12	9	α-Naphthol	325.	a. (0.1)	5.74	0.06	0.03	0.07	0.38	6.29
13	9	β-Naphthol	325.	a. (0.1)	6.06	0.05	0.03	0.07	0.43	6.64
14	9	Phenanthrene	319.	a. (0.1)	5.68	0.01	0.02	0.05	0.81	6.56
15	10	α-Naphthol	314.	a. (0.1)	2.33	0.03	0.00	0.13	0.59	3.07
16	10	Phenanthrene	326.	a. (0.1)	3.12	0.01	0.02	0.06	0.45	3.66

a. Cold system under vacuum.

Table 7 Continued :

Run No.	Coal No.	Solvent	Temp. (°C)	Press., (MPa) initial (final)	CO_2 (%)	C_2H_6 (%)	C_3H_8 (%)	CH_4 (%)	CO (%)	Total (%)
29	10	α-Naphthol	323.	3.2 (6.0)	3.24	0.00	0.00	0.15	0.00	3.39
30	14	α-Naphthol	321.	3.8 (6.4)	0.03	0.00	0.00	0.00	0.00	0.03
31	11	α-Naphthol	322.	4.2 (9.0)	7.51	0.00	0.00	0.23	0.00	7.74
32	9	α-Naphthol	325.	4.5 (9.6)	6.79	0.00	0.00	0.15	0.00	6.94
33	10	α-Naphthol	325.	4.5 (9.3)	3.77	0.00	0.00	0.08	0.00	3.86
34	14	α-Naphthol	314.	4.5 (8.6)	0.00	0.00	0.00	0.00	0.00	0.00

Table 7 Continued :

Run No.	Coal No.	Solvent	Temp. (°C)	Press., (MPa) initial (final)	CO_2 (%)	C_2H_6 (%)	C_3H_8 (%)	CH_4 (%)	CO (%)	Total (%)
35	11	α-Naphthol	322.	4.5 (10.1)	5.20	0.00	0.00	0.12	0.00	5.32
36	9	α-Naphthol	320.	4.8 (10.6)	5.49	0.00	0.00	0.00	0.33	5.82
37	10	α-Naphthol	270.	4.8 (9.3)	1.52	0.00	0.00	0.00	0.00	1.52
38	14	α-Naphthol	272.	4.8 (8.7)	0.00	0.00	0.00	0.00	0.00	0.00
39	11	α-Naphthol	269.	4.8 (9.7)	3.81	0.00	0.00	0.00	0.21	4.02
40	9	α-Naphthol	269.	4.9 (9.8)	3.24	0.00	0.00	0.00	0.13	3.37

Table 7 Continued :

Run No.	Coal No.	Solvent	Temp. (°C)	Press., (MPa) initial (final)	CO_2 (%)	C_2H_6 (%)	C_3H_8 (%)	CH_4 (%)	CO (%)	Total (%)
41	15	α-Naphthol	325.	4.8 (10.3)	0.23	0.00	0.00	0.00	0.00	0.23
42	16	α-Naphthol	324.	4.9 (10.3)	0.00	0.00	0.00	0.00	0.00	0.00
43	15	α-Naphthol	321.	5.2 (9.2)	0.44	0.00	0.00	0.00	0.05	0.49
44	16	α-Naphthol	326.	5.2 (9.7)	1.26	0.00	0.00	0.00	0.14	1.40
45	15	α-Naphthol	272.	5.2 (8.8)	0.03	0.00	0.00	0.00	0.00	0.03
46	16	α-Naphthol	274.	5.2 (9.0)	0.38	0.00	0.00	0.00	0.06	0.44

Table 7 Continued :

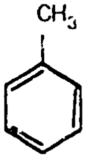
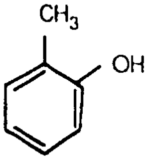
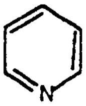
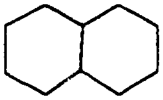
Run No.	Coal No.	Solvent	Temp. (°C)	Press., (MPa) initial (final)	CO_2 (%)	C_2H_6 (%)	C_3H_8 (%)	CH_4 (%)	CO (%)	Total (%)
47	15	α-Naphthol	318.	5.2 (10.2)	0.85	0.00	0.00	0.00	0.08	0.92
48	16	α-Naphthol	321.	5.2 (10.1)	0.81	0.00	0.00	0.00	0.07	0.88
49	10	α-Naphthol	325.	5.2 (10.0)	1.98	0.00	0.00	0.00	0.10	2.08
50	14	α-Naphthol	323.	5.2 (10.1)	0.86	0.00	0.00	0.00	0.07	0.92
51	9	α-Naphthol	324.	5.2 (10.1)	5.68	0.00	0.00	0.07	0.14	5.88
52	9	α-Naphthol	322.	5.2 (10.2)	7.25	0.00	0.00	0.09	0.21	7.56

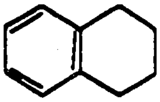
Table 7 Continued :

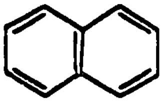
Run No.	Coal No.	Solvent	Temp. (°C)	Press., (MPa) initial (final)	CO_2 (%)	C_2H_6 (%)	C_3H_8 (%)	CH_4 (%)	CO (%)	Total (%)
53	11	α-Naphthol	321.	5.2 (10.8)	7.50	0.00	0.00	0.09	0.45	8.04
54	11	α-Naphthol	325.	5.2 (10.1)	7.82	0.00	0.00	0.06	0.32	8.20
55	15	α-Naphthol	323.	5.2 (9.5)	0.80	0.00	0.00	0.00	0.08	0.88
56	16	α-Naphthol	324.	5.2 (10.2)	0.56	0.00	0.00	0.00	0.06	0.61
57	10	α-Naphthol	325.	5.2 (10.1)	3.68	0.00	0.00	0.05	0.16	3.89

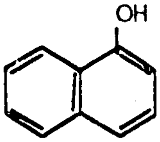
Appendix 3 - Some Common Solvents Used For Coal Extraction

Some Common Solvents Used For Coal Extraction

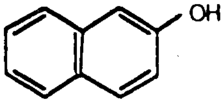
1. furan		C_4H_4O	b.p. = 32 °C
2. tetrahydrofuran		$C_5H_{10}O$	b.p. = 66 °C
3. benzene		C_6H_6	b.p. = 80 °C
4. toluene		C_7H_8	b.p. = 110 °C
5. o-cresol		C_7H_8O	b.p. = 191 °C
6. pyridine		C_5H_5N	b.p. = 116 °C
7. decalin		$C_{10}H_{18}$	b.p. = 196 °C

8. tetralin  $C_{10}H_{14}$ b.p. = 208 °C

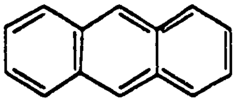
9. naphthalene  $C_{10}H_8$ b.p. = 218 °C

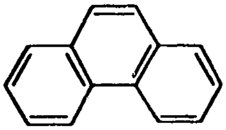
10. α–naphthol 

$C_{10}H_8O$ b.p. = 288 °C

11. β–naphthol 

$C_{10}H_8O$ b.p. = 295 °C

12. anthracene  $C_{14}H_{10}$ b.p. = 354 °C

13. phenanthrene  $C_{14}H_{10}$ b.p. = 340 °C